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1. **Combustion theory and modeling**
2. **SHS of micron, submicron- and nano- materials**
3. **Combustion of multilayered nano-structures**
4. **Nanoenergetic materials and processes**
5. **Biomaterials and coatings**
6. **Sintering and consolidation**
7. **Packing geometry in nano- and micro- scale**
8. **Space applications**
9. **Industrialization**
10. **Special Session in Memory of Professor A.G. Merzhanov**

Plenary Lectures

Alexander Rogachev (ISMAN, Russia),

In memory of Alexander Merzhanov: life and achievements of a distinguished scientist

Osamu Odawara (Japan)

Energy and mass saved space exploration aided by dimensionally-controlled SHS technologies

Frederic Bernard (France)

Dense SiC produced by reactive sintering from mechanically activated reactant mixture

Michael Zachariah (USA)

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Content

IN MEMORY OF PROF. ALEXANDER MERZHANOV: INVENTOR AND WORLD RECOGNIZED LEADER OF SHS

Prof. Alexander Merzhanov, inventor and world recognized leader of SHS, died on July 31, 2013 in Chernogolovka, Russia at the age of 82. Merzhanov made his first significant contribution to combustion science, while still quite young. He developed the Nonstationary Theory of Thermal Explosion in condensed media (1958-1966). This theory was highly considered and supported by N.N. Semenov and Ya.B. Zel'dovich and played an important role in the practical design of solid rocket propellants and has still not lost its contemporary R&D significance. In 1967 he led the work, which resulted in discovery of the “solid flame” phenomenon. Based on this discovery, Merzhanov and his coworkers elaborated a novel method to synthesize advanced materials called *Self-propagating High-temperature Synthesis (SHS)*, followed by a new scientific discipline, structural macrokinetics, which explores the formation of material microstructures in realistic conditions of rapid high-temperature reactions.

Merzhanov also demonstrated his talent as a scientific leader and administrator. He was capable to establish a new institute of the Russian Academy of Sciences, the Institute of Structural

Macrokinetics (ISMAN), and became its first director. He founded the *International Journal of Self-Propagating High-temperature Synthesis* (Allerton Press) and has been its Editor-in-Chief for more than 20 years. This tremendous activity, which also includes organization of international symposia, workshops, conferences, numerous lecture tours in different countries, and publication of analytical reviews, resulted in worldwide recognition of this new scientific field. Currently, SHS is being studied in more than 50 countries, hundreds of papers are published on this topic every year, and several industrial ventures have been launched.

Prof. Merzhanov's contribution to basic and applied research has been recognized both in Russia and abroad. He was elected a Full Member (Academician) of the Russian Academy of Sciences (1997); an Academician and Member of the International Board of the World Academy of Ceramics, Italy (1994); an Honorary Member of the Materials Research Society of India (1997); Active Member of *Academia Scientiarum et Artium Europaea*, Austria (1996); an Honorary Foreign Member of the National Academy of Sciences of Armenia (2006); an Honorary Professor of several Russian and foreign universities; etc. Merzhanov was awarded the status of an Honorary Citizen of Chernogolovka (2001).

Alexander Merzhanov was not only outstanding scientist with exceptional intuition but also a dedicated educator. Indeed he brought up a vast group of scientists all over the world including Russia, FSU countries (Ukraine, Belarus, Armenia, Georgia, Kazakhstan), United States, China, Japan and many others. His teaching and supervision has resulted in 40 doctors of sciences and 150 candidates of sciences, many of which now occupy leading positions in numerous areas of chemistry, physics, mechanics, materials science, chemical engineering, catalysis, etc. No doubts that scientific directions established by him will have a long life in the works of numerous representatives of Macrokinetics School and this will be the best memory for the outstanding scientist and bright personality, Alexander Grigor’evich Merzhanov.

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1. COMBUSTION THEORY AND MODELING

HETEROGENEOUS COMBUSTION WAVE X-RAY RADIATION IN CASE OF NANODISPERSED Ti -B

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Recently it have been shown that during heterogeneous systems thermal explosion with condensed reaction products forming the high-temperature gas plasma and intensive electromagnetic radiation in UV and soft X-ray ranges (estimated quantum energy of ~4.5÷5.5 keV) have place [1-4]. This effect reveals themselves at start stages of chemical reaction at time range of $10^{-3}\div10^{-2}$ s. In [5, 6] has been proved that in course of Ni-Al wires twist combustion the non-equilibrium gas plasma with high electron temperature (more than 30000 К) is emitted from SHS zone. The temperature value is considerably higher than combustion adiabatic temperature. And forming plasma includes the metal vapors' in ground and ionic states.

In current work the additional study of emission spectra of SHS has been carried out in case of thin layer of nanodispersed mixture Ti + 31.5 (weight percent) B.

It is shown that combustion wave produce emission which give discrete exposure of X-ray film under Ti (20 μm thickness) and black paper (120 μm thickness) protecting screen. According to high-speed video-camera recording the wave velocity of about 0.2 м/s was estimated. The stochastic reaction sites (2÷5 мм) were observed. Probably these sites are radiation sources that explain the discrete exposure of the X-ray film.

Photometric measurements of X-ray films is shown that combustion wave spectrum corresponds to X-ray photon energy from 4.5 to 30 keV, and approximately 28 % of the flow give photons with E > 18 keV.

It might be supposed that during high-speed heterogeneous reactions in combustion wave the excitation of free electrons up to 30 keV energy values and higher values have place. The X-ray radiation is an effect of relationships between these electrons and protecting screen, correspondingly.

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SHOCK MODIFICATION OF REACTIVE MULTILAYERED MATERIALS

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Processes in chemically reacting systems are significantly multiparametric, and the macroscopic structure of concentration inhomogeneity of powder systems is the reason for the significant scatter of the observed conditions of synthesis and structure of the final product [1]. Layered (foil) chemically reacting systems are concentration-deterministic, that makes them an attractive object of study for construction a theory of multicomponent chemically reacting systems, and for experimental studies of the chemical processes kinetics [2]. Nature of the mechanical modifications of reactive medium is defined by the processes of energy dissipation in the local micro-volumes, characterized by different times of damage, phase transformations of components, initial conditions of non-stationary processes of dynamic compression, and, in turn, determines the degree of mechanical activation of the reacting components. The resonant modes of energy exchange in shock-compressed heterogeneous medium determined the conditions of shock initiation of chemical reactions in layered materials are studied. A dynamic theory of mechanical modification of layered materials, allowing predict the structure of the emerging activated areas of reagents is constructed. The possibility of changes in natural frequencies of microvolumes due to compression and change of the concentration-phase composition is taken into account. The feasibility of non-stationary processes of mechanical modifications, under the conditions of the resonant modes of shock compression is investigated. Evaluation of dynamic characteristics of the shock compressed reactive compacts allows to formulate a criterion for the onset of unsteady regimes of shock compaction and run of chemical reactions with taking into account the natural frequencies of structural elements (including the frequency of Rayleigh waves for multilayered compositions). The following scheme of investigation is suggested:

1. Determination of Rayleigh velocity of components;
2. Determination of the velocity of applied load;
3. Determination of natural frequencies of the elements;
4. Estimation of possible characteristic size of the texture of damaged material;
5. Estimation of energy balance during the process of shock modification, with taking into account the incubation time of damage;
6. Estimation of local parameters of the kinetics of chemical reactions;
7. Estimation of chemical conversion conditions.

The simulation of physiochemical processes in the Al-Teflon and Ni-Ti multilayered systems allow us to analyse the dynamic conditions of shock initiation of chemical reactions. Obtained results indicate the presence of a critical value of the amplitude of the shock pulse, the overcoming of which leads to a resonant mode at components and shock initiation of chemical conversions.

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COMBUSTION THEORY OF LAYERED SYSTEMS AND SYNTHESIS OF COMPOSITE MATERIALS IN A HIGH GRAVITY FIELD

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Combustion of heterogeneous systems in a high gravity field is an effective technology for the synthesis of composite materials [1, 2]. In this paper, we propose a mathematical model for combustion of a composite sample in a centrifugal unit. The initial layered structure is formed from mixtures with a different reactivity. The upper part of the sample consists of a mixture formed during combustion of a low-melting product (thermite mixtures). The lower part of the sample is a mixture formed during combustion of a high-melting porous product. Metallic melts (in the upper part of the sample) and high-melting materials, such as carbides, borides, etc. (in the lower part) can also be used in experiments. The mixture is ignited in the upper part of the sample. Under the action of capillarity and gravity, the melt flows into the pores, simultaneously initiates a chemical transformation, and forms a composite material.

The purpose of this study is to find the combustion characteristics of the porous gasless mixture in the lower part of the sample under conditions of conductive and convective forms of heat transfer; determine the propagation velocity of the combustion wave subjected to an overload and the stability, find the optimum conditions for the synthesis of composite materials in the high gravity field.

The numerical study of the mathematical model allowed us to find the critical conditions for ignition of the lower part of the sample depending on the overload a/g, porosity m_0 and parameters of external heat exchange (Fig.1). The decrease in porosity or centrifugal force below the critical value led to the fact that the combustion of the upper part of the sample did not ignite the lower layer. Under conditions of interphase and external heat exchange, the melt in the pores solidifies before the initiation of a chemical reaction in a porous media. In this case, the melt penetrates into the pores at a small depth.

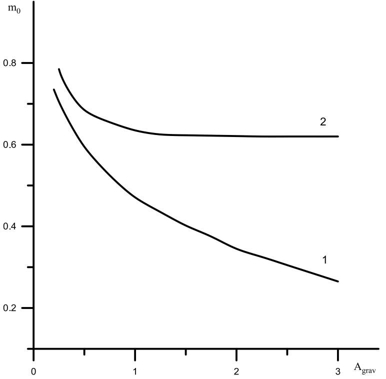

Fig. 1 Critical conditions for the ignition. External heat exchange B_0=0.001 (1); B_0=0.002 (2)

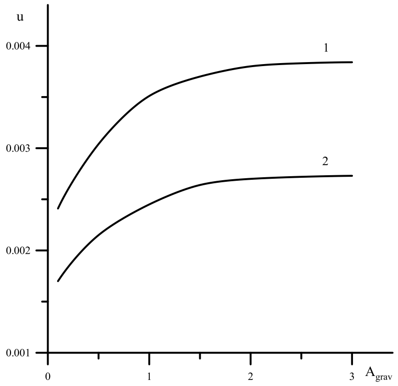

Fig. 2 The burning rate u vs. the gravity A_{grav}. Q=0.2 (curve 1), Q=0.1 (curve 2)

Figure 2 shows the numerical calculations for the combustion rate (u) of the lower part of the sample under adiabatic conditions depending on the overload and porosity. The influence of overload on the combustion rate can be explained by convective heat transfer from the zone of the reaction products to the heating zone of the porous layer in the direction of propagation of the combustion wave. A similar effect of increasing the combustion rate connected with heat recovery takes place during combustion of gasless compositions with a heat-conducting element [3]. For high values of the centrifugal force $A_{grav} \approx 3$, the dependence degenerates $u(A_{grav})$=const, which is explained by crystallization of the melt in the low-temperature part of the combustion wave and stopping the flow of a heat-transfer agent in pores. A similar dependence of the combustion rate was obtained in the experiments with the Ti-B system [4].

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SOLID FLAME PROPAGATION ALONG THE SPIRAL WIRE

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The theory of SHS processes considers two alternative mechanisms of the solid flame propagation: quasi - homogeneous (conductive), and heterogeneous (relay-race) ones [1]. In the former case, the temperature distribution over the medium particles is continuous, in the latter one - the temperatures of the neighboring particles differ by a finite amount. In papers [2, 3] the theory of a relay-race combustion was elaborated in application to the simplest model of a heterogeneous environment as a chain of individual reactive cells (particles) connected through heat exchange. A more comprehensive model of a heterogeneous environment was proposed in [4]. In that paper the experimental study of the solid state reaction wave propagation along the wire (thread) coiled into a spiral was conducted. In this system, there is a diffusion of heat along the wire, as well as the relay-race heat exchange between the spiral windings. Such a system is of theoretical interest, because it allows to track the interaction of quasi- homogeneous and heterogeneous mechanisms of solid flame propagation. Besides, there is a practical aspect of interest to the system of helical configuration linked to the issue of the possibility of temperature increase in the reaction zone, which is especially important for low-calorie SHS systems. For straight wire in which thermal interaction occurs only between nearest neighbors along the thread, the temperature in the adiabatic combustion wave may not exceed the value T_b, predicted by thermodynamic arguments. In the case of helical configuration, heat transfer occurs not only with nearest, but also with far neighbors, resulting in a direct transfer of energy stored in the products to unburned plots of the wire, which can lead to a temperature increase in the wave above the thermodynamic value T_b .

In this paper, the results of mathematical modeling of solid flame propagation in a spiral are presented. Analysis have shown that in the model under consideration a mechanism of the combustion wave propagation is determined by the value of quantity F

$$F = \frac{s^2}{12(1+As^2)}$$

Here A is the ratio of the characteristic times of heat release and heat exchange between the spiral windings, s - the ratio of the spiral coil length to the width of the preheated zone of the combustion wave propagated in a straight wire.

For $F<1$ the combustion wave has a typical for homogeneous system structure with a monotonic increase in temperature from the initial value T_0 up to a thermodynamic value T_b. A spiral wire configuration manifests itself in the effective thermal conductivity of the medium (λ_S), exceeding the thermal conductivity of thread material (λ) and a corresponding increase in the burning rate (U_S) compared with the burning rate of straight wire (U):

$$\lambda_S = \lambda(1+As^2),$$
$$U_S = U\sqrt{(1+As^2)}$$

The width of the combustion zone ($\Delta X_T \sim \lambda_S / U_S$) increases with the growth of A and s. With the rapid interturn heat exchange the heat penetration includes several turns of the spiral, and the system loses its heterogeneous features. Visually, it is perceived as wave propagation along the cylinder formed by a spiral, rather then propagation along the individual thread coil. An existence of similar combustion mode was observed in the experiment [4].

In the case of $F > 1$ (small values of A and $s >> 1$), the regime of combustion named in [4] pseudo spin is revealed. Combustion zone is much smaller than the length of the spiral coil. The reaction is localized at the spot with a temperature T_{m} greater than the thermodynamic value T_b.

The change of the settings A and s is an effective means of controlling the speed and temperature of the spiral wire combustion. For a fixed value $s >> 1$ the decrease of A causes superadiabatic increase of the temperature in the reaction site and the fall of the wave velocity, which is characteristic of a relay-race combustion mode. Increasing the length of the spiral coil is accompanied by an increase a speed of the wave and the significant temperature increase in the reaction zone, when the transition from quasi-homogeneous to the relay-race mechanism of the reaction wave propagation occurs.

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TOWARDS TO CONTINUOUS FILTRATION SHS PROCESS IN A COFLOW REACTOR

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SHS reaction in Metal–Gas systems under conditions of forced infiltration of gaseous reagent into a coflow reactor is one of promising techniques for synthesis of metal nitrides and hydrides. Similar scheme is being widely used in numerous technological applications such as production of pig iron, calcination and agglomeration of ores, regeneration of catalysts, oil extraction by in-situ combustion, etc.

Basic advantages of SHS processes in conditions of forced infiltration of gaseous reagents have been outlined in several publications [1–5]. One of these is the use of gas reagents diluted with an inert gas, which favors the elimination of impurity gases dissolved in solid particles of a solid reagent. Another is the feasibility of regulating the combustion temperature within relatively wide limits. At a sufficiently high gas permeability of porous medium, continuous autowave infiltration-mediated technological combustion can be organized on an industrial scale [4]. A drawback of coflow SHS reactors is a typically low gas permeability of metal powders used as a solid reagent. Last study showed that this problem may be essentially overcome by using a granulated mixture of green powder [3].

There are also some gas dynamics problems in conducting of SHS process under conditions of forced infiltration of gas reactant. It has been shown [6] that, in conditions of forced infiltration of gas reagent, the planar combustion front may become unstable and acquire the shape of the Saffman–Taylor fingers. Self-structuring of reaction fronts into fingering configuration in diverse physicochemical processes is also of current interest for general nonlinear physics. In technological SHS processes, the effect of fingering instability is exceptionally undesirable since in this case the conversion of green mixture into product turns out incomplete. In this context, a theory of such processes must be able to predict process conditions at which the combustion front retains its planarity over the entire reactor width (cross section) as a prerequisite for utmost extent of conversion.

The results [6] were obtained under the assumption that the width of combustion zone was negligibly small compared to that of the reactor channel, which implies an infinitely high rate of physicochemical processes taking place within the combustion wave. In this work, we numerically modeled frontal filtration combustion (FC) using the thermo-diffusional and kinetic factors that ensure a finite width of combustion wave commensurable with the width of the reactor channel, with special emphasis on planar front stability issues. A mathematical model includes the basic equations describing FC process [5] and takes into account that during combustion the porosity, thermal diffusivity, and gas permeability of the medium may change. The time dependent initial value problem was considered in 2D geometry simulating a slit-like reactor. The results of computations showed, that at certain conditions the initially planar combustion front is transformed and takes a form of the finger as Fig.1 illustrates. In particular, a finger effect appears in the case when a permeability of porous medium increases due to conversion of green mixture into the product. If permeability of the burned mixture exceeds that of green mixture, a steady planar reaction front propagation establishes no matter on the ignition conditions.

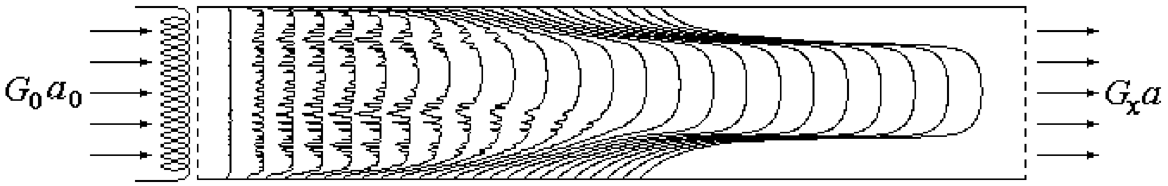

Fig.1 Dynamics of the reaction front propagation after a planar FC wave initiation.

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CHARGE TRANSFER DURING COMBUSTION SYNTHESIS OF SULFIDES

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Our recent numerical and experimental investigations [1] have revealed the critical role of gaseous phases in charge transport during the combustion synthesis of sulfides (CSS). Nevertheless, it is well known [2, 3] that distribution of electric resistance of solid in a combustion wave may have the strong effect on the wave mode stability and propagation under absorption of an external electromagnetic field and consequently under the similar conditions it may influence on charge transport in CSS also. In this paper we report the experimental results and based on them theoretical predictions of the impact of solid phases into charge transfer during CSS. Thermal instability of the CSS front caused by the distributed resistance in solid which turns out as an alternative way to charge transfer by gas convection. The experiments demonstrated that for different argon pressures the combustion front velocity by the reaction Zn + S = ZnS doesn't exceed ~7 mm/s.

Figure 1 shows the temporal electric voltage (with absolute value of 4 V), electric resistance and temporal reaction temperature generated by a planar thermal front during the combustion synthesis of ZnS. Duration of the voltage rise appears to be much shorter (0.2 s) than that of the voltage decay (0.8 s). We should notice that in each experiments we always measured a negative potential on the upper electrical probe. The upper probe is charged negatively independently on the ignition place (top or bottom) as well as on the sample length. These experimental facts may be explained by generation of a negatively charged gas during the CSS reaction only. To describe numerically the complex electro- and gas-dynamic features of the CSS we used two-level approach developed by Markov [4] who investigated cooperative multiphase processes in the course of Chemical Vapor Deposition (CVD).

While the CSS model equations with the exception of kinetics on a microscopic level are completely similar to those in the carbon combustion synthesis of oxides (CCSO) model [5] on the macroscopic level they are strongly different from those. The purpose is that in addition to mass transfer they describe also transfer of the charged carriers: ions, cations, as well as electrons and electron holes. The law of conservation of matter in gas phase follows to:

$$\frac{\partial \chi \rho_{\mathrm{g}}}{\partial \mathrm{t}} + \nabla \cdot \left(\chi \rho_{\mathrm{g}} \mathbf{u} \right) = \left(1 - \chi \right) \mathrm{J}^{\mathrm{macro}}_{\mathrm{s} \to \mathrm{g}}$$

Here is similar to the quasi-steady approximation in which the fluxes $\mathrm{J}^{\mathrm{macro}}_{\mathrm{s} \to \mathrm{g}}$ of gas-solid interaction are determined by the reaction kinetics.

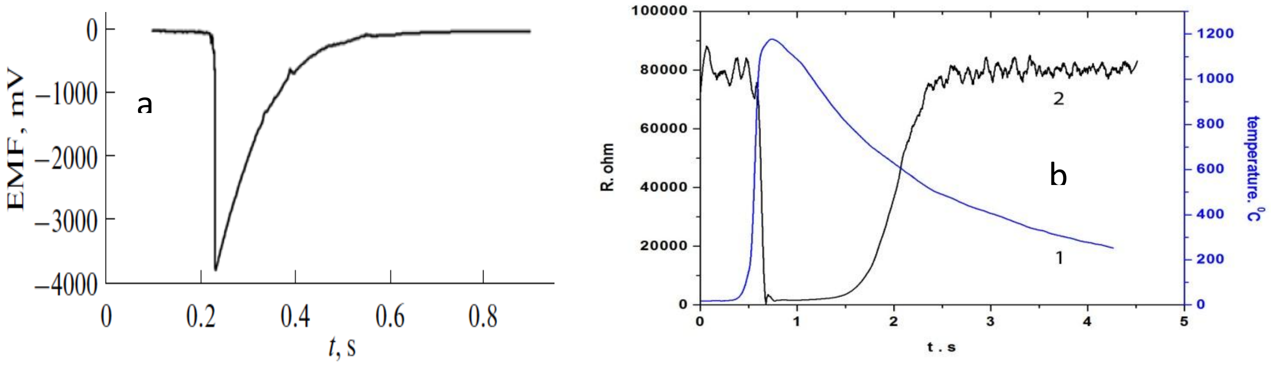

Figure 1. (a) – Temporal temperature, and (b) - Temporal electric resistance of solid during CSS (curve 2) and temporal temperature of Zn + S = ZnS (curve 1) measured in-situ.

The simulation demonstrated that the rate transfer of solid components is limited by their diffusion and is slow, while motion of sulfur vapors, which contain charged ions and electrons proceeds much faster, forming a vapor cloud charged negatively ahead of the combustion front.

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WAVE PROPAGATION LIMITS FOR FILTRATION COMBUSTION

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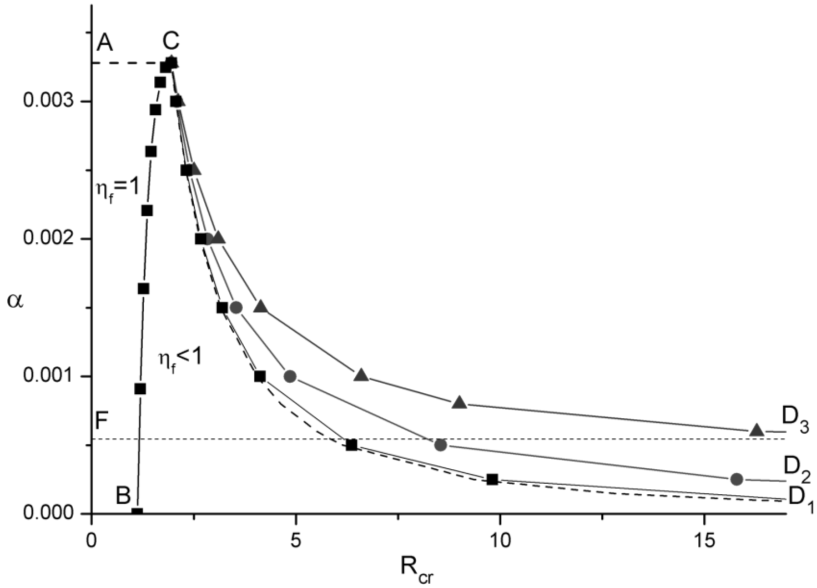
In SHS practice, gas-solid combustion modes with natural infiltration of oxidant are most popular. In reality, combustion is always proceed on conditions of heat sink to the environment, which leads to a decrease in combustion temperature and hence in burning velocity. The presence of heat sink is known to result in appearance of wave propagation limits, the critical drop of combustion temperature is a characteristic interval and accordingly the burning velocity decreases by a factor of $\sqrt{e}$ [1]. In the theory of filtration combustion, the effect of heat losses was analyzed only for the case when all sample boundaries are gas impenetrable except for one which is open to exchange with a large bath of gas [2]. The reaction is initiated at the opposite end of the sample and all gas to combustion front is supplied from outside (the initial gas content in pores was not taken into account). It has been shown that in this case two combustion modes are possible, with complete (a) and incomplete (b) conversion. In case (a), the combustion limit exists in full accordance with general combustion theory [1] but in case (b) there was no any combustion limit. At high pressures, the amount of gaseous reactant in the pores becomes sufficient for maintaining combustion even without external gas supply. Such a situation was analyzed [3] for steady filtration combustion in adiabatic conditions. The effect of heat loss in the absence of external gas exchange was analyzed in [4] and the existence of combustion limits was found for both cases (a) and (b). In view of the above discrepancy, it seemed interesting to revise the effect of heat losses on the basis of a generalized mathematical model.

The results of analytical solution to the problem are presented in the Figure showing the dependence (CD_i curve) of critical value of parameter R (that defines a combustion mode) on heat-transfer coefficient α for three initial gas pressures p_0. At a given level of heat losses (α), combustion is only possible for $R < R_{cr}(\alpha)$. The range of combustion mode (b) ($\eta_f < 1$) is under the BCD_i curves. Transition from mode (b) to mode (a) takes place on the curve BC.



Horizontal straight line AC corresponds to the extinction of mode (a). The dashed curve close to CD_1 ($p_0 = 0.1$) corresponds to the boundary of mode (b) within limits of low initial pressure (this border approaches asymptotically to the abscissa axis). With an increase in p_0, the CD_i curves at large R approach not to the abscissa axis but to some horizontal asymptote such as FD_3 (in case of p_0 = 0.7). Position of such asymptotes is defined by some critical value of α for the steady combustion sustained only by the gas reactant initially located in the sample pores [4]. The larger p_0, the higher is position of the respective asymptote. For a given p_0, the combustibility limits are confined by the ACD_i curves. Beyond this region combustion is impossible because of too high heat losses.

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MODES OF SOLID-PHASE SYNTHESIS DEPENDING ON THE DISPERSITY OF THE MIXTURE AND DURATION OF THE SHOCK WAVE

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Prospects for production of new materials with improved properties are connected with obtaining metastable compounds in non-equilibrium conditions. Explosion loading provides great opportunities to control the creation of such materials. These processes are accompanied by structural changes and often chemical reactions. As previously thought, high temperatures were a sufficient condition for initiation and development of exothermic reactions. In fact, the initiation, subsequent development and total completion of chemical reactions in the shock wave depends on the amplitude and duration of the shock wave, and high temperatures are an additional contribution to the development of synthesis. The initial dispersity of the mixture also influences on the initiation and development of solid-phase synthesis reactions. The lower the dispersity of components in the mixture, the less favorable conditions to complete the synthesis under identical loading conditions of multicomponent mixtures.

The purpose of this work is to numerically study the modes of solid-phase synthesis of aluminum sulfide (Al_2S_3) synthesis depending on the initial dispersity of the mixture from aluminum and sulfur and duration of shock waves on the basis of a multicomponent medium model [1].

Numerically in the axisymmetric formulation we considered explosive loading of a steel cylindrical ampoule that contained a porous mixture of aluminum and sulfur (Al-S). The composition of the mixture was 0.65 mass fractions of sulfur and 0.35 mass fractions of aluminum, which corresponds to the stoichiometric ratio of the Al_2S_3 formation. The action of explosives surrounding the ampoule was simulated in the calculations by the action of pressure from explosion products on the horizontal layer of the ampoule. The detonation velocity was 3.3 km/s on the basis of experimental estimates [2]. The duration of the shock wave was changed depending on the diameter of the explosive.

In the paper we assumed that the pressure criterion for the initiation of a chemical reaction, and the rate of reaction depend on the initial dispersity of the mixture. For the powders of aluminum and sulfur with a low dispersity, we chose the temperature criterion T_η = 933 K (the melting point of aluminum) and the pressure criterion P_η = 1.6 GPa. The rate of chemical reactions K_0 was 240.8 GJ/(kg*s). For the powders of aluminum and sulfur with a high dispersity, T_η = 933 K, P_η = 1.0 GPa. The rate of chemical reactions was 280.8 GJ/(kg*s). The initial porosity of the mixture (the ratio between the pore volume and the total volume) was 40%.

We found that the process of chemical transformations proceeds in three stages, including an intermediate stage when the reaction stops. Behind the front of a shock wave in the case with a low dispersity and short time of loading, the reaction stops, since the pressure criterion is not satisfied, and the temperature criterion for initiation of the reaction is not steel reached. Then the chemical reaction is again initiated due to performance of the temperature criterion and completed totally. In the case with a long time of the shock wave action and high dispersity of the mixture, the reaction proceeds in a two-stage regime: initiation in the passing shock wave due to performance of the pressure criterion and total completion behind the passing shock wave due to achievement of the temperature criterion.

We found out the contribution of pressure to the development of solid-phase synthesis in the lower part of the ampoule due to the shock wave reflected from the lid of the ampoule, but this effect is limited in time.

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COMBUSTION MODES OF TERNARY SYSTEM TITANIUM–ALUMINUM–NITROGEN

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The ternary system titanium–aluminum–nitrogen is of great interest from the scientific point of view as well as from the viewpoint of practical application of the obtained combustion products. The scientific interest consists in experimental investigation of filtration combustion regularities of the system in which several simultaneous competitive reactions are possible. In addition to two parallel gas–solid reactions such as titanium–nitrogen and aluminum–nitrogen with formation of nitrides, the reaction between solid reagents titanium–aluminum with formation of intermetallic compounds is possible. These compounds can react with nitrogen. Besides, the formation of triplex compounds titanium–aluminum–nitrogen is possible too. These compounds belong to MAX phases which are of great interest nowadays and they possess unusual combination of properties. On the one hand they are characterized by high electric and heat conductivity and machinability like metals. On the other hand they are distinguished by high thermal and oxidation stability like ceramic materials.

The aim of the present work was to investigate combustion modes of the ternary system titanium–aluminum–nitrogen depending on the chemical and phase composition of the initial mixture of solid reagents and the initial pressure of nitrogen.

For preparation of the initial mixture we used powders of titanium, aluminum and intermetallic powder TiAl. These powders were mixed in the planetary ball mill during 20 minutes. The prepared mixture with the bulk density was placed into the filter paper vessel of 15 mm in diameter and 50 mm in height. Thermal couples WRe5/WRe20 were installed at the preset destination for measuring the combustion velocity and temperature. The experiments were carried out in the reactor under nitrogen atmosphere. The burnt specimens were analyzed by means of X-ray phase analysis and scanning electron microscopy.

Video recording shows that in the system under study we can observe a large variety of combustion modes depending on the composition of the initial mixture and the initial pressure of nitrogen. Besides the well-known stationary combustion modes (layer-by-layer and surface burning), the multipoint (flickering) mode is observed. Sometimes the multipoint mode changes into the mode of several hot spots. And in some cases we deal with one hot spot moving in a spiral, so called a classical spin mode.

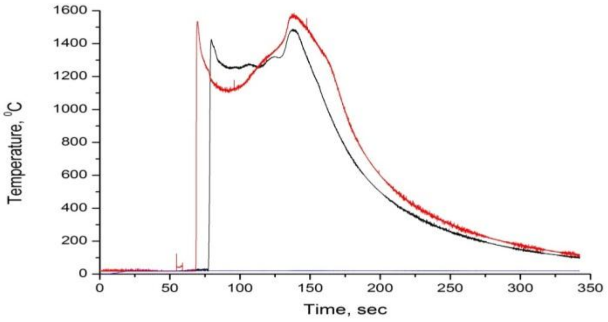

Figure 1. Thermocouple readings.

It is well-known that in the case of the surface combustion mode the stage of the front propagation is changed by the stage of after-combustion when the samples keep on lightening due to nitrogen consumption in the internal layers. Besides, a well-pronounced change of stages was observed in the system under study. After the shining front propagation the sample was cooled to disappearance of the visible lighting. And then it began shining again with the growing intensity. In fig.1 you can see the thermocouple readings for the combustion of TiAl and Ti powder mixture (molecular ratio 1:1) under nitrogen pressure of 2 MPa. The first sharp temperature growth corresponds to the combustion front propagation. The medium velocity was 2.2 mm/sec. Then the sample was cooled, the external lighting disappeared although the temperature in the sample axis was above 1000ºC. The second stage of the exothermic interaction was characterized by the temperature higher than that of the first stage. Moreover, it occurred in the whole volume of the sample. It was proved by the visible lighting of the entire sample and almost simultaneous achievement of the second temperature maximum registered by the thermocouples situated 20 mm apart.

To sum up, the carried out investigations of the ternary system titanium–aluminum–nitrogen revealed the interesting picture of this process with different combustion modes and put a set of questions. The answers to these questions should be found in our forthcoming investigations.

THE CELLULAR MODES OF FILTRATION COMBUSTION OF THIN LAYERS OF METAL POWDERS

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In conditions of instability, a planar front of infiltration-assisted combustion was found to split into individual hot spots (cells) propagating in an oscillation mode and leaving behind combustion products with the imprints of their periodic motion. Discussed are some subtle details of the phenomenon.

As reported in [1], the unsteady planar front of infiltration-assisted combustion, also known as filtration combustion, can (in conditions of limited supply of gas reagent) degenerate into individual self-sustained combustion spots (cells). Qualitatively, the process can be compared with formation of the cellular structure in gaseous flames [2].

We propose and justify a simple algorithm for the experimental study of filtration combustion for the experimental study of filtration combustion in a quasi-two-dimensional approximation. The nonlinear dynamics of cellular structure of the filtration combustion front have been studied using this algorithm. The pulsating mode of motion of cells of exothermic chemical conversion was found for the first time. It is shown that instability causes a flat filtration combustion front to “split” into individual cells of exothermic chemical conversion, which leave behind condensed products in the form of strips while moving in the condensed medium layer. The cell can grow and divide or, vice versa, reduce and die.

The titanium powder was used as the condensed porous reagent with a layer height equal to 2,5 mm. The gap between the quartz glass and the titanium layer was 4-3 mm. Atmospherics air was selected as the active gas reagent. It is known that titanium actively interacts with oxygen and nitrogen at high temperatures to form condensed TiO_2 and TiN. The powder layer was smoothed and slightly compressed. In the presence of gas-reagent deficiency , the rectilinear front broke up into separate cells of almost identical characteristics size with a certain distance between them.

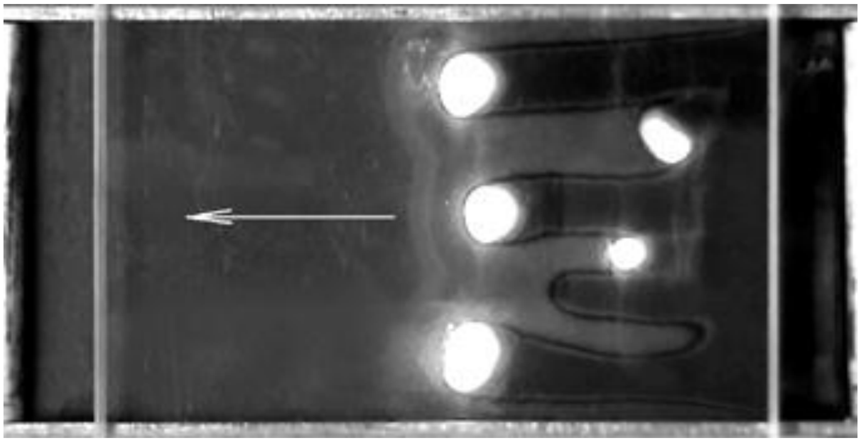

Figure 1. Top view on the reacting layer during the cellular combustion.

During the motion of cells, the products of combustion cooled and formed a trace that different in color from the initial titanium. The brightness of individual cells could vary time in time and be different cells. A direction of spot (cell) motion is defined by a local temperature at the edge and conditions of gas supply. Frontal expansion (degenerate combustion) creates a new reaction zone in front of cell. The instability of a planar front with such structure give birth to a new cycle of periodic front propagation. The process remind breaststroke swimming: strong stroke of hands ahead (thermal explosion), movement of hands aside (frontal combustion solid reagent), and preparation to a new cycle.

At limited access of a gas reagent, the cell tears off from the warm-up zone toward the direction of a gas infiltration and forms a new cell. We proposed and implemented a simple, visualy acceptable method of the experimental investigation of nonlinear dynamics of propagation of the cellular filtration-combustion front for condensed reaction products. We showed the possibility of occurrence of cellular structure of the chemical interaction as a result of destruction of an unstable filtration-combustion front. The periodic pulsing mode of the cell propagation was found.

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MATHEMATICAL MODELING OF COMBUSTION METAL POWDERS IN A QUASI-ISOBARIC FLOW OF THREE-COMPONENT GASEOUS REAGENT

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A mathematical model of two-zone infiltration-mediated combustion of a porous solid reagent (Ti) in an isobaric counter flow of three-component gaseous reagent (air) was constructed and numerically analyzed. We explored structural features, stability issues, and also the influence of inert impurity gas on the initiation and structure/stability of two-zone combustion waves.

Infiltration-assisted combustion (also termed filtration combustion, FC) is a kind of SHS processes promissory for industrial-scale implementation. Mathematical model of FC in porous media was suggested in [1-3] with special emphasis on stability issues.

Since in reality gaseous reagents are mostly multicomponent, this can result in the onset of combustion modes with spatially separated reaction zones. Multistage combustion of porous media is controlled by infiltration of gas reagents into a porous body. Moreover, the process is additionally complicated due to formation of inert product. At the same time, some solid reagents (such as Ti) are capable of reacting with both nitrogen and oxygen from such a gaseous reagent as atmospheric air. The process can also be affected by evolved inert gases (such as argon).

In the present study, we explored the structural features and stability of tandem-like double wave of infiltration-mediated combustion propagating over a porous solid reagent (Ti) in an isobaric flow of three-component gaseous reagent (air) and suggested an appropriate mathematical model.

The combustion geometry and top view of the reactor are presented in Fig. 1. During combustion, gas reagent (air) is allowed to enter inside at rate V through a slit left at the left. Infiltrating air is assumed to contain nitrogen in concentration c_1, oxygen in concentration c_2 and inert impurity (Ar) in concentration c_3.

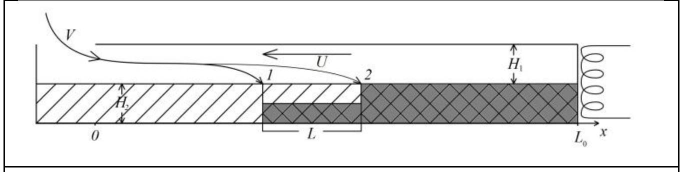

Fig. 1. *1*, first wave zone; *2*, second wave zone; *U*, burning velocity; *V*, rate of gas supply; H_1, air gap height; H_2, height of charge layer (Ti powder); and L_0, sample length

Transversal gas motion and temperature profile will be neglected. According to [2], the measured pressure difference before and behind combustion front was below $10^{-4}\,\text{atm}$. This gives us grounds for applying a quasi-isobaric approach to our analysis.

The analysis of non-stationary filtration combustion modes, taking into account the multicomponent gas mixture, showed high sensitivity of the filtration front structure to the concentration of inert gas. It is shown that the accumulation of inert gas components in the area of the products leads to a change in the structure and in the dynamics of a two-stage front. The conditions of control and separation modes have been found. It is shown that increasing the concentration of the inert gas in the mixture leads to increasing the distance between the reaction zones in control mode and decreasing the thermal interaction between the high-temperature zones. This reduces the velocity of the front and temperature in each of the reaction zones. It is shown that the maximum flow rate of gas is achieved in the transition area from the complete transformation of the condensed phase to the incomplete transformation. For small values of porosity, where we have the regime of incomplete burning, the speed of the front, temperatures in the zones of the two-step reaction front, depth conversions condensed components increases.

Stability of a two-zone combustion wave is defined not only by heat transfer parameters but also on the parameters of gas supply to the reaction zones. It was established that with increasing fraction of inert gas in a mixture the combustion front stabilizes.

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USE OF THERMODYNAMIC MODELLING FOR OPTIMIZATION OF SHS COMPACTION-BASED METHOD FOR PRODUCTION OF MATERIALS

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Functionally graded materials produced by SHS compaction are essential for civil and military aplplications including such important area as productioon of high-durability light armour. The quality of the SHS compaction product depends on its micro-structure and such characteristics as porosity, mechanical strength and hardness. These properties are strongly influenced by phase transitions and structure ransformations occurring during SHS of the material [1, 2]. Therefore, thermodynamic modelling seems to be a promising instrument for the optimization of SHS compaction-based production method.

The optimized thermodynamic modelling results in better understanding of important properties of the materials in question as well as allow one to improve the accuracy of their phase diagram plotting and analysis. The use of databases containing optimized thermodynamic model parameters lead to more reliable prodictions for characteristics of recently developed and novel materials.

With a view to the theoretical study of phase transformations in the Ti–B alloys and plotting the corresponding phase diagram, the compilation-optimization procedures were carried out for metals, compounds and irregular solutions of data bases (PURE, PSUB, SSOL, PBIN PKP) belonging to the Classical Version Thermo-Calc (TCC) [3]. These procedures involved determination of the number of the parameters characterising interactions between the elements of liquid and solid solutions and for metallic compounds and estimation of their values [4]. The obtained numerical values were entered into the Local Databases (TDB) of the program Thermo-Calc.
According to calculation of the phase equilibriums and the topological analysis for the binary Ti–B mixture, the minimum temperature for the $TiB_{0.6}$ synthesis is 1810 K. This limiting temperature is also preferable for the synthesis of high-density TiB. The minimum temperature required for the successful SHS compaction of TiB_2 was found to be significantly higher (2440 K). In general, these requirements can be explained by the necessity of the presence of liquid phase in the compacted SHS product which facilitates the plasto-elastic deformation shrinkage and a decrease in the closed porosity. As a result, one can obtain a desired high-strength material characterized by a minimum level of the residual stress ensuring higher resistance to internal structure collapse.

From the viewpoint of energy efficiency, for the optimization of the temperature status of the SHS compaction product the utilization of the heat released during the synthesis seems to be quite reasonable. For this to achieve, one needs to minimize the released heat loss before the compaction stage is complete. Some data on tests of a new press-die which design ensures a reliable heat insulation of the SHS-product due to its continuous vacuumization during the entire process of SHS compaction are presented. The rigid porous quartz band provides both required heat insulation of the hot SHS-product and impurity gases extraction into the vacuum piping connected to the press-die. The temperature of the walls of used press-die was found to reach only 120–170 ^{o}C which is significantly lower than the temperature of traditional press-dies (450–500 ^{o}C) heated-up during SHS compaction.

Obtained theoretical data on thermodynamic modelling of SHS compaction of the Ti–B-based individual and functionally graded materials are presented. Results of the testing of the new vacuum press-die for SHS compaction of the Ti–B-based materials are given.

Due to the improved heat insulation and press-die vacuumization, the SHS compaction product exhibited denser and stronger structure (Fig. 1).

Fig.1. Macrostructure of the functionally graded material

The photo of the fracture surface of functionally graded material obtained under regular SHS compaction is shown on the left side while the macrostructure of the same material sample synthesized in the new press-die provided the improved heat insulation and vacuumization is shown on the right side. The average value for the micro-hardness of the second sample in the TiB layer is 22900 MPa, in the TiB_2 layer, 31400 MPa.

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SIMULATION OF SHOCK COMPRESSED REACTIVE POWDER MATERIALS

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Exothermic chemical reactions in powder mixtures under shock compression are considered. The macroscopic structure of concentration inhomogeneity of components and specific pore volume formed during the preparation of the mixture and pre-compaction is taken into account. Element of the macroscopic structure is considered as a representative volume of the reacting medium - the reactive cell. Reactive system is represented by heterogeneous system of components with defined structural parameters, physical and chemical characteristics. Material of separate component is homogeneous and isotropic with specified physical properties. A model of physical and chemical processes in the shock loading reactive powder mixtures [1] based on the approach that combines elements of discrete and continuum approaches is developed. The mathematical model is represented by a set of non-stationary problems of thermal balance, shock modification of the powder material, forced filtration, macrokinetics of chemical reactions. The basic concept of modeling completed with taking into account the heterogeneity of plastic deformation of the powder particles, the incubation time of the phase transitions, the kinetics of the development of powder components damage during dynamic deformation. Thermomechanical state and phase composition of the reactive medium are considered at the macro and micro levels. A hierarchy of spatial and temporal structures of nonequilibrium physical and chemical processes leading to the formation of structures synthesis product, initiation and run of ultrafast chemical reactions in reactive powder mixtures at the shock pulse front is considered.

Simulation of the shock modification of reactive powder mixture is carried out on basis of the energy conservation law. The characteristics of the porous medium behind the shock pulse are considered as effective mechanical parameters of the final state of the powder compact. It is supposed that during the shock compression the energy is accumulated with a constant velocity. It is assumed that the dissipation processes can be separated into two states [2]: during pore closure and afterward. These processes lead to the increase in the reactivity of the reactive mixture – mechanical activation. At first state the plastic deformation of particles into pores takes place, and at the second state pore collapse is accompanied by shear localization resulting in destruction of particles surface layers. The shock pulse energy can be spent on work to eliminate the oxide and adsorbed layers from the particle surfaces. In this case, the existence of the incubation period of destruction, instant and current damage level of the particulate material, gives a chance for adequate modeling of the physical process at the shock pulse front [3]. This approach allows us to consider initial and the current levels of shock activation of reactive powder components.

The algorithm of the numerical solution of imitating simulation problems is developed on the basis of the created model, providing the solution of the connected problems of mechanical modification of a powder mixture during dynamic loading, a macrokinetics of chemical reactions, thermal balance and a filtration of a liquid phase in view of the kinetics of mechanical damageability and phase transitions. Every model parameters are refined via the iterations. The changes of components concentration, porosity, phase states are taken into account.

Product of mechanochemical transformations is a composite material composed of the structural elements of the initial mixture components and the reaction product. Linear dimension of the structural elements of the product of chemical reactions depends on the size of the mechanically activated zones of the particles of the reacting components.

The simulation of physiochemical processes in the Ni-Al and Ni-Ti powder mixtures allows us to analyse the influence of phase transition and the convective mechanisms of phase and mass transfer on the kinetics of different conditions of synthesis processes as well as the conditions of the formation of the macroscopic structure of physiochemical transformation product.

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ACOUSTIC EFFECTS IN A WAVE OF ORGANIC SHS, THEIR DIAGNOSTICS AND INTERPRETATION

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The emission of sound waves in the range of 20 Hz - 20 KHz accompanying appearance and moving of chemical exothermic waves in a mix of organic powders was studied for the first time at reaction of oxyhalogenation [1] and other.cExperimental device for acoustic diagnostics of organic SHS (OSHS) processes [2] has been designed and constructed. It includes the specific reactionary cell placed in the multilayered soundproof camera, the parabolic concentrator of sound, sensitive detectors, the computer recorder and the spectral analyzer of acoustic signals.

The technique for acoustic measurements at low-temperature interaction (less then 300 ^{o}C) of organic or inorganic powders mixes in mode of OSHS was developed. It includes registration and processing of signals of the acoustic phon, useful signals from the reacting medium and from the special acoustic labels entered in a reacting mixture.

Acoustic signals from reacting mix were written, their dynamics was investigated, the spectral analysis, including differential analysis, - was carried out. Correlations between macrokinetic and acoustic features of OSHS wave, and also structure of the final product are found out.

It is shown that the acoustic wave emitted from traveling wave of OSHS, have the spectrum specific to chosen reacting systems. It contains the information about reaction wave location, character of mass-transfer, cracking of crystals and other processes accompanied by movement of the reactionary medium. On the Figure 1 the spectra of acoustic emission from a reacting mix (top figure) in comparison with a phon signal (bottom figure) are resulted.

The possible assumption about the nature of acoustic waves at OSHS, relation of emission peaks in acoustic spectrum with concrete processes in the wave of OSHS was made.

Preliminary researches of organic crystals thermal cracking (> 15 kHz, high frequency range), formation of bubbles in reactionary melt and porous structure of the final product (~ 1,7 kHz, low frequency range) were carried out (Figure 2) on the basis of acoustic date.

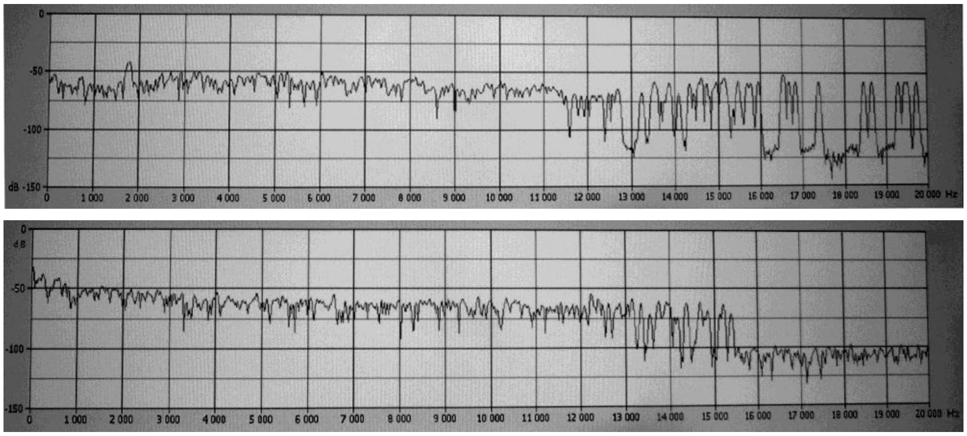

Figure 1. Acoustic spectra (intensity, dB – frequency, Hz).

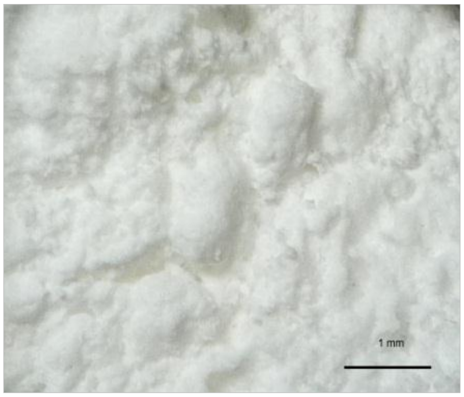

Figure 2. Microstructure of the product.

The study made has allowed tooffer above-mentioned acoustics techniques as effective in-situ method for diagnostics and studying of such thin features of OSHS mechanism, which are unaffected at studying with other traditional methods of research.

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ELECTRIC AND MAGNETIC FIELDS-RELATED EFFECTS IN THE COMBUSTION SYNTHESIS OF ALUMINIDES IGNITED BY MICROWAVES

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Microwave (MW) energy can be used to ignite combustion synthesis reactions in order to completely convert reactant mixtures and obtain peculiar microstructures [1, 2]. With respect to more conventional ignition techniques, the use of MWs suffers from usually poor reproducibility due to the possible electromagnetic field distribution-related ignition mechanisms. Indeed, ignition can occur by direct interaction of the reactants with the electromagnetic field, or by their indirect heating by the use of microwave co-absorbers or due to the possible occurrence of breakdown phenomena [3]. In the present study, microwave ignition of mixtures of powdered metal reactants, one of which is aluminium and the remaining one is of ferromagnetic nature (Ni, Co, Fe), was performed in regions of predominant electric or magnetic field of a microwave applicator operating at 2.45 GHz. These reactions, when a high heating rate is applied, are usually preceded by the formation of liquid aluminium, which then reacts with the other elements to form the corresponding intermetallic phases [4]. The aim of the work is to improve the process reproducibility and to propose new strategies to optimize the synthesis of high purity aluminide intermetallics.

Microwave ignition in predominant electric field regions resulted less reproducible than in case of magnetic field due to arc generation phenomena. In the experimental conditions investigated, ignition in predominant magnetic field resulted possible and occurred more rapidly, provided the Curie temperature of the ferromagnetic powders in the load is higher than the melting point of aluminium. The obtained experimental results were concurrently supported by a numerical simulation approach, in order to investigate the different microwave power penetration depth (skin depth) profiles, deriving from the different configurations of the load into the MW single mode cavity. In this way it resulted possible to predict the microwave ignition mechanism, as well as the ignition region of the exothermic reaction. With the same approach it resulted also possible to estimate the different contributions to the overall microwave power densities deriving from E and H field strength values, thus evaluating which configuration allowed also a moderate preheating of the reactive specimen prior to ignition. Moreover, despite the lower reproducibility, during combustion synthesis, and after its completion, it was found that the obtained aluminides can be heated more efficiently by exposure to electric field, and this can be proficiently exploited to provide energy to the reaction front, thus altering the products cooling rate and the resulting microstructure [2].

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COMBUSTION OF Ti–C POWDER BLENDS UNDER QUASI-STATIC PRESSURE

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Despite a huge number of theoretical and experimental studies on combustion of heterogeneous condensed systems, the influence of pressure applied to a burning sample on the parameters of combustion has not been studied so far and still remains unclear. Meanwhile, applied pressure could be expected to improve contact between reacting particles and thus to raise the thermal conductivity and heat release rate. Relative contribution from the processes of mass/heat transfer is a key point in the combustion theory of heterogeneous systems.

In this work, we investigated the phenomenology of combustion in compressed Ti + C powder mixtures. Ti + C mixtures were prepared from the powders of titanium (PTK, brand, mean particle size <180 μm, >99.5% pure, hereinafter Ti I), titanium (PTM brand, mean particle size <45 μm, >99.1% pure, hereinafter Ti II), carbon black (P804T brand, <1 μm, 99.5%) and diamond (DAGk 20, specific surface 30–60 m^2/g). Cylindrical green pellets (ϕ = 12 mm, l = 15–30 mm) with a relative density of 0.6 were obtained under a pressure of 200 kg/cm^2.

Compression pressure was varied between 1 and 100 MPa and kept applied during experiment. A voltage difference arising in the sample during combustion was detected with two electrodes made of a Ni foil 100 μm thick and 1 mm wide. Propagation of combustion wave was also monitored with photodiodes via two silica lightguides.

Figure 1 shows burning velocity as a function of applied pressure for Ti **I** + C, Ti **II** + C mixtures. With increasing of compression pressure, the values of burning velocities are seen to initially grow, attain their max value, and then gradually decline. The largest value of burning velocity was observed for Ti **II** + C mixtures, which is one order of magnitude greater than that in the absence of applied compression pressure.

Obtained results can be associated with the influence of several factors. It is known that combustion velocity is proportional to thermal conductivity of burning material, heat release rate and inversely proportional to the size of reagent particles. We assume that applied pressure improves the surface of contact between the particles of heterogeneous mixture. It leads to an increase in thermal conductivity of samples.

With increasing applied pressure, the combustion temperature decreased as well as the burning velocity. This was also supported by the data of elemental analysis of end product: with increasing of pressure, the free carbon content grew from 0.3 to 2.1 wt %.

Figure 2 shows burning velocities for systems Ti **II**–C (carbon black) and Ti **II**–C (diamond) as a function of carbon content (P = 8 MPa). Maximal burning velocity was attained during combustion of stoichiometric compositions. Deviation from stoichiometry leads to a decrease in burning velocity. In spite of different reactivity of carbon black and diamond, combustion limits are achieved at the same concentrations of carbon.

Maximum burning velocity for Ti **II**+ carbon black is 230 mm/s, and 40 mm/s for Ti **II** + diamond. The difference can be associated with different reactivity of carbon black and diamond, but critical burning velocities are almost equal. It is caused by increasing warm-up time nearby combustion limits and by phase transformation of diamond into graphite. Thus reactivity of carbon and burning velocity are increasing. The transformation of diamond into graphite was confirmed by XRD and SEM.

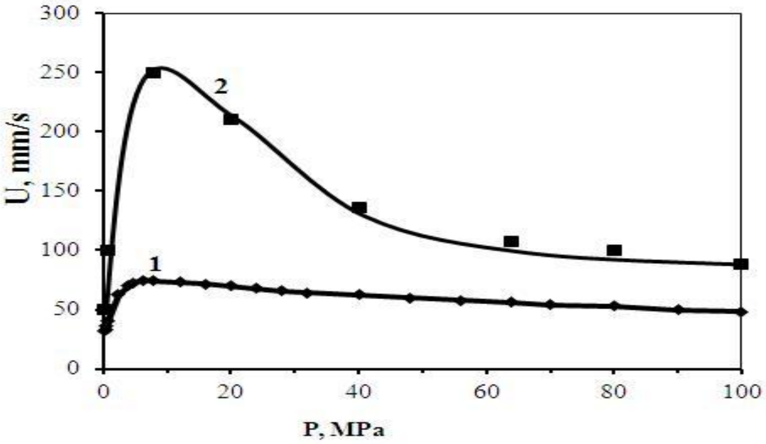

Figure 1. Burning velocity U as a function of applied pressure P for (*1*) Ti **I** + C, (*2*) Ti **II** + C mixtures.

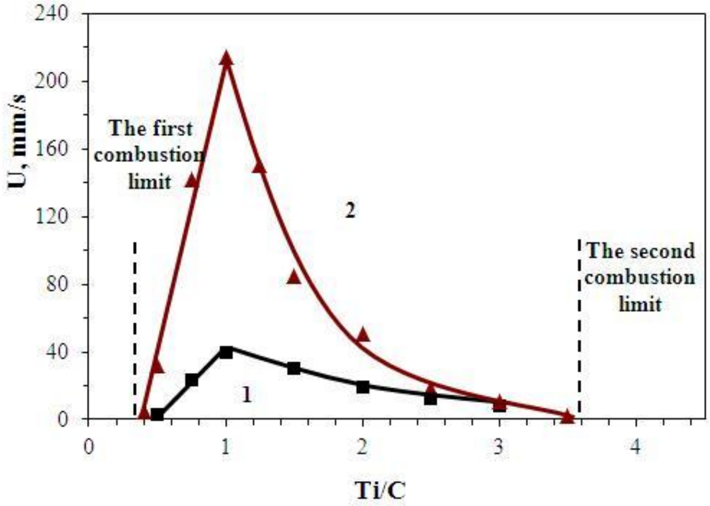

Figure 2. Burning velocity U as a function of Ti/C for Ti **II** + diamond (*1*) and Ti **II** + carbon black (*2*).

NUMERICAL SIMULATION OF CONTROLLED SYNTHESIS OF THE INTERMETALLIC COMPOUND ON THE SUBSTRATE OF CYLINDRICAL SHAPE

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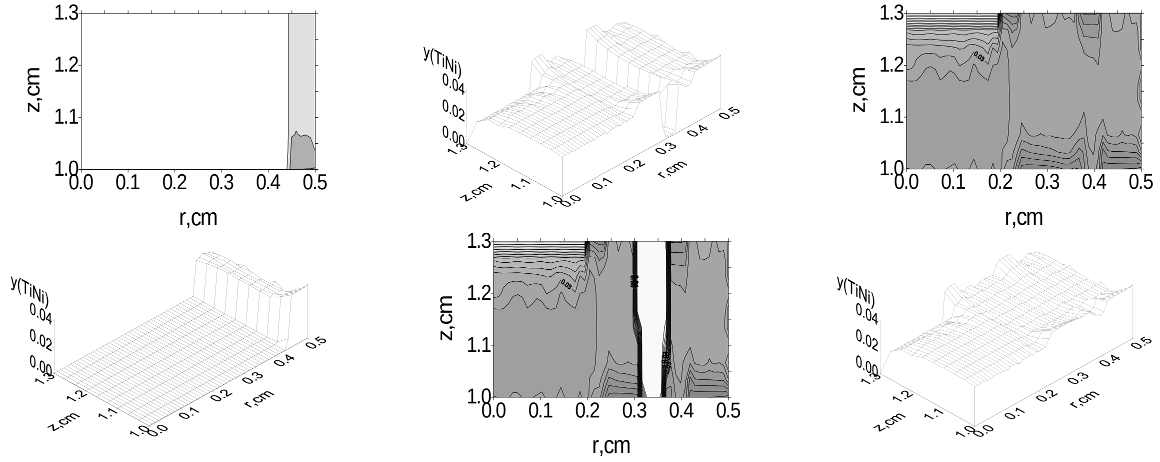
The joining formation between the coating and base or the transitive zone between materials may happen rarely during the synthesis process on the base. To form the transition zone additional heat treatment is required. Moreover under such conditions it’s not always possible to organize steady self-sustaining process. However the substrate that removes heat from the heating zone may considerably influence on the reaction regimes initiation and layer-by-layer propagation in the solid phase, similar to the effect of inert inclusions, inert rods, or the joined materials on the transformation regimes in such systems. Owing to heat loss by radiation and finite quantity of heat conduction coefficient, kinetic regularities can differ in various parts of the sample that as the result will lead to nonhomogeneous phase structure of final-product.

In the work investigated two-dimensional model of solid phase synthesis coating on the substrate under controlled heating takes into account the kinetic and heat phenomena [1]. As a model system the mix of the titan and nickel. The substrate - steel. The system of chemical reactions is written according to the phase diagram of Ti-Ni [2]. It is considered in the model that chemical reactions are decelerated by the product layer. In macrokinetics for reactions of this type (heterogeneous reactions) are special deceleration parameters [3]. The thermodynamic and physical properties are known from the experimental date or are calculated by special shape [4, 5].

The numerical decision of the problem on each step of time is run two stages. The first stage consists of the solution of the problem of heat conductivity by the method of splitting onto coordinates with the use of linear screw die. The second stage consists of the solution of the kinetic problem by Euler's implicit method. Function $\psi(T) = exp\left(-E_{aj}/RT\right)$ is displayed in Taylor series under the temperature from the bottom layer, limiting by composition of first-order of vanishing by $\Delta T = T^{j+1} - T^{j}$. In this work determines the distribution of temperature and concentrations of elements and compounds in different time.

Let's discuss the case when the first surface of the base is heated by steady source to temperature of T_{s1}=1200 K steady source. Then the coating surface is heated by the steady source of the smaller size. So, in figure 1 as an example space distribution of *TiNi* concentration, which is basically synthesized, are presented at the various moments of time. The dark area in figures is maximal value of concentration, white area - the minimal value of element concentration and transition region is defined by grey color «reaction front». It is seen, that initiation of the reactions are initially occurred on the surface in the contact with the base (fig.13, a – dark area). Since the beginning of the heated base to temperature of *T*=1200 K. Then the initiation reactions are initially occurred on the surface in the zone of influence of the external source (fig.1, b – dark area). It is visible that in this variant of processing it is the synthesis process in the entire region (fig.1, c – dark area). With increase in temperature of the base and or extension of radius of source influence the second area increases but distribution of elements in the whole reacted area becomes heterogeneous [1].



a) b) c)

Figure1. Spatial phase distribution of $y_3(TiNi)$ in coating in different times

a).– $t = 0.8c$; b).– $t = 1.6c$; c). $-t = 3.0c$

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CRITICAL PHENOMENA IN THE CELLULAR MODE OF FILTRATION COMBUSTION

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Critical conditions for combustion failure due to heat loss to the environment are examined. The process of filtration combustion is considered under conditions where a cellular structure of the front is realized, because the planar combustion front loses its stability and splits into separate cells of exothermic chemical conversion, which propagate in self sustained mode. The size and structure of the cells of chemical interaction depend nonlinearly on the governing parameters, including the rate of heat loss to the environment. Within the framework of a mathematical model of filtration combustion, the steady state dynamics of the combustion process and the structure of the cell of exothermic chemical reaction of a powder mixture with a gaseous reagent with the formation of solid products are simulated. The specifics of the evolution of the cell before combustion failure as a function of the heat loss rate are studied.

In [1], Ya.B. Zel'dovich formulated the foundations of the modern theory of the effect of heat loss on the combustion process. He showed that, despite the continuous dependence of the laminar flame speed in gases on the combustion temperature, the combustion process breaks down abruptly at a critical temperature, being realized only in a limited interval of high combustion temperatures. A nonlinear relationship between the rates of heat release and heat loss leads to the disruption of combustion. In the case of instability of a flat filtration front, again there is a need of further analysis of combustion failure. The combustion process was investigated using a three dimensional difference analogue of differential equations in conjunction with an implicit finite difference approximation and separation of coordinate directions.

In the cellular mode Fig.1 of filtration combustion of porous compositions, heat loss makes the combustion process concentrate in individual cells. In what follows, we examine the nonlinear dynamics of the evolutionary process in a cell at various intensities of heat loss within the framework of a quasi two mathematical model of filtration combustion.

The critical phenomena of distribution of the filtration combustion front under the influence of external heat loss are of scientific and practical interest. In studying the process of combustion, it is important to know the region of existence of the front, a factor that determines the reliability of the process for use in technology.

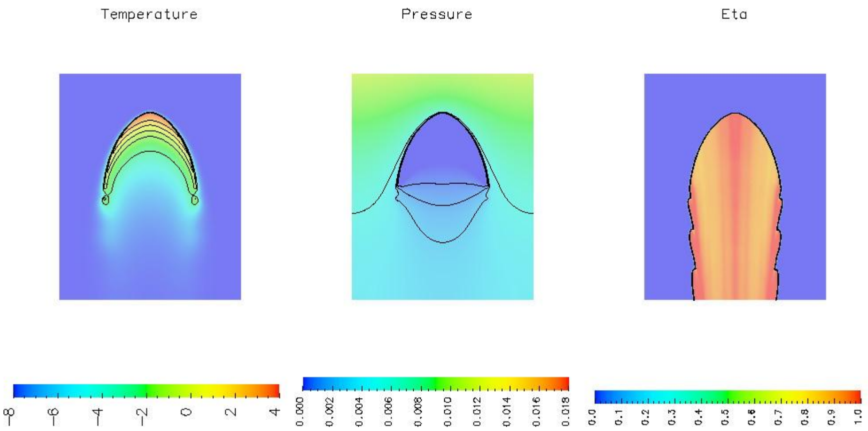

Figure 1. The structure of high temperature cells (fields of temperature, pressure, and extent of conversion).

The structural diversity of self sustaining combustion fronts, which arises due to the instability of the front, expands the scope of technological applications of the combustion process, but, at the same time, complicates the analysis of the safety of operation under such conditions. Various forms of frontal regimes require determining the parametric regions of their existence and analyzing their sensitivity to thermal impacts. A simplified one dimensional analysis of the possibility of exothermic interaction in these porous media may turn out to be incorrect because of a multidimensional cellular structure of the front. This is a rather complex nonlinear problem; therefore, the present work formulates no simple recommendations. The present study rate provides information on the possible process involved and outstanding problems.

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ATOMIC LATTICE SPACING AS A PREDICTIVE PARAMETER FOR FUNCTIONAL PERFORMANCE OF SPINELS MADE BY COMBUSTION SYNTHESIS

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It is now well accepted that the functionality of materials such as sensors, catalysts and pigments, is dependent upon the presence of atomic-level defects such as Schottky, Frenkel, etc which distort the atomic structure. Controlled defect structure of this type is usually obtained by doping with specific ions either during synthesis or by surface treatments. In this regard, it would be beneficial to be able to utilize knowledge of lattice distortion to determine or predict the performance of a new material. In this paper, we present evidence that atomic spacing of specific lattice layers, can be used as such a predictive parameter, which can aid in optimizing the catalytic performance of spinels such as catalysts, pigments and other materials.

The spinel structure is fairly empty and flexible in the accommodation of non-stoichiometry, and is characterized by an excess of bivalent cations, located at both tetrahedral and octahedral sites. Cations in the spinel structure can easily be substituted by many other cations to give multi-component systems, whose crystal lattice properties can be regulated by appropriate selection of dopant cations.

In the case of heterogeneous spinel *catalysts*, it is well known that local distortions of the primary crystalline lattice act as active catalytic centers. The nature and extent of such distortions depends on the atomic radii of the lattice ions, the type and parameters of the crystalline lattice and atomic bonds, the size and dispersion of the crystallites, the size and nature of the dopant ions etc. In the case of spinel nanostructured catalysts for the oxygen reduction reaction, changes in the crystalline structure of the catalyst with decreasing particle size remains virtually unstudied. Minor, but functionally significant, changes in the crystal lattice parameters of the active components of a spinel catalyst are usually caused by introducing various modifying additives, which increase the number of defects, but a comparable result can also be achieved by transition to the nanocrystalline state, in which the crystal lattice parameters change because of a sharp increase in the contribution of the surface forces and the necessity of balancing them. Actually, a decrease in the particle size of the active component may lead to either a desirable increase in the activity or to an abrupt decrease of it, which may also be caused by structural changes. This means that, for a particular catalyst and chemical process, there appears to exist an optimum amount of lattice distortion that gives high catalytic activity.

Recent studies of nanostructured catalysts for various processes tend to confirm this observation. For example comparable studies of SHS and solution combustion catalysts show that decreasing particle size - giving significantly increased surface area - lead to negative result for carbon dioxide reforming of methane. It has also been observed that, for carbon monoxide oxidation, reducing nanoparticle size decreases the crystal lattice spacing and decreases activity of a cerium catalyst. The results indicate that, it may be possible to predict or “tune” the activity of a catalytic system for a particular process, by appropriate “design” of the crystal lattice. This could be done by adding specific ions which are known to produce the needed amount of distortion. SHS and, to a lesser extent, SCS, appear to be ideal techniques for this, since the materials synthesised by combustion synthesis are often metastable and the atomic lattice remains distorted after synthesis due to the rapid heating and cooling rates. This has become clear during studies of the mechanisms of spinel formation in the combustion wave, secondary structure formation in the process of further reaction of components and final structure formation in the process of cooling and is particularly noticeable in the formation of intermediate and non-stoichiometric compounds. The influence of the existence of distorted atomic lattice on catalytic activity has been studied for a number of spinel systems. By comparing the published data for SHS and SCS catalysts for various processes, it was possible to confirm the above conclusion and develop predictive criteria for the composition and atomic crystal structure giving the highest catalytic activity. Specifically, the trend of crystal lattice spacing was found to correlate with the trend of the length of the bonds of organic substances which must be adsorbed, broken on the catalyst surface and recombined with others for the synthesis of the reaction product. As a result, it is possible to "tune" the lattice spacing for maximum catalytic activity by doping the material with ions of appropriate radii, thereby distorting the crystal lattice by the correct amount.

The above method for predicting and "tuning" the functionality of various spinels made by SHS is also applicable for spinel *pigments*. By the addition of appropriate dopants, it is possible to produce almost any colour and hue of the spinel-based pigments, as confirmed from the results of many years' work on colour formation in SHS materials. Recently, new systematic studies of solution combustion synthesis of pigments confirm the applicability of this predictive method for synthesising a large variety of nano-structured pigments of various colours and hues by regulating the crystal lattice spacing and particle size. It was found that the major factors responsible for production of colour in specific spinel pigments, were the type (Co, Ni, Mn, Cr, Fe, Cd, Cu etc.), atomic size and structure of the dopant and the lattice position in which it enters, which decides the size and type of lattice distortion. The ionic radius of the dopant metal ion was found to be correlated to the wavelength of the reflected light from each pigment, i.e. the colour of the pigment. For example, in the system Co-M-O (where M is the metal ion), the wavelength of the reflected light was found to decrease monotonically with increasing ionic radius of dopant metal ion.

It is expected that the above predictive process would be applicable to all types of functional spinels produced by SHS and SCS with ordered structure and composition. For example spinel is an important *semiconductor* material with narrow bandgap which increases efficiency for photovoltaic systems. Some semiconductor spinels are highly efficient and stable spinel photocatalysts for visible light catalytic degradation of organic contaminant. These include $ZnFe_2O_4$, $BaCr_2O_4$, $Cu/ZnMn_2O_4$ which have been reported as having photocatalytic activity under UV and visible illumination. The spinel structure is fairy empty and flexible in the accommodation of non-stoichiometry, which is characterized by an excess of cations, located both tetrahedral and octahedral sites. Thus cations in the spinel structure can be substituted by many other cations to give multicomponent system, whose properties can be regulated by proper selection of the cations, appropriate adjustment of composition and structure, lattice parameters.

2. SHS OF MICRON, SUBMICRON- AND NANO-MATERIALS

COMBUSTION SYNTHESIS OF SILICON CARBIDE NANOFIBERS USING WASTE SILICON FROM PHOTOVOLTAIC PANELS AND PTFE

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The unique Self-propagating High-temperature Synthesis (SHS) technique allows for an effective, energetically autothermal formation of different novel materials, including nanostructural and non-stoichiometric ones, and bearing new phases this all during fast reaction in the mixture of strong oxidant/strong reducer [1]. This all results from the specific process characteristics: high temperatures/pressures, short reaction times and very fast quench of gaseous reaction products during their expansion from combustion zone towards cooling zone. Silicon carbide as so-called refractory ceramics possesses very interesting physical and chemical properties, especially in case of its nanostructural morphology this including one-dimensional (1-D) nanostructures, and nanofibers SiCNFs [2, 3].

We earlier investigated a number of experimental systems using the parametric approach to optimize the SHS production of SiCNFs [4, 5]. The commercially available (Sigma-Aldrich®) reactants were commonly used as the stoichiometric mixture of micrometric silicon and polytetrafluoroethylene (PTFE) powders. The combustion was carried out in a high-pressure stainless-steel reactor provided with the observation port to monitor the process and measure the radiation from the reaction zone [6]. The ignition of combustion with an ohmically heated carbon tape leads to a rapid (less than 1 s) reaction, resulting in the formation of gram quantities of sponge-like solid product containing high content of SiC nanofibers having a diameter in the range of 10 to 100 nm. The nanofibres can be easily isolated and purified using a wet chemical protocol [5].

It is obvious that the cost of starting reactants distinctly influences the overall process performance and is one of the barriers in the production of nanomaterials. To improve the economics of SiCNFs synthesis, we propose here the replacement of relatively expensive commercial reactants by the silicon elemental (as reducer) from waste solar panels and waste PTFE (as oxidant) powders. Their overall cost is a few orders of magnitude (!) lower. Thus, such replacement will drastically reduce the costs of SiCNFs production since the operational costs of energetically autogenic SHS technique are obviously very low. It was found earlier that SiCNFs growth is favored by the presence of the oxygen in the growth zone. Thus, this aspect has been carefully studied within the present parametric investigations, with the use of carbon oxide (CO_2, CO) combustion atmosphere which proved to be superior during the former exploratory runs. The use of carbon dioxide (so-called ‘green-house gas’) looks here specially encouraging, both as an additional source of elemental carbon and of the oxygen which is a component of intermediate reaction compounds (gaseous SiO). Thus, not only the environmental aspect of such approach is worth to be mentioned, but also the presented preliminary testing brought very unexpected results: even so thermally stable compound as CO_2 can be, under probably partially non-equlibrium conditions of combustion, atomized to elements.

The diagram (Fig. 1) presents the proposed route to produce silicon carbide nanofibres using waste starting reactants.

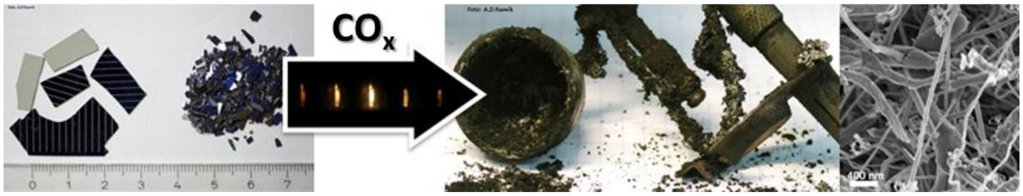

Fig. 1. The protocol to produce SiC nanofibers from waste PV Si panels via SHS route.

ACKNOWLEDGEMENTS

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KINETICS OF NICKEL OXIDE REDUCTION BY HYDROGEN AND METHANE

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In the literature nickel oxide reduction was mainly studied at relatively law temperatures (below 800-900°C) by using C, CO, CH_4 or H_2 as reducing agents. Recently, nickel oxide reduction was performed by our research group in combustion mode using organic compounds (polyethylene, polystyrene, melamine, etc.) as reducing agents [1,2] where the process temperatures reach or exceed 1000°C. It is assumed, that at high temperatures of combustion wave the main process of reduction took place through hydrocarbon fragments and hydrogen as a result of reductants' destruction. In this work the kinetics of nickel oxide reduction by hydrogen and methane was investigated at T=900-1200°C and P=1-100 torr. The experiments were conducted on high-speed scanning elektrotermography setup by using Ni wires 100 micron in diameter (NP-2 trademark, purity 99.5%). The latters were preliminary oxidized in air (P=1 atm., T=1300°C, t=150 s) with formation of NiO layer on metal surface with ~6 micron in thickness. Then the oxidized wires were reduced by hydrogen or methane at abovementioned conditions.

The kinetics of reduction process was investigated by gravimetry, SEM and X-ray analyses methods. The rate of heat release caused by Ni reduction was also determined by in situ measurements during the experiments.

It was found that the rate of hydrogen reduction is practically independent on gas pressure, and the wire weight loss is described by parabolic law (Fig.1a). The SEM examination of specimens' cross sections indicate, that during reduction a thin and uniform layer of reduced metal is formed on the surface of wire just at initial stage of the process, which is clearly separated from the intermediate oxide layer. During the reduction process this layer grows and eventually incorporates with metal core. Results of experiments testified that the reduction of nickel oxide by hydrogen occurs via the mechanism of reaction diffusion.

In contrasts to hydrogen reduction, reduction by methane is characterized by existence of a clearly marked induction period, followed by rapid acceleration of the process. As a result, the weight loss curve has a S-shaped form (Fig. 1b), which is specific for the topochemical reactions proceeding via stages of nucleation and growth.

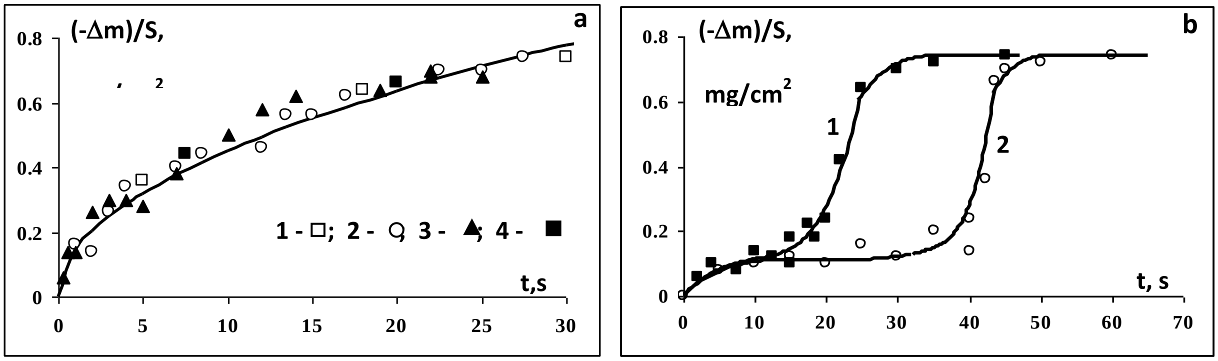

Fig. 1. Kinetic curves for nickel oxide reduction, T=1230°C.

a – in H_2:1- P=2; 2 - 5; 3 - 10; 4 - 100 torr, b – in CH_4: 1 – P=10; 2 – 5 torr.

It was shown that the increase of methane pressure significantly reduces the induction period, and moves the whole reduction process to the shorter time region. At that, if at pressure range from 2 to 10 torr the average rate of reduction by methane is lower than that with hydrogen, then at higher pressures (P=50-100 torr) the rate of methane-reduction exceeds the rate of reduction by hydrogen by a factor of 10-50.

The temperature influence on the reduction rate by methane and hydrogen has complicated character and as for methane, sharply depends also on gas pressure.

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DTA/TG STUDY OF TUNGSTEN OXIDE AND AMMONIUM TUNGSTATE REDUCTION BY (Mg+C) COMBINED REDUCERS AT NON-ISOTHERMAL CONDITIONS

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Metallic tungsten has an important role and applications in various fields of modern technology. The most widely used process for producing tungsten is based on a long route from either ore wolframite ($FeWO_4$) or from scheelite ($CaWO_4$). Salts are dissolved in acid and precipitated using ammonia to form ammonium tungstate which is subsequently calcined to form WO_3. The trioxide is then reduced with hydrogen to form metallic W. In recent years investigations are carried out towards the development of alternative methods of tungsten production, especially for direct and one stage reduction of tungsten oxide and it`s salts (ammonium, sodium and calcium tungstates) in combustion mode using combined reducers, such as (Mg+C) or (Mg+Zn) mixtures. This work is aimed to study the formation mechanism of metallic tungsten from tungsten (VI) oxide and ammonium paratungstate - APT ($(NH_4)_{10}W_{12}O_{42}*2.5H_2O$) at non-isothermal conditions using DTA/TG technique. In order to explore the phase formation dynamics, the reaction was stopped at preliminary chosen points and the quenched in inert gas flow products were examined by XRD analysis. Before the studying the reduction process of the WO_3 and APT with (Mg+C) combined reducers, it was studied behavior of binary mixtures (WO_3/APT+Mg) and (WO_3/APT+C) at linear heating.

1. DTA study of WO_3-Mg and WO_3-Mg-C mixtures In the WO_3-Mg binary mixture intensive reduction process starts in solid state (T≈560°C), with T_{max} = 570°C and practically finished at T≈610°C, thus till Mg melting point (640°C). XRD analysis performed for quenched from 700°C products shows the presence of Mo and MgO, which form by the following reaction:
$WO_3+3Mg=W+3MgO$

According to the results of the DTA investigations, carbothermal reduction of WO_3 till 850°C doesn't occur. Further studies are carried out with (Mg+C) reducing mixture. In the WO_3+0.5C+2Mg "stoichiometric" mixture reduction process starts by Mg in the solid state (~590°C) and is characterized by T_{max}=605°C. The reduction process is practically finished at ~660°C. Mg melting doesn't take place during all reduction process, but both reduction starting temperature and T_{max} shift towards high temperature range about 30°C.

2. DTA study of APT-Mg and APT-Mg-C mixtures It was shown that in all cases the reduction processes start after decomposition of APT, which was finished at ~450°C and WO_3 is obtained as a sole condensed product. Further, the magnesiothermal reduction of WO_3 takes place upon heating of mentioned mixtures above 560°C. The intensive exothermal reaction occurs at 580-630°C temperature range and is characterized with T_{max}=600°C. The results of XRD analysis of the products quenched from 700°C are presented in the Fig.1 (a).

The addition of carbon to the binary mixture leads to the shift of the reduction process at around 90°C towards high temperature.

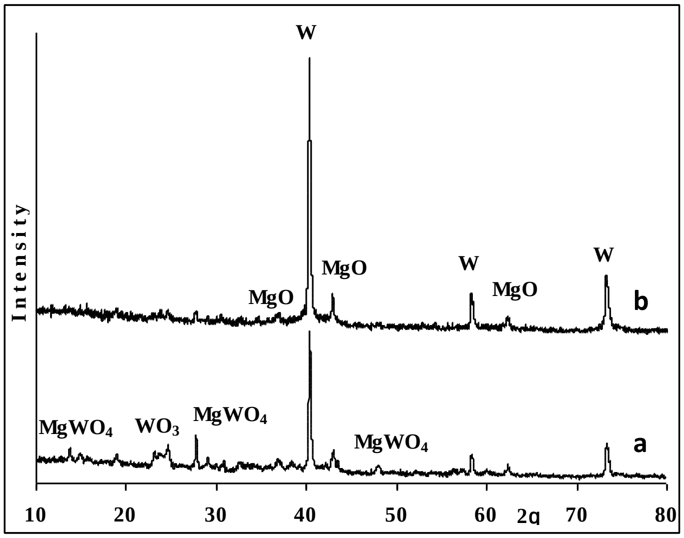

Fig.1. XRD patterns of APT+2Mg (a) and APT+2Mg+0.5C (b) reactions' products, quenched from high temperature

Thus in the APT+2Mg+0.5C ternary system the reaction starts just after melting of magnesium. According to the results of XRD analysis for quenched products, the reduction process of APT with Mg+C reducing mixture proceeds completely and metallic tungsten is obtained as target material (Fig.1b, 800 °C), unlike to the case of APT+2Mg binary mixture. It was shown, that in the WO_3-Mg-C and APT-Mg-C systems the shift of characteristic temperatures essentially depends on the amount of carbon which in fact doesn't involved in reduction process. Calculated values of effective activation energies for magnesiothermic reduction processes show the increase of activation energies in the presence of carbon.

CONCLUSIONS

1. The magnesiothermal reduction processes of WO_3 and APT at low heating rates started and finished in solid state;
2. The addition of carbon to the binary mixture leads to the shift of the reduction process towards high temperature. Thus in the case of APT the reaction starts just after melting of magnesium.

ACKNOWLEDGMENT

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HARD MAGNETIC FERRITES: SCREEN PRINTING AND PROPERTIES

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The feasibility of screen-printing process of magnetic nanoparticles produced by carbon combustion synthesis of oxides (CCSO) is investigated. In CCSO, the exothermic oxidation of carbon generates a smolder thermal reaction wave with relatively low temperatures at 600–1000 °C that propagates through the solid reactant mixture at a velocity of 0.1–4 mm/s converting it to the desired oxides [1, 2]. There has recently been increasing interest in the use of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ hexaferrite in the recording media applications with the emphasis on high-density perpendicular magnetic recording where nanocrystalline magnetic thin-film media is required. Furthermore, the nanoscale magnetic ferrites are of particular interest due to their chemical compatibility with biological tissues and their unique combination of electronic and magnetic properties such as very low electrical conductivity, high magnetic anisotropy, high Curie temperature, mechanical hardness, excellent chemical stability, and corrosion resistivity.

Barium and strontium hexaferrite nanoparticles were produced by CCSO via the following reaction: $MeCO_3+6Fe_2O_3+\alpha(C+O_2) = MeFe_{12}O_{19}+(\alpha+1)CO_2$ where Me is Ba or Sr. The high purity (99.9%) reactants mixture used in CCSO contained 11 wt. % carbon nanoparticles "carbon acetylene" with the average particle size of 5 nm (surface area ~ 80 m^2/g) and non-combustible iron oxide and barium or strontium carbonate reactants. The x-ray pattern of as-synthesized powders showed that combustion produced almost pure strontium and barium hexaferrite and did not require further calcinations to complete the reactants conversion. However, an x-ray pattern of as-synthesized $SrFe_{12}O_{19}$ powder shows a low intensity following suggestion that partial amorphous structure was presented, while for the $BaFe_{12}O_{19}$ powder was well crystalline and had a flat background indicating that no amorphous phase was present. The lattice parameters of the barium and strontium hexaferrites were a = 5.892 A°, c = 23.386 A° and a=5.889 Å, c=23.034 Å respectively (Fig. 1,a,b). The combustion products were predominantly rectangular particles with a range of particle size of 50–100 nm.

The samples show typical hard magnetic properties originated from high magnetocrystalline anisotropy (Fig. 1,c). The schematic diagram of the EFD dispenser printing system is shown in Fig. 1,d. The thin film layers are deposited onto the substrate within a predefined printed pattern. AFM image of the micro layer presented in Fig. 1(e) shows uniform strontium ferrite particles distributions and confirmed that the average particle size was predominantly 60 nm.

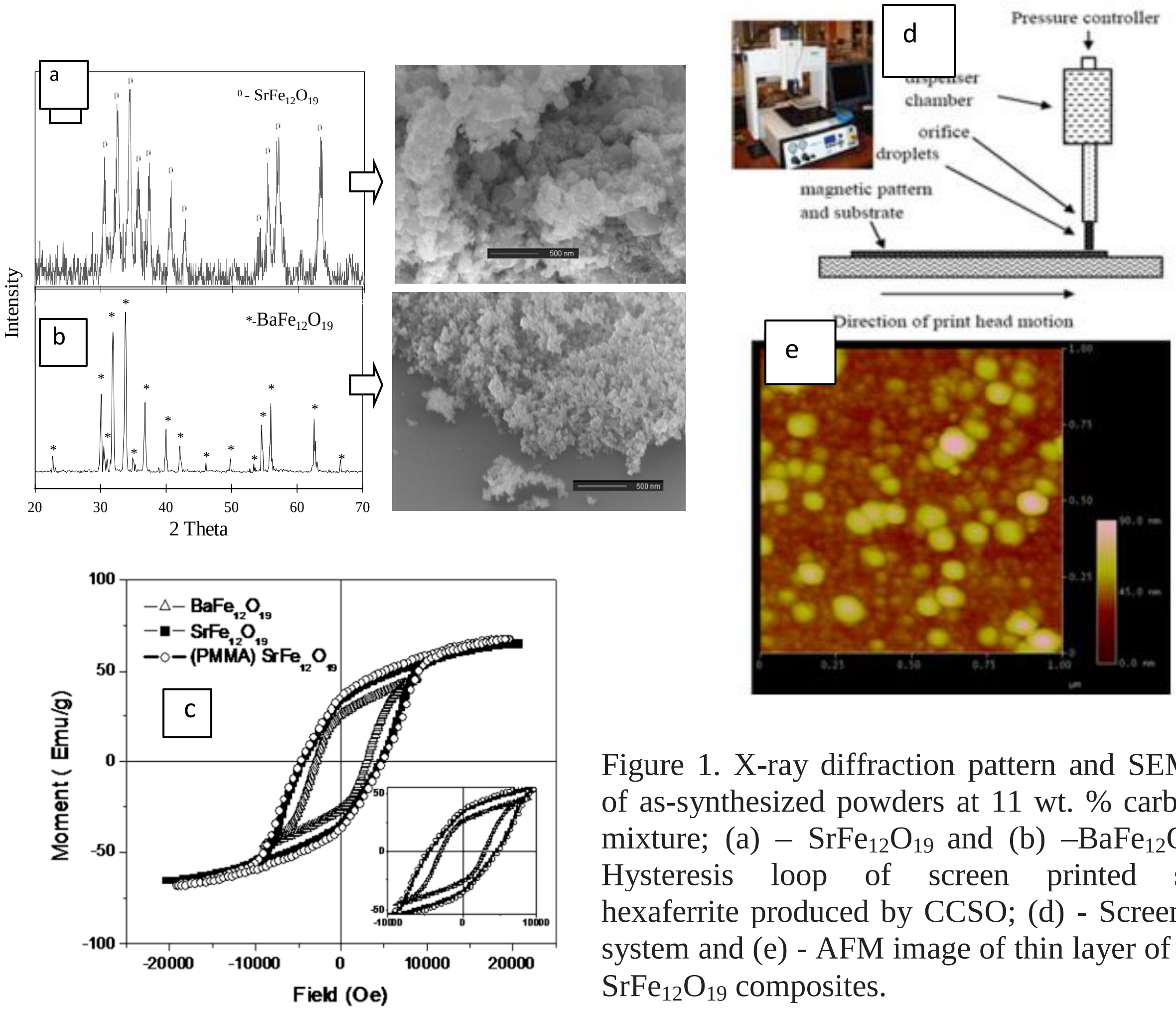

Figure 1. X-ray diffraction pattern and SEM images of as-synthesized powders at 11 wt. % carbon in the mixture; (a) – $SrFe_{12}O_{19}$ and (b) –$BaFe_{12}O_{19}$; (c) - Hysteresis loop of screen printed strontium hexaferrite produced by CCSO; (d) - Screen-printing system and (e) - AFM image of thin layer of magnetic $SrFe_{12}O_{19}$ composites.

The synthesized nanoparticles could be used to print permanent magnet structures for micro-sensors, motors, generators, actuators, and micro electro-mechanical systems (MEMs) applications.

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STUDY OF A HIGH TEMPERATURE KINETICS IN MECHANICALLY ACTIVATED NI-AL SYSTEM AT HIGH HEATING RATES

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One of the most rapidly developing new direction in the field of combustion synthesis is a mechanical activation of SHS compositions. Mechanical activation is a process of treatment the combustible mixture in high-speed planetary ball mills, vibratory mills and other devices in which the particles of the mixture subjected to mechanical impact with sufficient force for splitting of brittle and plastic deformation of viscous components [1]. During activation, not only reduces the size of the reactants but also increases the contact area between them, the contact surface is cleaning from the oxide films and other impurities, crystal defects are accumulating and all this leads to a high reactivity of the combustible mixture [2]. Many studies have a direct proof (electron microscopic images, etc.) that by the mechanical activation it is possible to obtain nanostructure composites with the size of structural components (phases) in the order of 10 - 100 nm. But even in those cases where such direct evidence is not provided, after mechanical activation observed a sharp changes in the properties of the reaction mixtures, for example, decreasing of self-ignition temperature in hundreds degrees. Furthermore, almost all researchers agree that activation reduces the ignition temperature of different reactive systems, extends combustion limits, facilitates more complete combustion and in some cases increase the propagation velocity of a combustion wave.

To explain these phenomena in the theoretical models assumes a hypothesis of a changing in the activation energy of the reaction due to mechanical activation on a certain amount of "delta E". However, there are no direct experimental data on the reaction kinetics of the mechanically activated mixtures. Kinetic studies on standard differential scanning calorimetry (DSC) does not provide the necessary data, since the heating rate in the standard DSC too small (1 – 100 °C per minute), whereby a further heating step is "annealed" nanostructured active reaction centers, and the resulting data does not match the actual kinetics in the rapid heating.

Here is reported the study of the kinetics of heterogeneous reactions in mechanically activated nanostructured composite materials by rapid heating. To provide controlled heating the high-speed temperature scanner (HSTS-1, Institute of Chemical Physics, Yerevan, Armenia), was used, allowing heating reaction mixtures up to rates 10^4 K/min by passing electric current through samples. Thus, we obtained data on the dependence of the activation energy on the activation time in the Ni-Al system. The results shown that the activation energy of the heterogeneous reaction strongly depends on the mechanical treatment of the reactive mixture.

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ELECTRO THERMAL EXPLOSION OF GASLESS SYSTEMS PLACED INTO ELECTRO CONDUCTING MEDIUM

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Experimental and theoretical investigation of electrothermal explosion (ETE) in the Ti–C system was carried out under conditions of quasi-static compression. The ETE parameters were found to depend on pressure, electric capacity, ratio of specific resistivity to thermal conductivity of green mixture and inert environment (TiC).

Experiments were carried as described elsewhere [1]. It has been shown that, at low compression pressure (8 MPa), the specific resistivity of the sample is several times higher than in the bulk. An increase in pressure lowers resistivity parameters while at still high pressures (> 240 MPa) the specific resistivities of the sample and bulk differ only slightly and remain intact.

The compression pressure affects temperature intervals of preheating and explosion. Thus pressure growth shifts the preheating interval toward higher temperatures. At 8 MPa, the sample temperature rises from 400 K to 1200 K and at 96 MPa it changes from ≈ 800 K to 1640 K.

Rise in electric capacity leads to a drop in ignition point and induction period from switching on to the sample ignition. This time interval includes inert heating the sample with electric heating source from initial temperature to the point when heat release from chemical reaction becomes considerable and period of induction of a reaction itself.

A rise of heating rate for the sample causes drop for ignition point and growth of maximum heating.

The process modeling [2] allows one to determine components of the full time of ignition. The calculated data agree with experiment.

Fast uniform heating of the heterogeneous mixture (heat sources were placed uniformly in bulk and sample volume) is a necessary condition for correct measuring the macrokinetic parameters of ETE.

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SELF-PROPAGATING EXOTHERMIC REACTIONS IN MECHANICALLY FABRICATED MATERIALS

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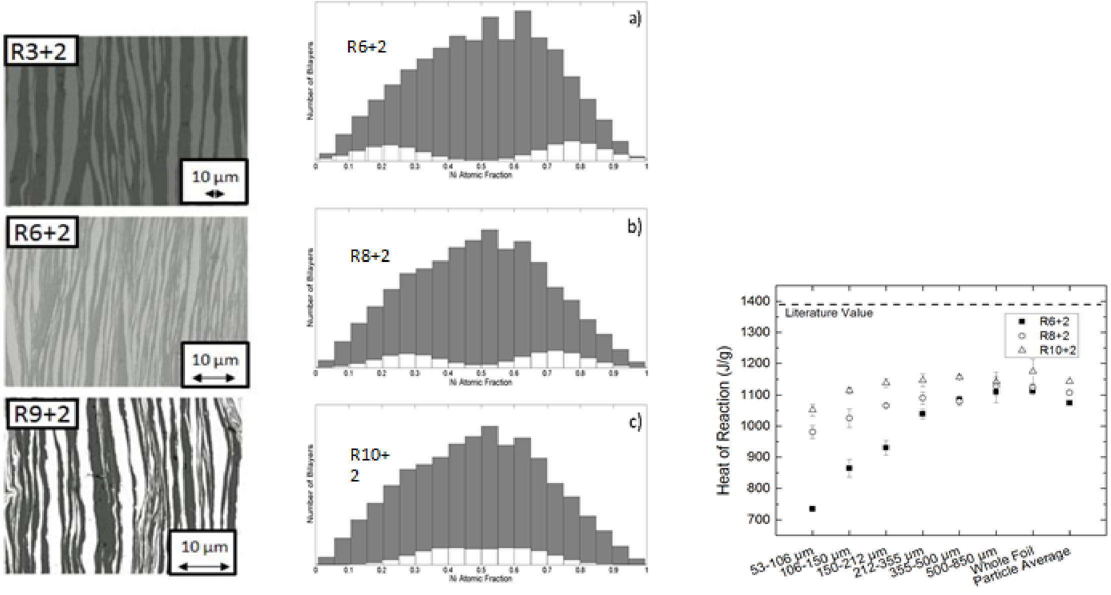
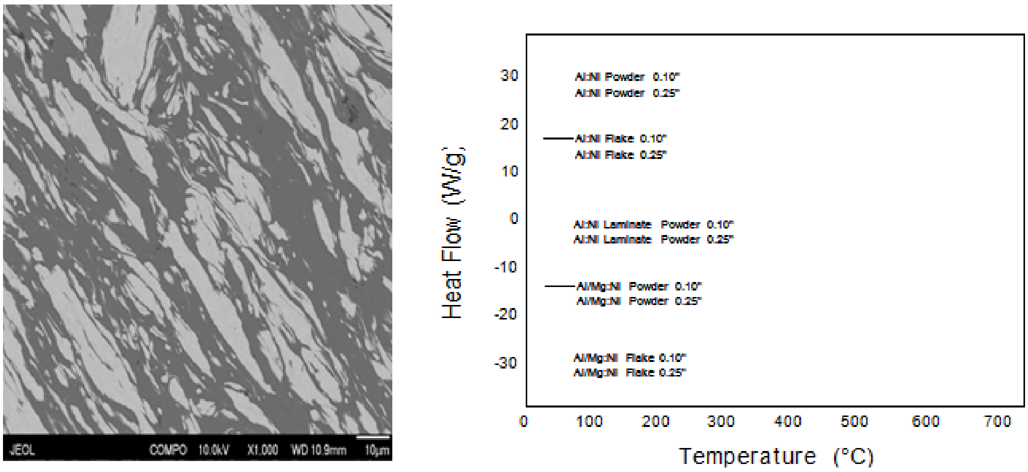
This presentation covers the mechanical fabrication of reactive materials and their resulting properties. Cold-rolling is used to fabricate thick, laminate foils from stacked sheets of Al and Ni, and the resulting foils are ground into laminate powders of various diameters. The reactive properties of these foils and powders have been characterized, and in many cases the average bilayer thickness and the average chemistry cannot explain the observed trends in reaction heats, temperatures and velocities. To help understand the trends we have gone beyond average values of layer thickness and chemistry and quantified distributions of the layer thicknesses and the local chemistries for these samples (Figure 1). In addition, we have used these distributions to explain variations in the maximum reaction temperatures and the reaction velocities for the foils and the measured heats of reaction for the particles.



(a) (b) (c)

Figure 1: (a) Micrographs of cold-rolled foils; the rolling direction runs parallel to the layers. (b) Statistical distributions of bilayer thicknesses according to their local chemistries, measured using 20 micrographs for each rolled sample. (c) Heats of reaction measured for the laminate particles as a function of particle diameter.

In contrast, we have used just cold-swaging to form fully-dense, Al/Ni composite rods from powders (Figure 2(a)) and we characterized changes in the properties of the rods as a function of the degree of swaging and the chemistry and geometry of the starting powders. Testing consisted of differential scanning calorimetry (DSC), hot-plate ignition studies, and velocity measurements. As expected, when the degree of swaging increased, exothermic peaks in DSC scans shifted to lower onset temperatures as shown in Figure 2(b); hot plate ignition temperatures decreased; and reaction velocities rose. We varied the initial chemistry by substituting Al 93 at%-Mg 7 at% powders for Al powders and found that the alloy powders yield lower DSC exothermic peak temperatures, lower ignition temperatures, and higher reaction velocities compared to similar compacts with pure Al powders. We also varied the shape of the initial reactants by substituting Ni flakes for Ni powders but found no improvement in reaction properties, due to clumping of the Ni flakes during the initial compaction steps. These observed trends will be described and discussed in detail.



(a) (b)

Figure 2: (a) Micrograph of cold-swaged Al-Mg and Ni powders and (b) DSC scans of multiple samples following two different degrees of swaging denoted by the sample's final outer diameter. Note that additional swaging shifts DSC peaks to lower temperatures suggesting finer microstructures.

PRODUCTION OF TiB_2 BY SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS

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Borides are one of the important sub-groups of advanced ceramics. TiB_2 is a transition metal boride which contains theoretically 31.1% boron. Its remarkable properties are high melting temperature, hardness, thermal and electrical conductivity, good wear, thermal shock and corrosion resistance [1, 2]. As a result of these distinguishing features, TiB_2 is mainly used in aluminum industry as Hall–Héroult cell cathode, electrode - thermocouple case and evaporation boat. Other utilization area is the production of various sintered materials such as armour materials and sputtering targets [3].

Various synthesis methods which are performed to produce TiB_2 have been reported in literature. Synthesis of TiB_2 via carbothermic process of TiO_2, B_4C and carbon is a commercially applied process. However, self-propagating high temperature synthesis (SHS) followed by acid leaching, molten salt electrolysis, powder metallurgy and aerosol processes are in use as well [3, 4]. SHS process is a prominent method to produce advanced ceramics with ultra-fine grain size, shorter process duration and high energy efficiency. One of SHS experiments in the conducted experiments is given in Figure 1.

In this study, SHS processes were performed according to Reaction (1). Investigated parameters were Mg stoichiometry as 90%, 100% and 110%, process atmosphere as open and argon atmosphere and effect of $MgSO_4$ (2.5% and 5% addition) as catalyst on the quality and grain size of synthesized TiB_2 powders.

Figure 1: SHS Reaction

$$TiO_2 + B_2O_3 + 5Mg \rightarrow TiB_2 + 5MgO \quad (1)$$

SHS reactions were carried out in a cylindrical copper crucible. For the experiments conducted with 100% of stoichiometrically required Mg, amount of charge materials was fixed at 100 g. Thus, quantities of charge materials were slightly changed owing to increase or decrease in Mg stoichiometry. SHS products were leached by using concentrated HCl solutions. Leaching parameters were 9.25 molar HCl concentration, 600 rpm stirring speed and 1/5 solid/liquid ratio. X-Ray Diffraction and chemical analysis techniques were performed for the characterization of leaching products.

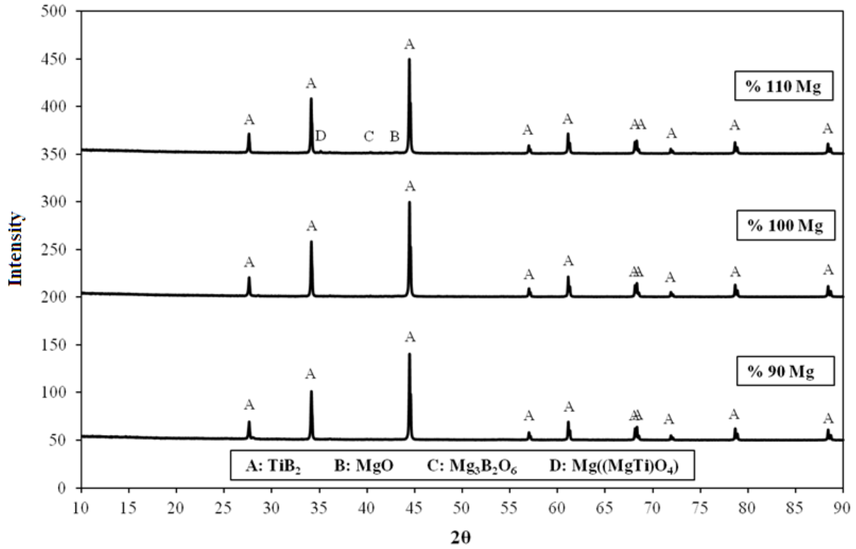

Figure 2. XRD Pattern of Leached SHS Products Synthesized Under Argon Atmosphere.

Results indicated that purer TiB_2 powders were obtained with the experiments conducted under Ar atmosphere particularly for 90% and 100% Mg stoichiometry. Powders which were synthesized under open atmosphere contained undesired $Mg_3B_2O_6$ and $Mg((MgTi)O_4)$ phases. The experiment with 100% Mg addition under Ar atmosphere had vey low level of Mg as 0.81%. It was observed that $MgSO_4$ addition as a catalyst had no remarkable effect on the synthesis of TiB_2.

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SYNTHESIS OF HIGH TEMPERATURE MATERIALS UNDER THE CONDITIONS OF SOLIDPHASE COMBUSTION

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Silicides are distinguished by many technically important properties – electrophysical, refractory, corrosion – resisting, wear resisting that make them promising inorganic materials for different fields of engineering having to do with the use of high temperatures, strength, wear resisting loads, corrosive media. For example, intermetallic compounds and silicides of the elements of groups IV – VIa are used as working surfaces of metal tools [1, 2].

Traditional technology of synthesis of intermetallics and silicides is based on the interaction of precleaned elements and production of a proper metal-cutting tool from synthesis products.

Apart from traditional technology, in order to solve the problem of producing items of particular hardness including different cutters, drills, ect., SHS technology has great prospects as it allows decreasing production expenses due to reduction of technological cycles, economy of production time and possibility to use instead of cleaned elements their oxides which are much cheaper [3, 4].

In this work SH-synthesis of refractory materials based on titanium silicide was carried out at room temperature in the atmosphere of air. The following systems were studied: TiO_2 – SiO – Mg, TiO_2 – SiO_2 –Mg. The mixture of the initial components: titanium oxide, magnesium, silicon monoxide and silicon dioxide was pressed in the form of cylindrical samples with d=20 mm, h=20-30 mm. XRD analysis was carried out using a DRON-4M diffract meter (Co-K_α radiation) in the range of $2\theta = 10–70°$.

The results of semi - guantitative X - ray phase analysis of SHS products for systems TiO_2 – SiO – Mg, TiO_2 – SiO_2 –Mg are presented in Table 1. As can be seen from Table 1, when using silicon monoxide, the yield of the target product is higher than when using silicon dioxide.

Table 1 – The results of semi – quantitative X-ray phase analysis.

Systems	Products, mass. %				
	MgO	Ti_5Si_3	Mg_2SiO_4	Si	TiO_2
TiO_2 – SiO – Mg	20,6	63,6	15,7	-	-
TiO_2 – SiO_2 –Mg	46.8	37.2	12.2	1.6	2,2

Thus, the possibility of synthesizing a composition material with maximum content of titanium silicide (Ti_5Si_3) up to 63.6 mass % which is easily separated from reaction by – products under the conditions of solid – phase composition is shown.

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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS COMPOSITES ON THE BASIS OF TiB_2-Al_2O_3

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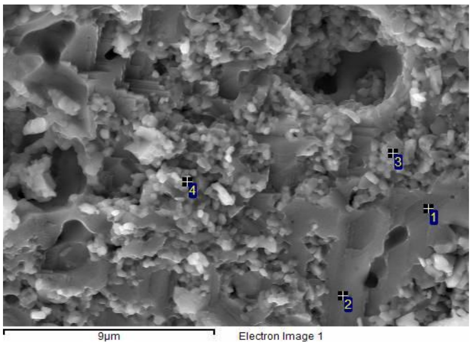
The SHS technique has been extensively applied to produce a great number of advanced materials such as borides, carbides, nitrides, suicides, and intermetallics [1-3]. When incorporated with thermite reactions based on Al as reducing agents, the SHS approach represents an in situ procedure for preparing ceramic, intermetallic, and metal matrix composites reinforced by Al_2O_3, because such thermite reactions are highly exothermic and produce a stable oxide Al_2O_3 [1, 2].

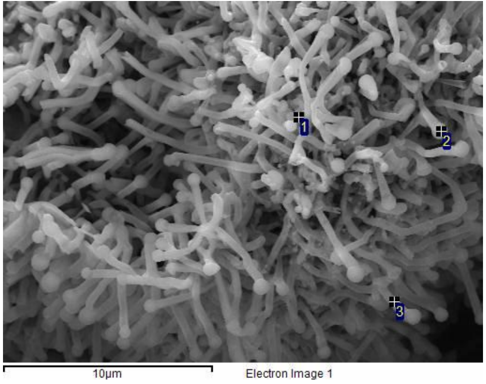
Preparation of TiB_2-Al_2O_3 composites with a broad range of phase composition was conducted by SHS involving reaction of different types. SHS was carried out in the constant-pressure chamber in argon atmosphere at 1 atm. Aluminum (99,1 % purity), TiO_2 (98% purity, anatase, B_2O_3 (96% purity) were used as initial components. The 2 cm diameter and 3 cm high cylindrical samples made up by the pressed powder mixtures have been used as the study object. The microstructure and phases composition of synthesized products were investigated using microanalyses-scanning electron microscope JCXA-733 (JEOL) «Superprobe» and Hitachi S-4800 FE-SEM, Japan and XRD.

To determine the processes occurring in combustion wave in TiO_2- B_2O_3-Al system the «hardening» method was used. The wave of SHS process followed by analysis of partially and completely part of TiO_2- B_2O_3-Al mixture. In Fig.1a it can be seen that initial reagents melt, then with boron oxide can be formed the titanium diboride crystals. The structure of the melt after SHS is a porous, strong material that has in some zones dendrite constituent and grainy inclusions, crystallized into six membered lamellar formation of titanium diboride in aluminum oxide matrix (Fig. 1a). Typical SEM micrographs in Fig.1a shows the grains of TiB_2 with a small and rather uniform particle size. This confirms the feasibility of applying the SHS technique to fabricate the soft-agglomerated composite powders with homogeneous distribution of the components. In comparison with conventional methods, the SHS-derived powders eliminate the less efficient mechanical mixing of both components, the prolonged grinding of disagglomeration, and the steps of removal of the impurities. Therefore, the SHS-derived powders enable simplification of processing ceramic materials by shaping, sintering and hot-pressing of powder.



Zone No.	Atomic ratio, %			
	B	O	Al	Ti
1		57.32	39.69	2.99
2	7.76	52.99	37.93	1.32
3	44.13	24.23	20.69	10.95
4	49.98	13.43	7.44	29.14

a)



Zone No.	Atomic ratio, %			
	B	O	Al	Ti
1		42.87	56.45	0.67
2	19.01	29.45	50.00	1.54
3	13.42	40.40	42.60	3.58

b)

Fig. 1 Microstructure of the products of TiO_2- B_2O_3-Al system produced by the hardening method: a) microanalyses of zone reaction b) formation of Al_2O_3 fibers in pores.

Figure 1b shows that the fibrous crystals of Al_2O_3 have different sizes. The length of fibers is about 0,5 µm and the diameter is 700 nm.

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SYNTHESIS OF TI-Nb-Cr-C-H CARBOHYDRIDES IN THE COMBUSTION MODE

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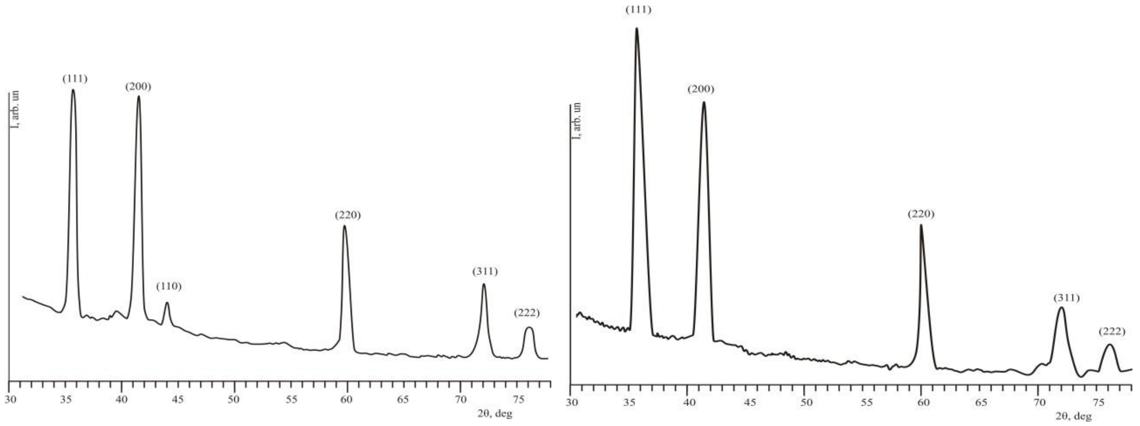
Solid metals, manufactured on the refractory carbides differ by high hardness, strength, wear, heat and corrosion resistance. The fields of their application are very broad. Carbide ceramics are used as constructional materials, refractory materials, for manufacturing of high-temperature heaters for electric furnaces, tools in the metal industry, etc.

The aim of this work was to study the interaction with hydrogen of Ti, Nb, Cr metals and carbon based variable composition charges in the combustion mode and getting new easily dispersible refractory compounds of transition metals. Such compounds are mainly used as hard alloys. There is also some interest in heat-resistant alloys based on Ti, Nb and Cr due to the fine allotments during formation of carbides in Ti-Nb-Cr and Ti-Nb-Zr-Cr systems, which are used for obtaining hydrogen by conversion.

In this work the results of study of SHS-processes in Ti-Nb-Cr-C-H system are presented. xTi + (1-x)(Nb + Cr) + yC mixture, where ($0.6 \leq x \leq 0.9$; $0.35 \leq y \leq 0.7$) was pressed to cylindrical tablet (P = 100 kN) and ignited in argon or hydrogen (P = 2atm). At combustion in the argon atmosphere, a mutual dissolution of niobium and titanium was not observed. Combustion products were a mixture of the two, titanium and niobium, carbides with fcc structure. At combustion of the initial charge in hydrogen atmosphere, in particular, at high content of titanium and carbon, a full mutual dissolution of titanium and niobium carbides formed in the combustion front occurred. This leaded to the formation of single-phase complex titanium and niobium based carbohydrides with fcc structure. In some cases, in dependence on the ratio of metals and carbon, a small amount of chromium remained. After grinding and dehydrogenation of the complex carbides, their single-phase character mostly was saved. In Fig. 1 the X-ray pictures of Ti-Nb-Cr-C obtained at combustion of charge in argon (A) and of Ti-Nb-Cr-C-H, obtained at combustion of charge in hydrogen (B) are presented.

In our previous paper [1] the differential thermal analysis of complex carbohydrides in Ti-Cr-C-H system, have shown that their dissociation occurred at temperatures 360 and 530°C depending on the composition. Differential thermal analysis of carbohydrides studied in the present work, Ti-Nb-Cr-C-H, showed that their dissociation occurred with one endo-effect at relatively low temperatures of 330-350°C. Hence, we have shown that the introduction of niobium into the multicomponent system leaded to the decrease of the temperature of dissociation of the resultant hydride.



A

B

Fig. 1. X-ray pictures of: **A** - Ti-Nb-Cr-C obtained at combustion of charge in argon;

B- of Ti-Nb-Cr-C-H, obtained at combustion of charge in hydrogen

It is known that the hydrogen incorporated into the crystal lattice of the interstitial phase strongly embrittles it and allows easily dispersion. This property is often used in powder metallurgy for grinding [2, 3]. The multicomponent carbohydrides of variable composition, synthesized in this work, are easily dispersible to fine carbide Ti-Nb-Cr-C.

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Proceedings of the XII International Symposium on Self-propagating High-Temperature Synthesis

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PATTERNED PRECURSOR MEDIA FOR MODEL EXPERIMENT IN COMBUSTION SYNTHESIS

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In this report, we are describing a large scale patterning capabilities to investigate the application of combustion synthesis (CS) to patterned reactant multilayers. Significantly, patterning enables information on the interactions between individual reactive particles in the reaction zone, which is difficult if not impossible to attain in powder mixture. The approach enables quantitative analysis of temperature rise, heat generation and front propagation during the CS. A number of parameters can be varied in the patterned reactant multilayer approach including individual layer thicknesses, the number of layers, the spacing between patterned islands and island size, and substrate choice to control heat losses.

We have studied a self-assembly of diblock copolymer on solid substrates to fabricate patterned structures. Many types of block copolymers (e.g., diblock, triblock, etc.) have been used for nanoscopic patterning by several research groups. Here, we are interested in the self patterning of polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymer which is one of the most common block copolymer studied. We have developed the conditions to generate a nearly defect-free cylinder orientated PS-b-PMMA pattern. This can be obtained by utilizing the solvent-vapor annealing which has become widespread recently instead of high temperature annealing. A thin PS-b-PMMA film (ca. 14 nm) was prepared by spin coating 0.3 wt % toluene solution of the diblock copolymer on piranha-cleaned silicon wafer at 2000 rpm for 45 seconds. Then, this thin film was placed in a sealed chamber for solvent vapor annealing using acetone overnight before characterization. We also tried using a sputter deposited-palladium film on silicon wafer as the substrate and a comparable structure was obtained, as shown in Figure 1,a. Furthermore, the selective removal of PMMA in thin PS-b-PMMA film can be performed to create nanoporous materials (Figure 1,b). In our study, we exposed the thin film to ion beam using our colleagues' home-made helium ion beam irradiation system. The irradiation causes the PS matrix to cross-linked, but not the PMMA domains. Therefore, by soaking the resulting film into concentrated acetic acid would remove the PMMA moieties; leaving the PS matrix with cylinder orientated pores on the solid substrate, as confirmed by XPS data in Figure 1,c.

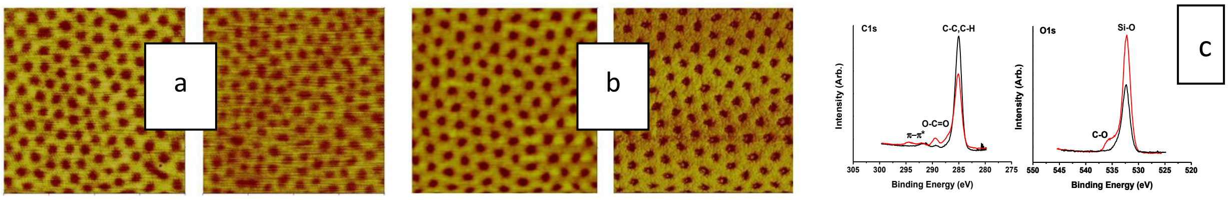

Figure 1. (a) - AFM images (scale 1×1 μm) of PS-b-PMMA pattern showing cylinder orientated PMMA embedded in PS matrix prepared on Si (left) and Pd (right) substrates; (b) - AFM height (left) and phase (right) images (scale 1×1 μm) of PS matrix with cylinder orientated pores with ca. 10-12 nm deep. (c) - XPS data showing C1s and O1s peaks for the

thin PS-b-PMMA film before (red) and after (black) ion beam exposure. The disappearance of O-C=O and C-O indicated the successful removal of PMMA.

Next, the possibility of SLIM process using a commercial Oxford 100 Plus reactive ion etcher, RIE, was explored. It should be noted that the process explored here is not “reactive” ion etching but rather a version of ion milling/sputtering utilizing using RIE equipment. The RIE system used to further study the SLIM processing had a base pressure of 3.75×10^{-2} mTorr and a process pressure of 10 mTorr. The RF power was set to 70 W with the resulting DC bias of 250V. It should be noted that the process pressure here is 20 times higher than the process pressure used in ion milling and while the bombarding ion energy is a half of what was used in ion milling. This low energy of argon ions is advantageous with respect to the reduced ion damage of the underlying materials. A 60 nm diameter on a 100 nm pitch dot array transformed into ~80 nm square patterns after being etched by argon plasma for 4 min. is shown in Figure 2.

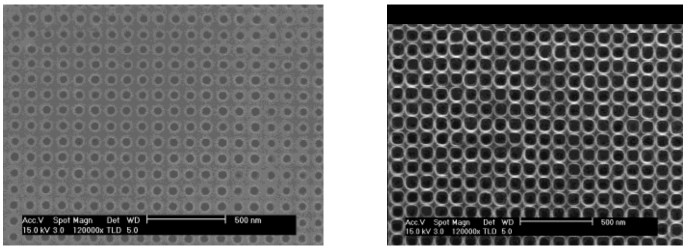

Figure 2. (left) A SEM image of ~60 nm diameter, 100 nm pitch dot array on a square grid formed in PMMA using e-beam lithography. (right) A SEM image of ~ 75 nm length square patterns on a 100 nm pitch after 4 min etching.

According to recent experiments, we observe that it is more difficult to convert densely packed square patterns with good uniformity as the structure size decreases, likely due to the resolution limit of the e-beam writer used.

FEATURES OF ALUMINOTHERMIC SHS REDUCTION OF ZIRCON IN THE NITROGEN ATMOSPHERE

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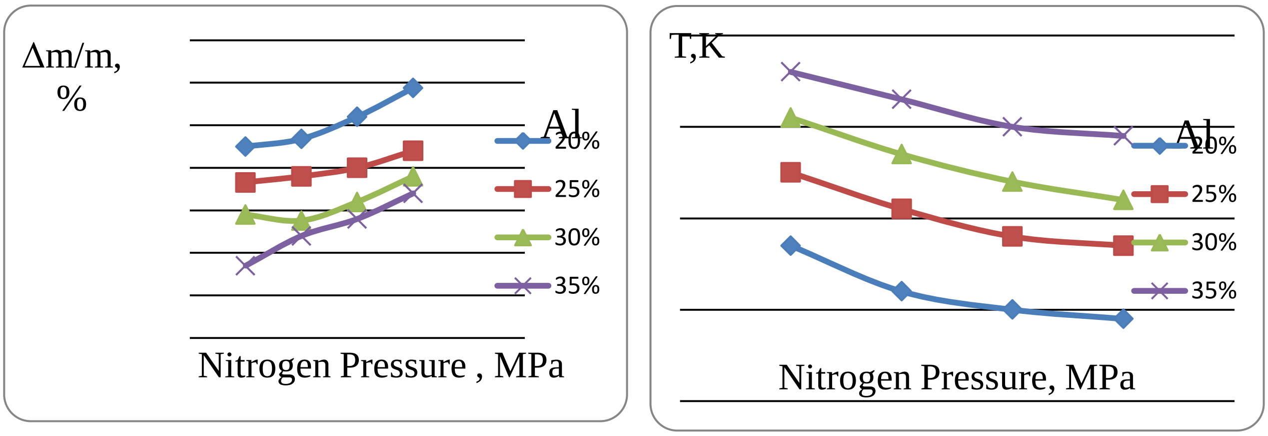
Zircon (zirconium silicate) is a major raw material used for production of elementary zirconium, zirconium oxide, fire-resistant and composite materials, and pigments. There are numerous methods currently applied to produce new composite materials containing zirconium and its compounds and having a wide range of useful properties [1, 2]. The purpose of this survey is study the zircon aluminothermy features when the nitride-containing composite ceramics is produced in the SHS mode in the conditions of nitric atmosphere at higher pressures. Related experiments have been carried out in the tubular furnace placed inside the high pressure reactor. The nitrogen pressure in the reactor varied from 0.5 up to 2.0 MPa. Initially used mixtures consist of aluminum and zircon powders with various ratios. 10 % mass of zirconium powder has been added to all mixtures to provide steady SHS combustion. The combustion temperatures have been measured by means of the thermocouple method. The experiments accomplished in the high pressure reactor with preliminary heating of the samples have demonstrated both steady spontaneous ignition and steady synthesis for all the compositions. There has not been revealed any noticeable effect of the external nitrogen pressure on the starting synthesis temperature that is within 850 °C. All the compositions have shown tendency towards combustion temperature decrease with the increase in the nitrogen pressure as well as tendency towards combustion temperature increase with the increase in the aluminum contents (Figure 1a).



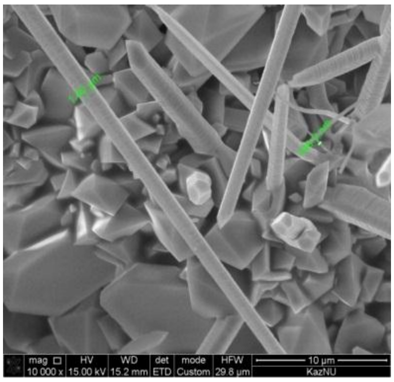
a) b)

Figure 1. Combustion temperatures (a) and relative changes in the samples mass (b) depending on the nitrogen pressure and aluminum contents.

The reason is that basic heat generation occurs due to the aluminothermic reduction of zirconium and silicon, whilst growth of the external pressure sharply increases gas heat conductivity resulting in increased heat loss and lower temperature in the system. In all the cases the SHS process leads to increase in the samples weight within 2-4 % mass due to the reaction capture of nitrogen with subsequent formation of the nitrides (Figure 1b). The nature of the mass increase such as decrease in the degree of the mass increase with growth of the nitrogen pressure seems to be quite unexpected. Peculiarities of a sample mass increase depending on the nitrogen pressure can be explained based on the results of the X-ray phase analysis of the SHS products according to which growth of the nitrogen pressure in the system leads to increase in the oxynitride contents while the zirconium nitride contents providing basic mass gain decreases increases. Absence of any elementary zirconium and silicon in the synthesis products indicates that reduced zirconium is extremely active and at immediately reacts with nitrogen forming nitrides, and excessive aluminum leads to complete reduction of silicon and zirconium that form zirconium disilicide through their interaction.

Figure 2 illustrates the electronic microscope pictures of the nitride-containing composite products synthesis.

(a)



(b)

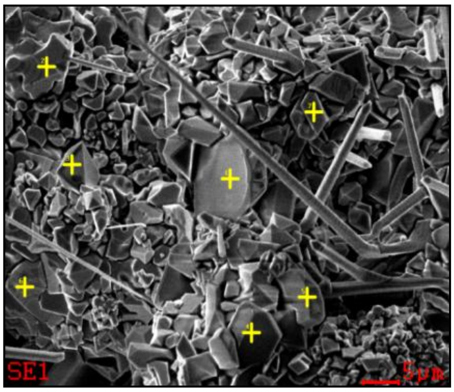


Figure 2. Electronic microscope pictures of the synthesis products: (a) General view and morphology of composites; (b) Typical microcrystals size.

Figure 2 illustrates long rachislike crystals of zirconium nitride; polyhedrons crystals correspond to aluminum oxide in the corundum modification. Apart from that, the synthesis products have certain amount sof zirconium silicide and aluminum oxynitrides. Unreduced zirconium oxide has been found in the products when the aluminum contents in the system is less than 28 %. Thus, the results of the study of the aluminothermic synthesis of the zircon based composite materials carried out in the SHS mode in the nitrogen atmosphere at increased pressures prove that formed products are high-refractory and chemically inert materials that are of considerable practical interest for chemical and metallurgical industries.

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GAS-PHASE SYNTHESIS OF NANOSTRUCTURAL CERAMICS BY METAL COMBUSTION

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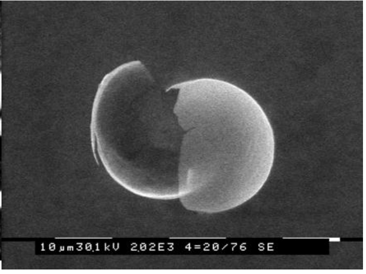
SHS is considered nowadays not only as combustion waves in single-phase solid systems but also as the synthesis in multi-phase systems. For majority of SHS-processes combustion of metallic components is the most important source of energy and useful products. That is why the subject of this paper is combustion of metallic particles (aluminum, titanium, zinc, and zirconium) in different gas-phase mixtures (air, nitrogen, oxygen, carbon oxides), and application of this process for the synthesis of nanostructured ultra-porous ceramics. Specific attention is given to the influence of pressure and composition of the gas medium on the combustion products, their stability and structural macro-kinetics.

It is known that among molecules forming a condensed particle the surface molecules are more energetic than molecules located inside the particle. Increasing the part of such particles (specific surface area of particle) can significantly change physical properties of the material. The proportion of the surface molecules is equal approximately to 50% for the particles containing 1000 molecules [1]. The typical size of these particles is approximately equal to 1 nm. Ratio of the surface molecules is inversely proportional to the particle size. It becomes negligible for the particles having size of 100 nm [1]. Therefore, for the synthesis of nanostructured materials, the most important are particles whose size does not exceed a few tens of nanometers. The synthesis of such ceramic nanoparticles in metal combustion is the main purpose of technologies presented in this paper. We represent some original technologies for production of nano-sized ceramic particles and nano-structured ultraporous ceramic materials. These technologies are based on the methods and installations designed in ICP RAS to study the mechanism of condensed products formation in combustion of metallic energetic compositions [2-5]. These installations allow one to examine combustion of single free particles, and combustion of assemblies and jets of metal particles.

The particle-to-size distribution of the condensed phase of combustion product (*c*-phase), typically, has two distinct modes: a submicron (nano-sized) mode and a large mode which is comparable with the size of initial metallic particle. This is due to the existence of two mechanisms for metals combustion: the first is the oxidation of the metal vapor in the volume around the particle, and second is heterogeneous oxidation on the surface of the particle. To increase the yield of ceramic nanoparticles and to reduce their size we have to stimulate oxidation in the gas phase, stimulating evaporation of metallic particles. This is facilitated by reducing the pressure, however, as the results of our investigations, the pressure can strongly influence the composition of the *c*-phase. Moreover, the oxidizing gas pressure and size of the original metal particle impact on the structural macrokinetics forming final ceramic material after combustion.

The study of single free particle combustion in the falling combustion chamber allows to discover mechanism of metallic particles ignition and combustion under controlled conditions [2]. The experimental investigations of combustion of free aluminium particle in low gravity conditions [2] first have shown formation of ultraporous nanostructured snake-like aggregates of Al_2O_3 –nanoparticles (aerogel), see Fig. 1. In normal gravity conditions, experiments with single free particle combustion, as well as with combustion of assemblies and jets of metal particles do not give the snake-like aggregates but other types of ultraporous ceramics (aerogels). For example, *c*-phase of Zr- particle combustion product consists of hollow spherical particles having nano-sized walls (see Fig. 2); *c*-phase of product of zinc vapor combustion in the air consists of the needle aerogel structures (see Fig. 3).



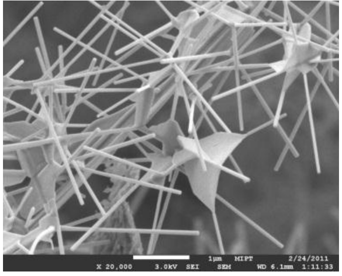


Fig. 1. Macro-assembly of nanoparticles of *c*-phase of aluminum particles combustion in 80% N2 +20% O2 under 60 atm.

Fig. 2. Hollow spherical particles of combustion products of zirconia particle in 80% N2 +20% O2 under 1 atm.

Fig. 3. Needle aerogel structure, formed during combustion of zinc vapor in the air.

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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS, PHASE COMPOSITION, STRUCTURAL PARAMETERS AND MAGNETIC PROPERTIES OF COMPLEX STRONTIUM HEXAFERRITES

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Among commonly used ferrites, the oxide ferrimagnetics with a hexagonal structure are of great interest, in particular, strontium hexaferrite $SrFe_{12}O_{19}$ (Sr-M) with high values of magnetization, magnetic crystalline anisotropy field (MCAF), and a high stability of these characteristics in a wide temperature range.

One of the main ways to control these characteristics is the introduction of various dopes of paramagnetic cations with an electronic structure different from that of iron ions to the main composition. For strontium hexaferrite the replacement of Fe^{3+}iron ions with a complex of $Co^{2+}Ti^{4+}$ leads to the significant decrease in magnitude of a magnetic crystalline anisotropy field and the frequency shift of the natural ferromagnetic resonance, and, accordingly, the operating frequency shift of radar absorption to the low-frequency microwaves.

Industrial production of these ferrites is based on the traditional multioperational ceramic technology that includes, in particular, the prolonged solid-phase sintering of components at high temperatures.

In recent decades, the Institute of Structural Macrokinetics RAS and the Scientific and Production Center of SHS (Armenia) have developed new progressive resource-saving methods for production of ferrites. These methods are based on self-propagating high-temperature synthesis (SHS) in the mode of filtration combustion of a powder mixture from iron and oxides of other elements in the atmosphere of reactive gases (oxygen or air).

The purpose of this work is to obtain the complex strontium hexaferrites $SrFe_{12-2x}Co^{2+}{}_xTi^{4+}{}_xO_{19}$ (replacement interval varies between $0 < x < 1.0$), and study the phase composition, structural parameters and fundamental magnetic properties of the synthesized materials using these methods.

Self-propagating high-temperature synthesis (SHS) in the mode of filtration combustion does not result in obtaining a single-phase product, the content of the targeted M-phase is 60-65 vol.% depending on the composition. Ferritization in air at 1200°C for 2 hours increases the main M-phase up to 75-90 vol.%.

We found that after the short-term (2 - 3 min) mechanochemical activation (MCA) of a mixture from the reagents in a planetary mill with subsequent SHS, the concentration of a targeted phase significantly increased and was about 75-87 vol.%. Subsequent ferritization increases the content of the main phase up to 95-96 vol.%.

After SHS, and also SHS and ferritization at 1200°C for 2 hours, the coherent scattering regions (CSR) were nanosized. When we obtained the M-phase using the mode of

MCA + SHS + ferritization at 1200°C for 2 hours, the CSR values were nanosized for most of compounds, but sharply increased at 1250°C for 2hours.

Thus, the method of SHS in combination with pre-mechanochemical activation and subsequent ferritization provides a product with a high content of the M-phase of complex strontium hexaferrites.

The specific magnetization and anisotropy field of strontium ferrites, including the replaced strontium ferrites decrease with the increase in concentration of the CoTi complex. In this case they are close to the literature data for powder samples prepared by the conventional ceramic technology. Thus, the mode selected for obtaining complex strontium ferrites, including mechanochemical activation allows us to produce ferrites with the distribution of cations close to equilibrium.

The analysis of the concentration and temperature dependences for the magnetic characteristics shows that the synthesized oxide ferrimagnetics are promising materials for thermostable radar absorbing devices and coatings within the frequency range of 20-25 GHz.

We have proposed the resource-saving methods to produce complex strontium hexaferrites based on self-propagating high-temperature synthesis. These methods reduce the number of operations and the cost of production compared to the ceramic method.

CAST METAL-MATRIX COMPOSITES BASED ON Ni ALUMINIDES BY COMBINED CENTRIFUGAL CASTING–SHS PROCESS

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The metal-matrix composites (MMCs) have been found [1] to show a unique combination of properties: high strength and excellent corrosion resistance in conditions of heavy loading and friction at high temperatures. Due to their attractive functional properties MMCs are regarded as promising candidates for use in marine and aerospace propulsion engineering, power engineering, gas/oil transportation, as heavy-current electric contacts, structural engineering materials, armoring materials, etc. [2]. Three processing methods are primarily used to design metal-matrix composites (MMCs): powder-metallurgy, pressure-assisted casting, and high-pressure diffusion. Main drawbacks here are high energy requirements, complexity, and expensive equipment.

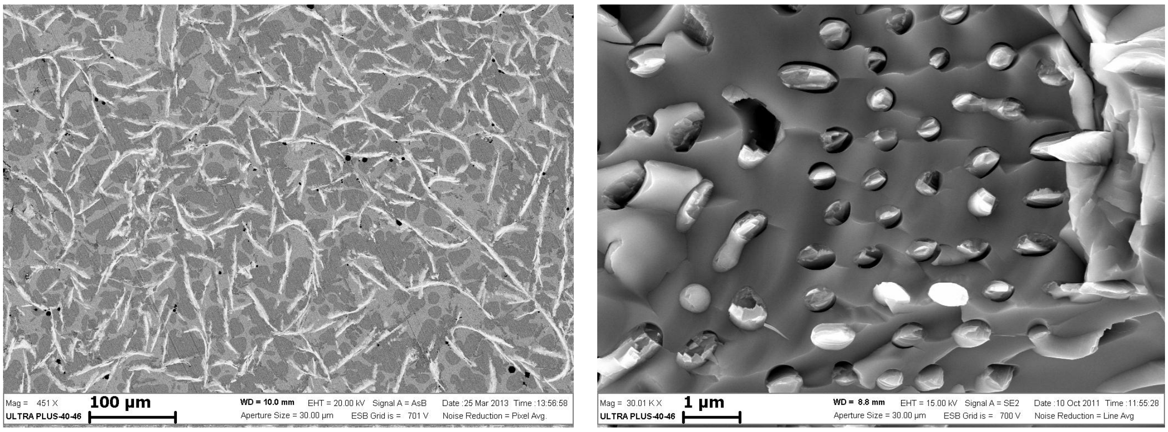
In this work, we attempted to fabricate cast MMCs on the basis of Ni aluminides (Ni–Al/Mo(Nb)–B, Ni–Al/Ti(Mo)–B, Ni–Al/Zr–B *etc.*) by combustion synthesis which combines the advantages of metallothermy and Self-propagating High-temperature Synthesis (SHS). Since the combustion temperature of typical thermite-type SHS mixtures is in the range of 2500–3500 K, this technique affords fabrication of cast materials [3]. This work aimed at searching reactive systems and process parameters that would ensure simultaneous preparation of both metal matrix and boride filler in a single process.

Combustion was performed at centrifugal acceleration $a = 10–400\ g$. In this way we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product composition more uniform.

Figure 1 exemplifies the microstructure of cast MMCs. Here dark areas correspond to matrix material while the brighter ones, to hard filler. The synthesized samples have not been subjected to additional thermal treatment; the pattern formation took place during the SHS process (in situ).

Detailed investigation revealed formation of a two-storey architecture of material microstructure. The first level is formed by a metal/ceramic structure. This is a basic structural element of synthesized MMCs. At higher magnification we could also discern the spatially strengthening body-structured units of the metal matrix. The second storey is formed by intermetallic/intermetallic elements. According to our EDS data, composition of these deposits is formed by nickel aluminides. Addition of alloying agents into green mixture was found to markedly change the microstructure and morphology of resultant MMCs. The Vickers hardness of synthesized MMCs was found to vary between 9.5 and 14 MPa.

The process can be recommended for practical implementation in production of cutting tools, tribological materials, moulds, and deposition of protective coatings. The present results can be expected to make a theoretical background for industrial-scale manufacturing of new tungsten-free MMCs with valued properties.



(a) (b)

Figure 1. SEM micrographs of cast MMCs: (a) polished surface of Ni–Al/Mo(Nb)–B and (b) fracture surface of Ni–Al/Ti(Mo)–B composite.

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COMBUSTION SYNTHESIS OF TWO-DIMENSIONAL NANO-CRYSTALS

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Exfoliation of atomically thin carbon sheet, named graphene, from bulk graphite spurred great interest in two-dimensional nano-crystals. It was suggested that layered compounds (e.g. MoS_2, WS_2, $MoSe_2$, $NbSe_2$, $NiTe_2$, hexagonal BN and WO_3) may also be exfoliated into two-dimensional (2D) thin crystals. Recently we discovered several novel schemes [1-3], which allow to produce graphene and other 2D nano-crystals (e.g. MoS_2, WO_3) and composites (e.g. H_2WO_4-W, WO_3-W, graphene - prorous carbon) using different self-sustained exothermic reactions. For example, the combustion synthesis of free-standing graphene flakes (Fig.1a) is based on fundamentally unusual type of self-sustaining reactions between a refractory ceramic compound (silicon carbide) and a halogen containing polymer (polytetrafluoroethylene, PTFE) under the inert atmosphere. The synthesis of MoS_2 2D nano-crystals (Fig.1b) have been achieved by controlled ball-milling induced exothermic reaction between $MoCl_{5a}$ and Na_2S in the inert atmosphere. Tungsten oxide based 2D-structures (Fig.1c) were produced by solution combustion synthesis of different tungstates followed by their further chemical treatment with different agents.

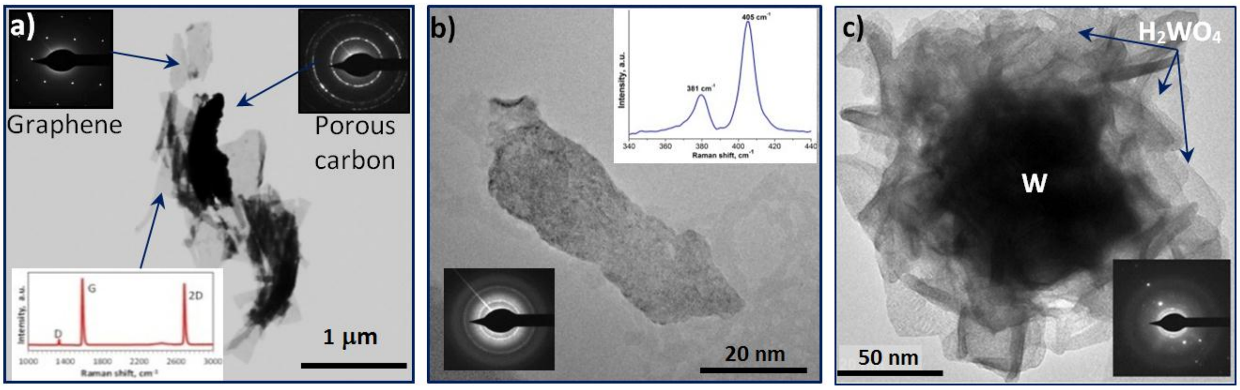

Figure. 1 The results of TEM analysis and Raman spectroscopy for different 2D materials produced by CS: graphene-porous carbon (a), molybdenum disulfide (b) and H_2WO_4-W composites (c).

We thoroughly investigated the effect of synthesis conditions (e.g. maximum combustion temperature, heating and cooling rates, pressure of inert gas, used additives, ball-milling and post-synthesis treatment) on phase composition, crystallinity, microstructural characteristics (shape and size of flaks) of combustion-derived 2D nano-crystal. It is found that the most important factors influencing at composition and microstructure of materials (e.g. number of layers) are maximum combustion temperature and the value of an inert gas pressure. For example, fine tuning of reaction conditions allows us to change the ratio of crystalline and amorphous

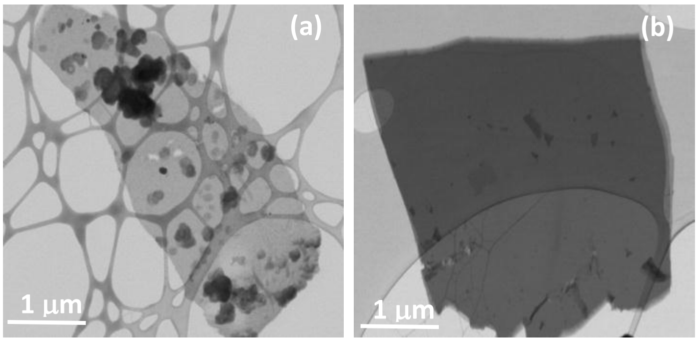

Figure 2. The microstructures carbon sheets produced at 1150 (a) and 1600°C (b) temperatures.

carbons with different pore sizes (micro- or measo-pores) and their distributions [1,2]. It is more important that fine control over the reaction temperature also allows to a gradually vary the thickness of carbon nano-sheets (Figure 2).

We used combination of different dynamic diagnostic techniques (differential thermal analysis, mass-spectroscopy, infrared temperature measurement, etc.) coupled with high-resolution TEM analysis to understand the mechanism involved in synthesis of 2D nano-materials. Those investigations suggest that in SiC+PTFE system tetrafluoroethylene (C_2F_4) gas, released due to PTFE decomposition, reduces SiC to tetrafluorosilane (SiF_4) gas and disordered carbon particles with folded “native” graphene layers on their surfaces. The continuous supply of carbon (in the form of C_2F_4) enables further rapid growth of “free-standing” graphene flakes on the surface of those graphene-coated particles. Relatively low temperatures and used additives in ball-milling induced combustion provide synthesis of exfoliated 2D MoS_2 nano-crystals. Other strategy to produce 2D nano-crystals involves combustion synthesis of layered materials and their subsequent exfoliation by a post-combustion process. This new pathway provides synthesis of doped 2D nano-materials (e.g. Zr doped WO_3) and self-assembly structures (WO_3/W and H_2WO_4/W) involving 2D nano-crystals [3]. More details on synthesis conditions, mechanism governing the growth of 2D nano-crystals and some important applications of resulting materials will be discuses.

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COMBUSTION AND MICROWAVE SYNTHESIS OF TUNGSTEN AND MOLYBDENUM CARBIDE CATALYSTS

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Catalytic systems based on carbon coated tungsten carbides (WC/C and W_2C/C) and molybdenum carbide (Mo_2C/C) were prepared by two methods: (1) *impregnation combustion synthesis* (ICS) [1, 2] and (2) *microwave synthesis* (MS) [3]. In the first case (ICS method) water soluble salts or peroxocomplexes of metal as reagents are used, which on carbon (or γ-alumina) carrier are impregnated. In recent years interesting results are obtained in synthesis of carbides by microwave heating method [3]. It allows to obtain tungsten and molybdenum carbides (WC, Mo_2C) with grain sizes <50 nm, which shows promising results in fuel cells. This method has some advantages compared with previous method, it provides:

- uniform heating of bulk sample,
- opportunity to synthesis carbides nanoparticles (particle size <50 nm) and high specific surface areas (up to several hundred m^2/g),
- target end-products purity (absence of wastes like MgO) and high yield**.**

By MS method MeO_3-C, MeO_3-C-Al_2O_3 and MeO_3-C-SiO_2 systems are investigated to synthesis carbides with different phase composition and on different carriers.

Metal powders, as well as their salts (ammonium tungstate, sodium tungstate, ammonium molybdate) as raw materials were used. It was shown, that precursor's nature, initial mixture composition and combustion conditions have significantly affect on the composition of final products. Optimal conditions for carbides (WC, W_2C, Mo_2C) synthesis were found. Carbides also on other carriers, like carbon and γ-alumina (250 and 200 m^2/g specific surface area, respectively) were supported.

In the first case (ICS method) carbidization of metal under combustion mode in the presence of magnesium is performed. In the case of MS carbidization is possible without magnesium, which solves the problem of leaching, as well as increases yield of process. Thermal regimes of processes of reducing and carbidization can be regulated by changing combustion temperature and get products: tungsten and molybdenum carbides (WC, W_2C, Mo_2C), as well as systems on different carriers (WC/C, Mo_2C/C, WC/Al_2O_3 etc.). Both methods have the chance to get nanopowder and homogeneous carbides with developed specific surface areas.

The obtained carbides catalytic activities were tested for the following reactions: (i) isopropyl alcohol dehydration (very high activity) [4], (ii) cyclohexane dehydrogenation and (iii) dry reforming of methane. These carbide catalysts will be applied also in hydrazine decomposition [5]. Hydrazine catalytic decomposition has two practical importances: as a fuel for rocket engines

$$N_2H_4(g) = 4NH_3(g) + N_2(g), \qquad \Delta H = -37.5\ \text{kkal/mol} \qquad (1),$$

and as a source of hydrogen in the fuel cells

$$N_2H_4(g) = N_2(g) + 2H_2(g), \qquad \Delta H = -22.8\ \text{kkal/mol} \qquad (2).$$

Our prior investigations have shown that phase Mo_2C prepared by modified SHS method performed high catalytic activity [6] in the mentioned (1) reaction at low temperature and (2) reaction at high temperature.

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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF COMPLEX OXIDES FOR THERMOELECTRIC APPLICATIONS

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Large amount of waste heat (20.90x1015 Btu) is produced by transportation in the US [1]. Most of the energy heat loss is in the exhaust of automobiles, which can reach temperatures of about 600 ºC. This heat, if recycled, can be used to power various electronic equipments in an automobile. Thermoelectric materials are compounds that can utilize temperature differences to generate electrical current. The Seebeck effect describes the generation of an electrical current in a closed loop when there is a temperature difference between two leads[2]. In recent years, the Seebeck effect is used to generate electrical power for electronic equipment in automobiles from their exhaust heat. Thermoelectric materials are characterized by their thermoelectric figures of merit, ZT, defined by equation (1):

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T \quad (1)$$

where α is Seebeck coefficient, σ is electrical conductivity, T is temperature, and κ is thermal conductivity. Calcium cobaltates (e.g. $Ca_{1.24}Co_{1.62}O_{3.86}$) are good candidates for thermoelectric applications in oxidizing environment [3] because their resistance to oxidation and thermal stability at elevated temperatures. Calcium cobalt oxides have good thermoelectric properties due to their intricate layered structure, which combines the electron conducting CoO_2 and insulating Ca_2CoO_3 substructures [4]. In the work, Self-propagating High-temperature Synthesis (SHS) was used to produce $Ca_{1.24}Co_{1.62}O_{3.86}$ for thermoelectric applications.

Surface temperature of the surface during the SHS reaction was measured by an IR thermal imager. Product after SHS reaction was not pure. Reacted pellet was dark grey in the center and light grey near the surface, suggesting incomplete reaction due to low temperature on the surface. X-ray powder diffraction of synthesized sample showed no desired product nor any starting reactant and its oxides. Synthesized product was an unknown compound, most likely a calcium-cobalt oxide of unknown stoichiometry or lattice constant. Products of SHS reaction were then heat-treated in air for 30 minutes at 850 ºC to obtain pure product and tested for their thermoelectric performance. At 500 ºC the ZT value of the prepared calcium cobaltate was 0.13. Even though the electrical conductivity was lower then samples prepared by others, high Seebeck coefficient of our sample compensates for the deficiency.

To improve the thermoelectric properties of the calcium cobaltate small amount of calcium was replaced by silver. Substitution of calcium with silver resulted in a decrease in thermal conductivity. The decrease was especially significant at lower temperatures. For example, at 50 ºC the thermal conductivity was decreased by 30% for a sample containing 5% of Ag. The decrease in thermal conductivity is though to be caused by increased rate of phone scattering, which is the result of the defects introduced by the Ag ions. Silver has different ionic radius (1.26 Å) than calcium (0.099 Å) and which causes disturbance in the crystal lattice. The decrease of thermal conductivity therefore increases the figure of merit (ZT) value.

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DESIGN OF NEW COMPOSITE MATERIALS VIA MASHS

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Mechanochemical synthesis under conditions of intense mechanical activation (MA) of the reactive mixture is widely used for preparation of green exothermic mixtures to be used in SHS- technology [1-7]. The advantages of MASHS are related with quickness reactions, preventing the annihilation of the stored charge of energy. The basic idea of the application of MA in the SHS process is to increase the reaction ability of the mixture.

At the same time the most important technological problem is a search for optimal conditions of the MA which allow to produce the desired product of a given composition and properties. Various authors have proposed methods for analytical calculation of the energy parameters of MA, but they are based on a simplified scheme of interaction of grinding media with a mixture of components, and at best can be used for the qualitative characteristics of MA. The most suitable parameters for evaluation of the MA contribution seem to be amount of released heat and change in the activation energy for formation of targeted product. From these data we can determine the amount of heat released during combustion per gram of mixture and calculate the temperature of combustion. [1-4]. Thus, we can predict the mode of SHS process for a specific compound or composite material and to conduct evidence-based selection of the appropriate SHS technology and equipment.

Another important factor is structure of mixture after MA. The structure of the starting powders during MA as a result of repetitive processes of destruction and cold welding is changing. Formation of a particular type of structure is determined by the nature of the components of the mixture, equipment and mode of MA. By changing the parameters of MA can form different types of structures consisting of

- evenly distributed over the volume components;
- agglomerates of the mixture components which differ in composition and size;
- granules, wherein the components of the charge jumbled practically at the atomic level.

Mixtures of the same composition with a different structure have different combustion rate and heat evolution. As a result, the microstructure of MA mixtures contributes the significant effect on the combustion parameters and the final product structure and properties [3-4]. In a paper the effect of MA on structure of initial mixtures, combustion characteristics, and final products structure and properties an example of binary and ternary compositions (Ni-Al, Fe-Al-ZrO_2, Ti-Cr-Al-C, Mo-Si-B) were studied.

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TREATMENT OF ACIDIC WASTE SOLUTIONS OBTAINED FROM SHS PRODUCED TUNGSTEN BORIDES

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Self-propagating high temperature synthesis (SHS) is an alternative production technique for a variety of advanced ceramics, intermetallics, oxygen free single crystals, polymers and other organic and inorganic compounds. In the SHS method, after initiation, the reaction becomes self-sustaining and propagates in the reactant mixture. In case of advanced ceramic production by magnesiothermic SHS method, the product will certainly contain some mixture of unwanted compounds. So a subsequent acidic leaching process is unavoidable to purify the target product. However, waste leach liquor is an environmental concern when it contributes to groundwater contamination. In our previous study, calcium tungstate was reacted with magnesium (Mg) and boric acid (B_2O_3) mixture to produce boride powder by SHS process according to the reaction 1.

$$\mathrm{CaWO4 + 0.5B2O3 + 4.5Mg = WB + 4.5MgO + CaO} \qquad (1)$$

Then, magnesium and calcium containing byproducts (i.e. MgO, $Mg_3B_2O_6$ and $Ca_3B_2O_6$) found in the SHS product were leached out by using concentrated hydrochloric acid (HCl) solution to obtain pure tungsten boride powder.

In this study, the recycling conditions of magnesium, calcium and boron containing spent liquor obtained after the leaching of above mentioned SHS product were investigated. Before the experimental study, a computational thermochemistry simulation was carried out by FactSage to understand the interactions and effects of additives on the present acidic SHS waste solution. Different precipitates were obtained after the controlled additions of Na_2CO_3 or NaOH solution to the spent liquor by arranging pH conditions. The experimental flowsheet is shown in Figure 1. The effects of chemical reagents, pH, stirring speed & contact time and temperature were investigated in detail. The obtained products were characterized by using X-ray Diffraction and Atomic Absorption Spectroscopy.

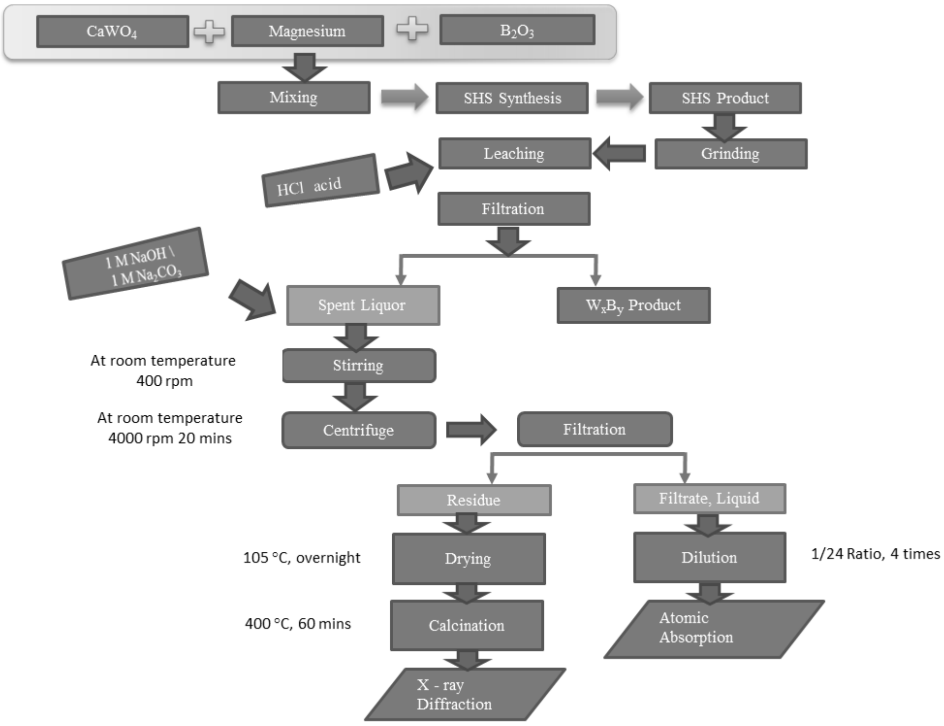

Figure 1. Experimental flowsheet

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Mo_2NiB_2 AND Mo_2FeB_2 BASED COMPOSITES AND PROTECTIVE COATINGS BY CENTRIFUGAL METALLOTHERMIC SHS

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Phase diagrams of Mo–Ni–B, Mo–Fe-B, W–Co–B, etc. systems suggest that complex borides Mo_2NiB_2, Mo_2FeB_2, W_2NiB_2, and MoCoB may come in thermodynamic equilibrium with a metal matrix of Ni, Fe or Co. This circumstance gives hope for preparation of stable metal-matrix composites (MMCs) in the form of a ductile metal matrix doped with uniformly distributed particles of hard and refractory transition-metal borides. Such MMCs have shown a unique combination of properties [1]: high strength and excellent corrosion resistance in conditions of heavy loading and friction at high temperatures.

In this work, we attempted to fabricate cast MMCs containing Mo_2NiB_2 (**I**) and Mo_2FeB_2 (**II**) by centrifugal metallothermic SHS [2] which combines the advantages of metallothermy and SHS. Since the combustion temperature of typical thermite-type SHS mixtures is in the range of 2500–3500 K, this technique affords fabrication of cast materials and protective coatings (SHS surfacing). We carried out a search for reactive systems and process parameters that would ensure simultaneous preparation of both metal matrix and boride filler in a single process. Then the above systems were use to deposit protective coatings of ternary borides directly onto commercially available Ti and Fe alloys during the SHS process.

Combustion was performed at centrifugal acceleration a = 10–400 g. In this way we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product composition more uniform.

As follows from Table 1, cast MMCs **I** contained orthorhombic Mo_2NiB_2 and $MoNi_4$ intermetallic, and some admixture of MoNi. The material has a clearly pronounced composite structure. The material of largely Ni matrix is filled with Mo_2NiB_2 particles 20–30 μm in their size uniformly distributed over the cast material (Fig. 1a).

The MMCs **II** have a Fe matrix impregnated with Cr and Ni in the form of sold solutions (F_{ss}). The boride Mo_2FeB_2 acts as a filler. Its particles about 10 μm in size are uniformly distributed all over the volume of cast material.

Table 1. Nominal and actual composition of cast MMCs I and II.

Nominal (wt %)		Actual (wt %)						
		Ni	Mo	Fe	B	Al	Cr	V
I	Ni–58Mo–6B	bal.	57.8	–	5.8	1.0	–	–
II	Fe–49Mo–6B–2.5Cr–2.5V	–	49.1	bal.	5.8	0.8	2.3	2.5

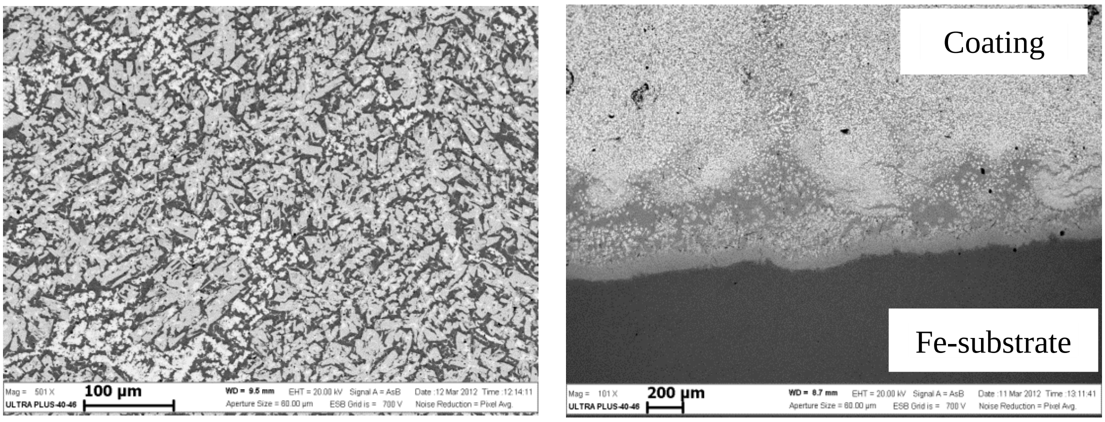

Figure 1**.** SEM micrographs of cast MMC **I** (a) and (b) Fe substrate with composite coating.

The Vickers hardness of synthesized MMCs was found to vary between 9.5 and 12 MPa. This makes such MMCs promising candidates for use in marine and aerospace propulsion engineering, power engineering, gas/oil transportation, as heavy-current electric contacts, structural engineering materials, armoring materials, etc. The process can be recommended for practical implementation in production of cutting tools, tribological materials, moulds, and deposition of protective coatings. This work can be regarded as the first positive experience of SHS surfacing of Ti substrates carried out in open air.

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MECHANICALLY ACTIVATED SHS COMPACTION OF MOLYBDENUM DISILICIDE BASED COMPOSITES

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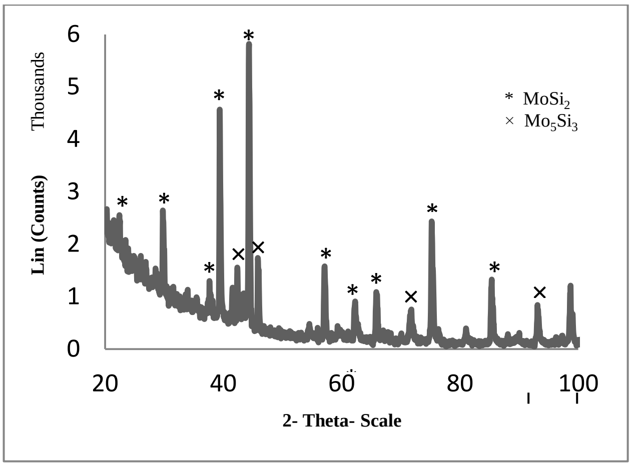
Molybdenum disilicide ($MoSi_2$) has been recognized as a promising high-temperature structural material due to the combination of attractive properties such as a high melting point (2030°C), a reasonable density, excellent high temperature oxidation resistance, and a brittle-to-ductile transition in the vicinity of 900°C. Thus, $MoSi_2$ can be used in oxidizing environments at temperatures that significantly exceed 1100°C, the limit for nickel-based super alloys currently used in advanced boilers and turbines. Further, $MoSi_2$ is non-toxic, environmentally benign, and suitable for electro-discharge machining. Molybdenum disilicide, however, has some problems, which can be overcome by adding secondary phases such as Mo_5Si_3 and WSi_2. Although SHS of $MoSi_2$ has been studied by many researchers [1-4], change in the stoichiometry and addition of other components decreases the exothermicity. This problem can be reduced with the so-called mechanically activated SHS, successfully used for fabricating $MoSi_2$ alone [5] or with secondary phases SiC [6] and WSi_2 [7]. The porosity problem of SHS products is overcome in SHS compaction, where the reacting mixture is compacted immediately after combustion, leading to the formation of dense, non-porous materials. In the present paper, both mechanical activation and SHS compaction (quasi-isostatic pressing) are used for the combustion synthesis of $MoSi_2$ – based composites. Molybdenum and silicon powders were mixed according to the desired $MoSi_2$-Mo_5Si_3 composition in a three-dimension inversion kinematics tumbler mixer and then milled together in a planetary ball mill. The as-milled powders were compacted into cylindrical pellets using a hydraulic press. The pellets were ignited in either a windowed steel chamber filled with argon or in a special die for SHS compaction, where silica powder was used as a pressure-transmitting medium. The die was placed under the hydraulic press, which was operated immediately after the end of combustion. The obtained combustion products were subjected to compressive tests. The milled powders and combustion products were characterized by XRD and SEM. It has been shown that mechanical activation of the reactants significantly accelerates combustion and enables stable, self-sustained combustion without preheating. Quasi-isostatic densification immediately after synthesis led to a 55–60% increase in the product density as compared with the materials obtained after combustion in argon atmosphere. XRD pattern of the products shows (Figure 1) that $MoSi_2$ is the major phase and Mo_5Si_3 is the secondary phase of the composite. Most particles have a size of 0.5–1 μm; they are agglomerated and form a three-dimensional network structure (Figure 2).



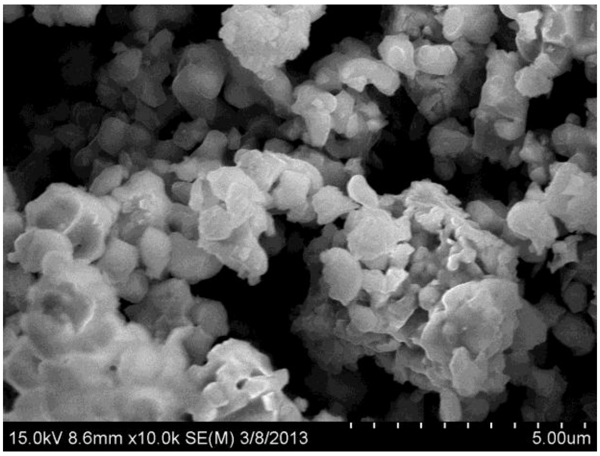


Figure 1. XRD pattern of the combustion products. Fig. 2. SEM micrograph of the combustion products.

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An INVESTIGATION on Co-BASED TERNARY ALLOY SYSTEMS PRODUCED by SHS METHOD

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Self-propagating high temperature synthesis processes are one of the highly productive and economically reasonable methods for the metallurgy industry. The synthesis of materials (compounds) by self-propagating high temperature takes place as a combustion reaction of reactive raw materials and the following chemical reaction by heat transfer that allows an easy production of ceramic and intermetallic materials.

This study covers information about our previous investigations on production and the thermodynamic aspects of Co-based cast alloys via self-propagating high temperature synthesis (SHS) methods. In order to reduce the number of examples, the thermodynamic aspects of the SHS processes were carried out firstly by using Factsage 6.2 thermochemical software in order to graph ternary phase diagrams and to calculate adiabatic temperatures and molar composition changes of the cast alloys such as Al-Co-Ni, Al-Co-V and Co-Fe-V. The initial mixtures were prepared from dried powders, and were calculated to produce the estimated alloys given in Table I.

Table I. Estimated alloys compositions of SHS reactions, wt.%

Al – Co – Ni System	Al – Co – V System	Co – Fe – V System
10.0 Al – 65.0 Co – 25.0 Ni	10.0 Al – 75.0 Co – 15.0 V	37.5 Co – 50.0 Fe – 12.5 V
10.0 Al – 40.0 Co – 50.0 Ni	10.0 Al – 55.0 Co – 35.0 V	25.0 Co – 50.0 Fe – 25.0 V
10.0 Al – 20.0 Co – 70.0 Ni	10.0 Al – 30.0 Co – 60.0 V	12.5 Co – 50.0 Fe – 37.5 V

The reaction mixtures were mixed thoroughly 15 minutes in a turbula mixer and powder mixtures (150 g) were charged into Cu crucible and compacted. Copper crucible was designed as two pieces; a base plate and a cylindrical part. The cylindrical part has 140 mm height with 50 mm outer diameter and 40 mm inner diameter. The bottom part of base plate has 50 mm outer diameter and top part of it has 40 mm outer diameter which is fitted with the cylindrical part. Cr-Ni wire was placed at the top of copper crucible and the reaction realized by passing current through the wire. After initiation, a highly exothermic reaction became self-sustaining and propagated throughout the SHS mixture. The obtained SHS products were discharged from the crucible after cooling.

The refining process was realized after obtaining SHS alloys by using Edmund Buehler MAM-1 mini vacuum arc melting system. The maximum 20 g of SHS alloys could be remelted at a time. By using a vacuum pump, air in the chamber was vacuumed out at 1 torr (10^{-3} bar), then high purity of Argon gas (99.998 %) were purged into the chamber. The arc was generated between tungsten (W) electrode and copper base plate under inert Argon atmosphere. The copper vase plate has a water-cooling-system to prevent to melt or react with the SHS alloy.

The phase compositions of the SHS products were characterized by X-ray diffractometer (PANalytical PW3040/60, Cu Kα radiation) equipment with using X'Pert HighScore+ software and ICDD, ICSD databases. The morphologies of the products were characterized by electron probe microanalysis (EPMA, CAMECA SX-100) with using three

WDS (Wavelength Dispersive Spectrometer) units. Wet chemical analyses were realized by using atomic absorption spectrometer (AAS, Perkin Elmer Analyst 800). Microhardness values of SHS and refined SHS alloys were measured by Struers Duramin A300 microhardness tester. A diamond based certified Vickers indenter was used and 0.3 kg (2.94 N) force had been loaded into the alloy surface during 5 seconds. Microhardness and standard deviation values were calculated within 15 hardness measurements.

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THE ROLE OF NH_4F ON THE MAGNESIOTHERMIC REDUCTION OF Na_2MoO_4

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The one stage obtaining of refractory metals from oxygenous raw materials is in the focus of our current research. Particularly, sodium molybdate, which is an intermediate product of Mo ore processing and available source, is of great interest for direct reduction. In our previous work magnesiothermic reduction of sodium molybdate by self-propagating high-temperature synthesis (SHS) method was performed [1]. Although Na_2MoO_4+Mg interaction characterized by sufficient exothermicity, but reaction proceeds partially, moreover, sodium and sodium oxide formed as unwanted aggressive compounds, which complicate the process and make it not safe. To avoid from the above-mentioned disadvantages it was suggested using CaF_2, which allowed to overcome the formation of sodium and sodium oxide, as well as to reach quantitative yield of target product. Thus, the experiments show that addition of 1 mole calcium fluoride to the stoiciometric Na_2MoO_4+3Mg mixture substantially influences on the combustion parameters, namely combustion temperature increases by 500°C, velocity – about 3 times. Moreover, reduction proceeds completely and according to XRD patterns at optimum composition of green mixture (Na_2MoO_4+3Mg+CaF_2) and process parameters (P=2 MPa) combustion product represent as molybdenum, MgO, CaF_2 and NaF. Note, that MgO, CaO and NaF byproducts easily removed due to acid leaching. The aim of this research was to study the use of NH_4F instead of CaF_2, which will increase the effective yield of Mo powder, as well as to simplify the process of acid leaching. In the case of ammonium fluoride, when using two moles of NH_4F combustion temperature increases by 300°C and velocity 2 times compared with just (Na_2MoO_4+3Mg) interaction. It also promotes the complete reduction of sodium molybdate leading to the formation of fine molybdenum particles. The using of NH_4F has one more privilege; it doesn't form additional byproducts, as in the case of CaF_2. The synthesis process is controlled by ambient gas pressure and sample parameters.

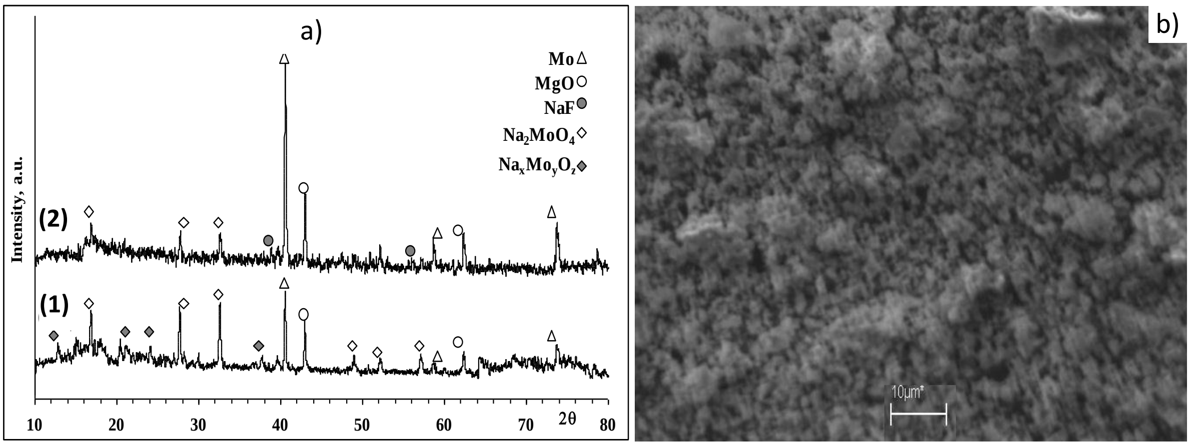

Fig.1. XRD patterns of combustion products of Na_2MoO_4+3Mg (1) and

Na_2MoO_4+3Mg+2NH_4F (2) mixtures (a) and SEM micrograph of combustion product of Na_2MoO_4+3Mg+2NH_4F mixture (b).

Thus, the possibility of complete magnesiothermic reduction of sodium molybdate and the positive influence of various additives was confirmed. Optimum conditions for obtaining molybdenum fine powder according to initial mixture composition, additive type and its amount, inert gas pressure, etc. found out.

ACKNOWLEDGMENT

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AMMONIUM PARATUNGSTATE REDUCTION BY COMBINED Mg-Zn REDUCERS IN COMBUSTION MODE

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Nowadays, nanosized refractory metals (tungsten, molybdenum) have received much attention in nanotechnology because of their unique physico-chemical properties. However, the complexity and expensiveness of their preparation methods impede their wide application.

In the work a new, effective method for obtaining of tungsten nanopowder by combustion synthesis approach was developed. As starting material the intermediate product of tungsten mine processing (ammonium paratungstate, APT: $(NH_4)_4W_5O_{17}\cdot 2{,}5H_2O$) was used. (Mg/Zn) combined reducers were chosen to perform combustion processes in mild and controllable conditions to obtain tungsten nanopowder.Preliminary thermodynamic analyses of the APT-Mg-Zn system were performed using the “ISMAN–THERMO” software. Adiabatic combustion temperature (T_{ad}) and equilibrium composition of the final products were calculated. Calculations showed that while magnesiothermic reduction of APT is too exothermic ($T_{ad} \sim 3100^oC$), the zincathermic reduction is low exothermic and cannot proceed in a self-sustaining mode. The coupling of mentioned high and low exothermic reactions allows to perform combustion reaction in the $(NH_4)_4W_5O_{17}\cdot 2{,}5H_2O$ - xMg - yZn system in mild and controllable temperature regime due to varying Mg/Zn ratio [1].

Particularly, decreasing Mg amount in the initial mixture from x=15 to 5 moles, leads to decreasing combustion temperature 2 times, and combustion wave propagation velocity - 15 times (fig. 1). At 4 moles content of Mg combustion lower limit was observed (fig. 1). According to XRD analysis of combustion products, one may conclude that x=8 value was found optimal for APT complete reduction. At x>8 values characteristic lines of tungstates and tungsten oxides were appeared in the XRD patterns of combustion products. Taking into account the implication of gaseous products in the process, as well as possible evaporation of Mg and Zn, the influence of ambient gas pressure on the combustion laws and relative mass loss (□m/m_o) of the initial ($(NH_4)_4W_5O_{17}.2{,}5H_2O$ + 7Zn + 8Mg) samples were investigated. It was shown that increasing ambient gas pressure above P=2 MPa obviate the removal of both reducers from sample and complete reduction of APT takes place. Note, that ZnO and MgO byproducts are easily removed by 10% HCl treatment. SEM and XRD analyses showed that

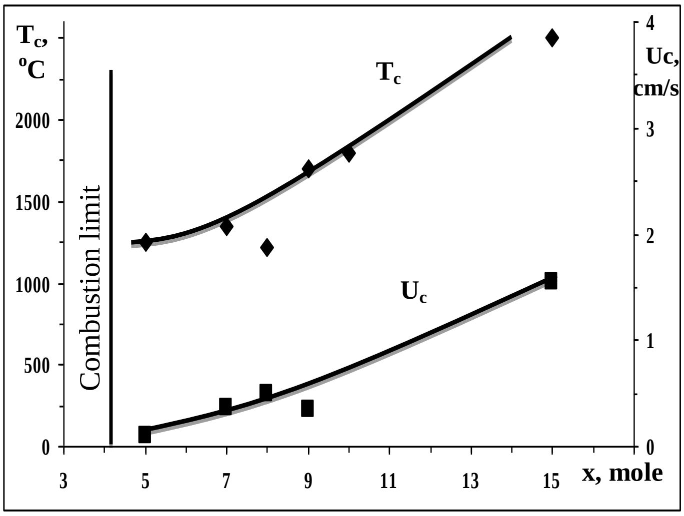

Fig.1. Combustion parameters of APT + xMg + (15-x)Zn system vs. Mg amount (x)

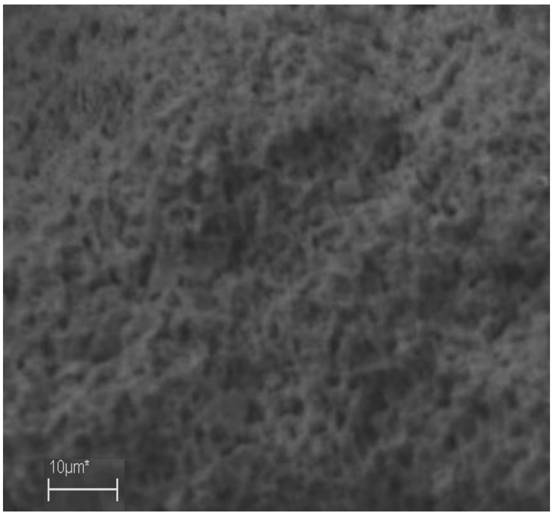

Fig.2. SEM micrograph of combustion product APT + 8Mg + 7Zn mixture

combustion product after acid leaching represent as submicron particles of tungsten (fig. 2).

Thus, the possibility of APT reduction by Mg/Zn combined reducers in the combustion mode was shown, the optimum parameters for the preparation of tungsten fine powder were determined according to initial mixture composition, ambient gas pressure, as well as sample geometry and density.

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The authors acknowledge the financial support of the State Committee of Science of the Republic of Armenia (Project no. 11_1d167).

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COMBUSTION SYNTHESIS OF Mo-Cu NANOCOMPOSITES BY CO-REDUCTION OF MOLYBDENUM & COPPER OXIDES

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Composite materials (such as Cu - refractory metal), which are composed of two or more metals with distinctly different physical properties, are widely used due to their multiple functionalities in heavy-duty electronic contacts, welding electrodes, vacuum technology, military fields, aeronautics, portable apparatus and some other advanced fields. These new type of materials combine the properties of both metals, even leads to the optimization of alloy properties, such as high thermal and electrical conductivity, low and alterable thermal expansion coefficient, low weight, nonmagnetic and well high-temperature behavior. Among such type of alloys Mo-Cu alloys have been attracted a great interest in both scientific and practical points of view. The increasing scientific interest in Mo-Cu alloys is caused by the facts, that despite the 1) significant difference in lattice parameters of metals (a(Mo) = 0.314nm, a(Cu) = 0.361nm) and 2) the high difference of melting points of copper ($T_{Cu}=1083^oC$) and molybdenum ($T_{Mo}=2625^oC$), as well as their insolubility in both solid and liquid states, they form a material with absolutely new structure, so called pseudo-alloys.
Mo–Cu composites are generally fabricated by Cu infiltration in Mo skeleton or liquid phase sintering of Mo–Cu powder mixtures. Since the Mo–Cu system exhibits mutual immiscibility or negligible solubility, Mo–Cu powder compacts show very poor sinterability, even by liquid phase sintering above the melting point of the Cu. Moreover, in most of the applications, high-dense Mo–Cu materials with homogeneous microstructure are required for high performance, which is possible by applying ultra-fine and well-dispersed powders.

In the present work it was suggested a new approach for manufacturing of Mo-Cu composite nanomaterials via co-reduction of Mo and Cu oxides in combustion mode by combined (Mg+C) reducers. The magnesiothermic reduction of MoO_3 and CuO are too exothermic (T_{ad} ~ 3000^oC), while carbothermic reduction is low exothermic and cannot proceed in a self-sustaining mode. The proposed approach allows to perform joint reduction of oxides in controlled combustion regime and to obtain Mo-Cu composite material.

At first, for estimating the value of adiabatic combustion temperature (T_{ad}) and equilibrium composition of the final products, preliminary thermodynamic analyses of the MoO_3–CuO–(Mg+C) system were performed using the “ISMAN–THERMO” software developed for multicomponent heterophase systems. Calculations showed that reactions in the MoO_3–CuO–(Mg+C) mixtures are characterized by significant exothermicity and can proceed in the self-sustaining mode with Mo-Cu single product formation.

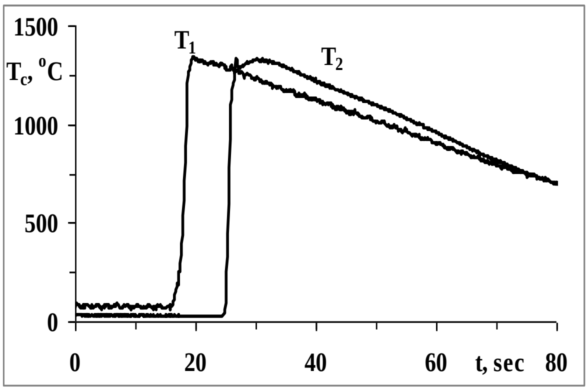

Fig.1 Combustion thermograms of the MoO_3-CuO-(Mg+C) mixture, P=0.3 MPa.

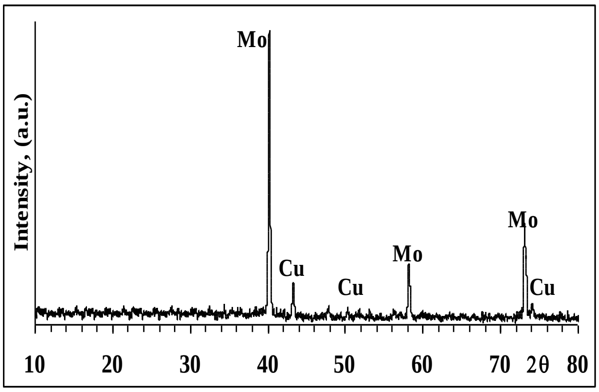

Fig.2 XRD pattern of combustion product of MoO_3-CuO-(Mg+C) mixture after acid leaching, P=0.3 MPa

Based on the thermodynamics, combustion experiments were performed in the MoO_3 – CuO –(Mg+C) system with appropriate compositions. It was shown, that combustion parameters (T_c, U_c), as well as products composition and characteristics are controlled by varying initial mixture composition (mainly Mg/C ratio) and ambient gas pressure (up to 0.3 MPa N_2). The analysis of both temperature profiles (fig.1) and XRD patterns (fig.2) showed the possibility of complete joint reduction of MoO_3 and CuO oxides by combined (Mg+C) reducing mixtures in mild combustion conditions. During the magnesiothermic reduction apart from the Mo-Cu composites, MgO produces as a byproduct, which is easily removed from the main product by acid leaching.

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COMPOSITE CERAMICS ON THE BASIS OF β-SIALON USING Fe-Si-Al

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β-sialons are solid solutions with a variable composition ($Si_{6-z}Al_zO_zN_{8-z}$) produced on the basis of β- Si_3N_4 by replacing Si → Al and N → O (z is the number of substituted atoms of silicon and nitrogen in the formula of silicon nitride, varies from 0 to 4.2), have a stability at high temperatures (1500-1800º C), high corrosive, heat-and wear-resistance, high hardness and strength [1, 2]. Traditionally, the synthesis of sialons is combined with hot pressing of mixtures from the previously prepared powders of Si_3N_4, AlN and Al_2O_3, which causes the high cost of ceramic materials. For simplifying a process for the production of sialon ceramics and reducing its cost, it is appropriate to use raw materials not subjected to deep chemical purification, such as natural silica-aluminia minerals or iron-containing alloys. Especially attractive materials are ferroalloys containing in the composition both nitride-forming elements which enter into the composition of sialon: aluminum and silicon.

This paper presents the study of the ceramic composite synthesis on the basis of sialon in the mode of self-propagating high-temperature synthesis (SHS) using aluminum ferrosilicon (AFS) as a row material.

Aluminum ferrosilicon (FS65A15) was used as a row material. According to the data of X-ray phase analysis (XPhA), the original AFS was a multiphase material consisting of silicon and high-temperature leboit ($FeSi_2$). According to the results of X-ray microanalysis with the use of the CAMEBAX-MICROBEAM analyzer we found that aluminum was represented as a solid solution in the phase of $FeSi_2$. The impurity phases were Al_2O_3 and $Al_{0.5}Fe_{0.5}$. The results of chemical analysis have shown that the content of silicon in the alloy is 60.1 wt. %, aluminum - 13.2 wt.%, the rest is iron. The AFS powder was placed in the cylindrical tubes constructed from a metal mesh 30 ÷ 60 mm in diameter and burned in the installation with a constant pressure using the method [3], when the pressure of nitrogen was varied from 1 to 6 MPa.

The experimental results have shown that the maximum temperature of AFS combustion is 2120±15ºC and exceeds the temperature of ferrosilicon (FS 75) combustion by approximately 100ºC. This fact is probably connected with the exothermic reaction between aluminum and nitrogen in the combustion wave, which leads to the formation of aluminum nitride with high heat of formation (259.4 kJ/mol).

The AFS combustion product is a multiphase material consisting mainly of β-Si_3N_4 and FeSi. A significant amount of iron monosilicide (FeSi) in the combustion products indicates a low degree of nitration for the products of combustion. To achieve the highest nitration degree of the synthesized products and obtain β-sialon with a composition of $Si_3Al_3O_3N_5$, we added alumina (α-Al_2O_3) to the row material in the amount of 5 - 22 wt.%. Combustion of aluminum ferrosilicon was not initiated after adding Al_2O_3 in the amount more than 22 wt.%.

A detailed study of the diffraction profile for the combustion products of AFS in the presence of the Al_2O_3 additives showed the displacement of all diffraction peaks towards the smaller angles (2θ). We found that the increase in Al_2O_3 additive approximated the parameters of a crystal lattice to the reference values for β - $Si_3Al_3O_3N_5$ and the maximum compliance was in the case when the Al_2O_3 additive was 22 wt.%. In this case it is formed almost a two-phase product of combustion consisting of β - $Si_3Al_3O_3N_5$ and α-Fe. To obtain pure sialon it is enough to process the combustion product with a weak solution of hydrochloric acid.

The obtained material (β - $Si_3Al_3O_3N_5$ - α-Fe) was tested as a catalyst for degradation of dissolved organic compounds (phenol, formaldehyde, oxalic acid, etc.) for purification of waste and industrial water. High chemical resistance of sialon allows us to use a synthesized material in the most aggressive media.

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SYNTHESIS AND OPTICAL PROPERTIES OF A NITRIDE PHOSPHOR VIA THE SELF PROPAGATING HIGH TEMPERATURE SYNTHESIS METHOD

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Nitride phosphors have been reported to be potential for applications in solid state lighting. However, presently available methods for the synthesis of nitride phosphors all require relatively severe conditions such as high temperature, high pressure and long duration time. In this presentation, we report the development of a new method for the synthesis of a nitride phosphor (i.e.,$CaSiAlN_3$) based on self-propagating high temperature synthesis (SHS) reactions. The reactants used for the synthesis include calcium, silicon, aluminum, silicon nitride and europium oxide. These powders were mixed and pressed into compacts. The reactant compacts were then wrapped up with igniting agent (e.g., $Mg+Fe_3O_4$). The reactant compact was ignited by electrical heating under a N_2 atmosphere of 5-7 atm. The $CaSiAlN_3$ phosphor could thus be produced under a low pressure, and a short duration time. We also investigated the effects on the properties of the product of several important experimental parameters including compositions and different reaction pressure. The results showed that the luminescence intensity and wavelength of the $CaSiAlN_3$ phosphor are affected by experimental parameters. A typical product has an excitation spectrum in the range of 220-500nm and a single broadband emission in the range of 400-670nm upon excitation at 380nm.

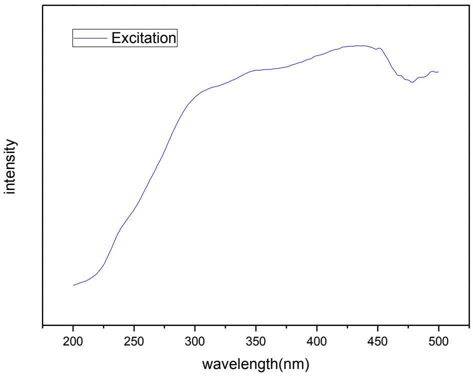

Fig..1. Excitation spectrum of the synthesized CaSiAlN3: Eu^{2+} phosphor.

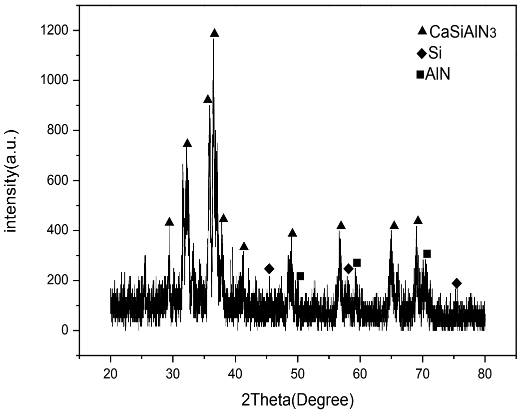

Fig.. 3. XRD Pattern of the synthesized CaSiAlN3: Eu^{2+} phosphor.

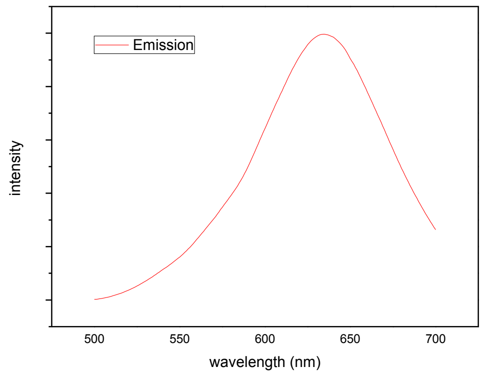

Fig.2 Emission spectrum of the synthesized CaSiAlN3: Eu^{2+} phosphor.

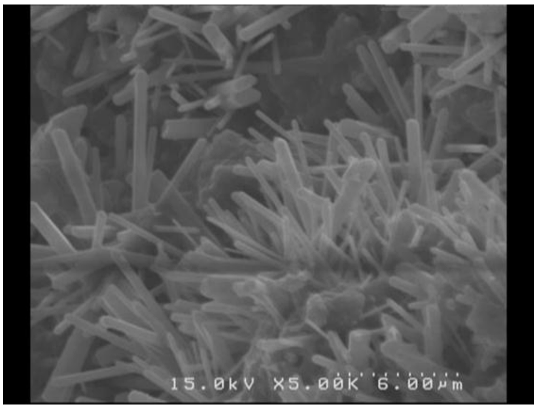

Fig.4 SEM Photo of the synthesized CaSiAlN3: Eu^{2+} phosphor.

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COMBUSTION SYNTHESIS OF A NICKEL SUPPORTED CATALYST: EFFECT OF METAL DISTRIBUTION ON THE ACTIVITY DURING ETHANOL DECOMPOSITION

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Solution combustion synthesis method is used to prepare Ni catalysts supported on γ-Al_2O_3 pellets with controlled metal distribution as described in Figure 1. It was shown that impregnation time of the SCS solution onto the pellet determines the distribution of the Ni in the pellet which in turns affects the catalyst selectivity towards hydrogen production during ethanol decomposition.

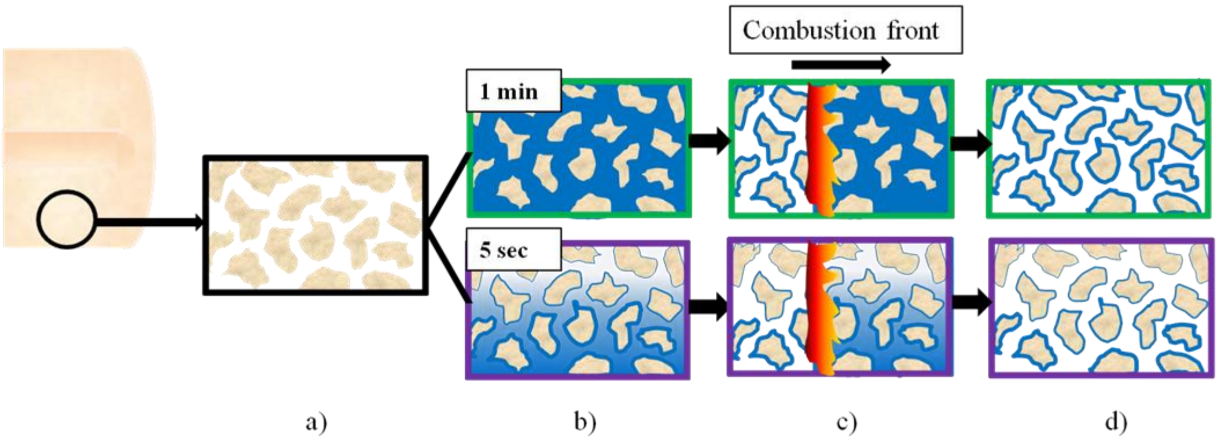

Figure 1. Direct Combustion Synthesis of Supported Catalyst: the alumina support (a) is impregnated with the reactive solution (b), the combustion wave is initiated and propagates through the pellet in the form of reaction front (c) producing highly dispersed metal in the pores of the inert support (d) with the desired metal distribution along the bulk of the sample.

Based on an optimization study for the synthesis of pure metals,[9] an aqueous solution of nickel nitrate hexahydrate and glycine with a φ value of 1.75 was used. A series of γ-Al_2O_3 pellets with a ring geometry were immersed into the reactive solution for different time intervals ranging from 1 s to 30 min to allow for variations in active metal distribution in the radial direction. The uptake of the liquid is surprisingly fast and the pellets are saturated after about 10 seconds of impregnation. Two impregnation times were chosen for further study, 5 seconds and 1 minute representing a partially and fully loaded reactive solution, respectively.

The combustion reaction was initiated on the pellets placed on the hot plate (~515 °C) and the reaction propagated in a self-sustained manner along the pellet as a combustion front. Figure 2a shows a sequence of IR images at various times in the 1 min impregnated sample. The IR intensities measured at the top of the pellet translated to temperature vs. time for the two samples as shown in Figure 2b. The reaction front for samples impregnated for 1 min propagates faster and exhibits a higher combustion temperature (330 °C) compared to 5 s (300 °C) due to shorter impregnation times and less uptake of reactive solution, reducing the energy density of the combustion mixture leading to a lower combustion temperature and velocity.

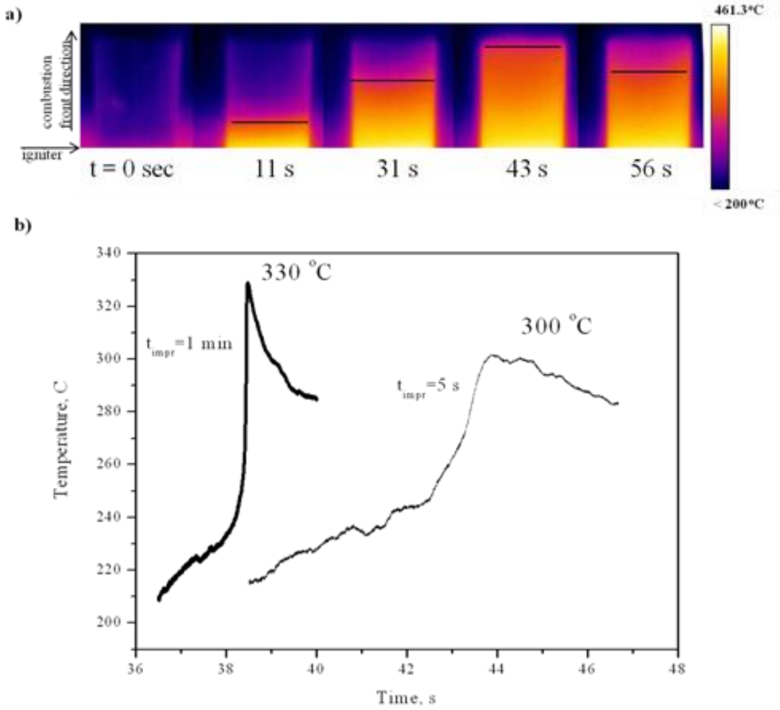

Figure 2 a) Combustion front propagation as captured by infrared camera and b) temperature profile of combustion front in 1 min and 5 sec samples.

TEM and EDS data was also collected and will be presented, along with reaction data that shows the change in Ni distribution leading to a change in reaction conversion and selectivity.

It can be seen that SCS of Ni supported catalyst takes place via the self-propagating mode under highly diluted conditions in a compacted porous alumina pellet. The impregnation of the metal in the pellet is very fast with only a minute required to obtain a uniform distribution of the metal on the pellet. Shorter impregnation times yields a non-uniform distribution that it is preserved during SCS, and which affects the selectivity of the reaction when the support itself is active and this effect can be used to tune the selectivity of the reaction.

REGULARITIES AND MECHANISMS OF AUTOWAVE SYNTHESIS OF ALUMINUM AND CHROMIUM OXYNITRIDES (Al-Cr-O-N)

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During burning thermite highly-exothermic mixtures with an excess of aluminum in a nitrogen atmosphere to 2-3% (by weight) of nitrogen is a part of the oxide phase combustion [1-4]. Adding of aluminum nitride in the initial mixture can increase the nitrogen content and get cast aluminum oxynitrides with a nitrogen content of 8-10%.

The present study is aimed at obtaining oxynitrides Al-Cr-O-N, as well as the research of the principles and mechanisms of their synthesis. For the synthesis of cast oxynitrides mixtures of oxide of chromium, aluminum and aluminum nitride were used. The synthesis was performed in a laboratory reactor under nitrogen pressure of 0.1 to 16 MPa. Mass of the initial mixture ranged from 10 to 100 g. The mixture was burned in graphite refractory or transparent quartz glasses. During the experiments video, thermocouple measurements, quenching of the intermediate states were taken. The synthesis products were examined by classical chemical analysis and metallography, X-ray and local X-ray spectrometry analysis.

Visual observations and video, thermodynamic calculations and analysis of the synthesis products provided a general idea of the autowave Al-Cr-O-N synthesis. After ignition of the mixture a flat flame front formed, which moved in the mixture at a constant speed. In the combustion wave the mixture was converted into the combustion products.

After the completion of the combustion process during the subsequent melt cooling the final product phase composition and structure were formed.

While the experiments the detailed study of burning of CrO_3 + Al with different content of AlN (α) in it was carried out. The product of this mixture combustion at $\alpha = 0$ had cast look and presented solid solution of Al_2O_3 x Cr_2O_3.

With α increasing from 0 to 60% the linear burn rate decreased monotonically from 7 to 0.7 cm / s and reached a limit burning at $\alpha = 60\%$, and the nitrogen content in the final product increased from about 1 to 10% by weight. In the interval $0 \leq \alpha \leq 25\%$ the single-layer combustion product had cast form, and at $25 \leq \alpha \leq 60\%$ - sintered. The X-ray analysis showed that, depending on the nitrogen content in the products they represented oxynitrides Al-Cr-O-N with different nitrogen content in them.

To detail the mechanism of chemical reactions in combustion waves of the studied mixtures the possibility of burning $CrO_3 + \alpha AlN$ mixtures was studied. The experiments showed that the mixture combustion was possible in the range of possible $0.25 \leq \alpha \geq 4$. Maximum calculated temperature of combustion was achieved at $\alpha = 1$ and made 2800K. Products of combustion mixtures with combustion temperature above 2500 K had two-phase structure: large particles of chromium nitride were distributed in cast oxynitride matrix.

The maximum content of nitrogen in the oxynitride matrix was ~ 8% (by weight). The obtained results showed that at combustion of mixtures $CrO_3 + Al + \alpha AlN$, aluminum nitrides might be involved not only in the formation of oxynitrides (Al-Cr-O-N), but also in the reconstruction of chromium oxide.

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HSTC STUDY OF MoO_3/MoS_2 CO-REDUCTION BY COMBINED Mg/Zn REDUCERS

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In our previous work direct zincathermic reduction of MoS_2 in the combustion mode was performed by coupling (MoS_2+2Zn) low exothermic reaction with (MoO_3+3Mg) high caloric one. At that zincathermic reduction of MoS_2 proceeds in the self-sustaining mode even at quite small amounts (starting from ~10wt.%) of high-caloric (MoO_3+3Mg) mixture. It was shown that thermal coupling in this system is distinguished with its unique flavor, such as selective interactions (MoS_2+2Zn) & (MoO_3+3Mg) take place that were confirmed also by preliminary thermodynamic analysis. This fact is caused that Mg has more affinity to oxygen, but Zn - to sulphur, which makes possible to avoid from the formation of easily hydrolysed and undesirable sulfide byproducts (MgS, $Zn_{0,68}Mg_{0,32}S$).

To explore the interaction mechanism in the above-mentioned system in this work model experiments were performed with initial mixtures at high heating rates. For this purpose, high-speed temperature scanner (HSTS-1) was used coupled with XRD analysis method of samples obtained at different stages of the process [1].

The latter allows studying the kinetic features of highly exothermic reactions taking place in powdered mixtures at fast heating. For performing experiments the powder mixture under study (5-100 mg in weight) is placed into the mini envelope made from Ni or Ni alloy foil (thickness: 50-100 μm) and is heated directly by electrical current according to the preliminary given way. The heating way of the sample is controlled either by the temperature of powder mixture (T), or electrical power (W). Heating rate of samples can be varied from 10 to 10.000^o/min. Temperature range of scanning: from room temperature to 1300^{o}C. The experiment can be stopped automatically at preliminary given time or temperature with subsequent fast cooling of samples (up to 200^o/s) from reaction temperature. The cooled down samples were examined by XRD and SEM.

The experiments can be performed in vacuum, air and inert gas medium at $P \leq 1$ atm. (static conditions). Custom Microsoft Windows-based software and intuitive graphical user interface have been designed for the current HSTS-1 model.

The behavior of target quaternary (MoS_2+MoO_3+3Mg+2Zn), as well as ternary (MoO_3+2Mg+Zn), (MoO_3+Mg+2Zn), (MoS_2+Mg+Zn), (MoS_2+MoO_3+5Mg), (MoS_2+MoO_3+5Zn) and binary (MoO_3+3Mg), (MoO_3+3Zn), (MoS_2+2Mg), (MoS_2+2Zn) mixtures were investigated at high rates of linear heating. The experiments were performed at $V_h=300\div3000^o$/min heating rates of initial samples in argon medium at 1 atm pressure. In fig. 1 the HSTS curve of MoS_2 + 2Zn mixture and XRD pattern of sample quenched from point "A" were brought as example. As it can be seen from the results obtained, physicochemical transformations can be clearly distinguished on the temperature profile.

At first zinc melts at ~420°C, then the first exothermic interaction takes place at temperature range 570÷730°C leading to self-heating of the system by ~100°C. At 850°C evaporation of non-reacted zinc starts and the interaction is continued with participation of gaseous zinc. The latter leads to additional self-heating of the system and process completes at 1090°C. According to XRD analysis quenched sample at 1130°C mainly represent as Mo and ZnS.

It was shown that in spite of simple thermodynamic nature, the interaction mechanism for ternary and quaternary mixtures have quite complicated character.

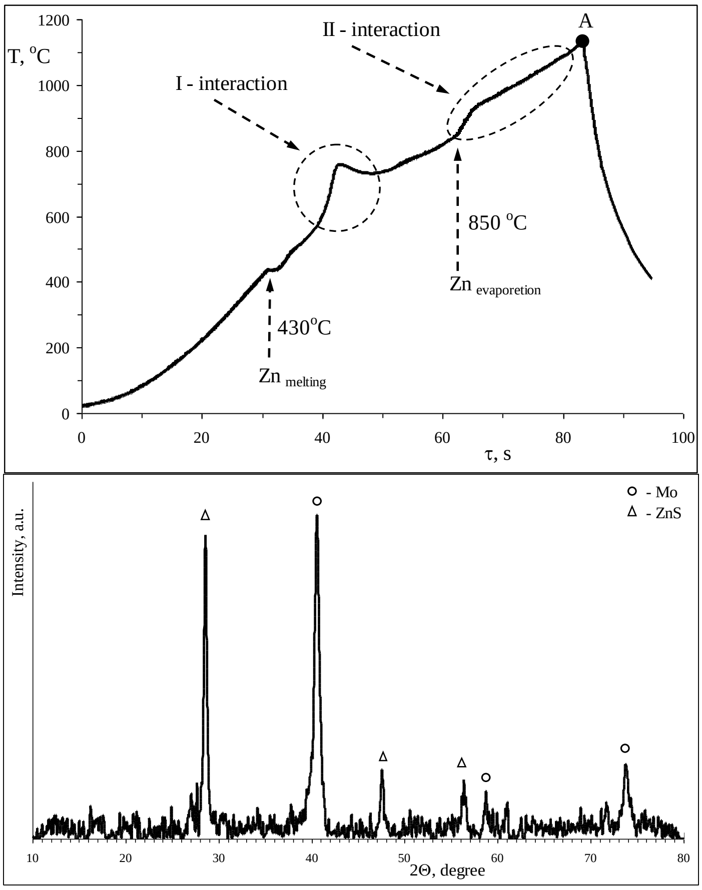

Fig.1. HSTS curve of MoS_2 + 2Zn mixture & XRD pattern of sample cooled down from high temperature

(point “A”). V_h= 780°/min, m_o=50mg

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SHS PROCESSING OF METAL SULFUROUS COMPOUNDS INTO METAL POWDERS

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The possibility of cobalt powder preparation from sulphate raw material in the double stage combustion process was investigated. In the present study, cobalt (II) sulphate crystalline hydrate ($CoSO_4.7H_2O$) as precursor and polystyrene (PS) as reducing agent were used. The first stage of the combustion process is obtaining of cobalt oxide (CoO or mixture of oxides CoO and Co_3O_4) from $CoSO_4.7H_2O$, and the second one - reduction of oxides to metallic cobalt. In order to implement above mentioned two stages in self-sustaining manner, the reactions thermal coupling approach was applied [1]. The endothermic (decomposition $CoSO_4.7H_2O$ - I stage) or weakly exothermic (Co_xO_y+PS - II stage) reactions were coupled with high exothermic NH_4NO_3+xPS (high caloric mixture - HCM) one.

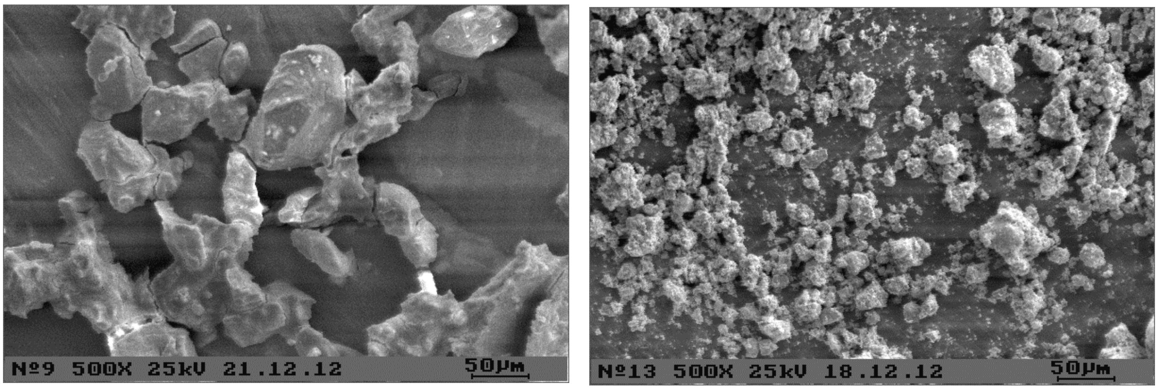
The self-sustaining decomposition of Co precursor was carried out in metallic boat (in an open reactor), and the second reaction - in the constant pressure reactor in nitrogen atmosphere. To measure the main combustion parameters (T_c and U_c) thermocouple technique was used. After the combustion process was over, cooled down samples were examined by XRD and SEM analyses methods. Simultaneously, the mass losses of burnt samples were measured, as well as magnetic properties of obtained products were checked.

Combustion peculiarities in the [$CoSO_4.7H_2O$ - m(HCM)] and [Co_xO_y-PS-n(HCM)] systems depending on the initial mixture composition (amount of "HCM" additive) and sample size were explored. The dependences of T_c, U_c and mass loss (□m) vs. aforementioned parameters were determined; combustion regimes, chemical and phase composition of combustion products, as well as microstructure characteristics were investigated.

It was established that the systems under study are characterized by different combustion regimes, such as autooscillation and stationary ones. The existence of combustion limits by the HCM amount in the initial mixture was also found out.

The degree of cobalt sulphate desulfurization and reduction depth was estimated by mass loss of samples. Complete reduction of metal in the combustion process can be confirmed both by XRD analysis and magnetic properties of the final product.

In the first stage of the process multiphase products are obtained, basically composed of cobalt oxides (CoO and Co_3O_4) and in some cases, small amount of $CoSO_4$. At this stage, both autooscillation and stationary combustion regimes are realized. In the second stage (reduction of Co_xO_y by PS-HCM system), mainly steady-state combustion was observed. At that at complete reduction, regardless of ratio of CoO/Co_3O_4 oxides and sulphate content, pure cobalt powder is obtained. In the Fig.1 the microstructure of the initial sulphate (fig.1, a) and final product (fig.1, b) are presented.



(a) (b)

Fig.1. Microstructures of the initial cobalt sulphate (a)

and the obtained cobalt powder (b)

Based on the results obtained, characteristic features of double-stage preparation of cobalt powder from sulphate raw material in the combustion mode were revealed and the main parameters, influencing on the combustion laws, composition of the final products and microstructure were explored. It was shown that complete desulfurization of cobalt sulphate (first stage) and metal reduction (second stage) may be controlled by varying the HCM amount in the initial mixture and the sample size.

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SELF-PROPAGATION LOW TEMPERATURE FLAMELESS COMBUSTION SYNTHESIS OF Ni and Al NANOPARTICLES: TIME-RESOLVED XRD STUDY

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Exothermic decomposition of some energetic materials such as cellulose nitrates in filled polymer systems can proceed in a mode of frontal low-temperature flameless combustion [1]. The distinctive features of the process are the absence of flame, relatively low temperatures (260–600°C) and incomplete conversion of fuel and release of reactive gaseous products. A happy confluence of several factors—such as formation of low-temperature combustion wave, evolution of reactive gaseous products, and the presence of polymer binder—allowed us to suggest a novel method for preparation of new high-porosity composite materials containing nanoparticles of some transition metals and their compounds.

We explored the kinetics for formation of Ni and Ag nanoparticles during low-temperature combustion of cellulose nitrate in ballasted systems by using the method of Time-Resolved X-Ray Diffraction (TRXRD) [2]. In our experiments, we used the commercially powders of cellulose nitrate, $C_{20}H_{16}N_4$ (I, $\bar{d}$ = 20–40 μm, nitrogen content 12.6%) as a fuel; a diffraction-silent nickel hydroxycarbonate, $NiOHCO_3$ (II, Ni content 46.9%) as a precursor of Ni; and silver carbonate Ag_2CO_3 (III, pure grade) as a precursor of Ag. Hexamethyldiisocyanurate (HMDI) was used as an organic binder, Si - as an etalon.

Flameless frontal combustion yielded porous composites containing metal nanoparticles of Ag and Ni. Our estimates for crystallite size gave L = 5–10 nm in case of Ni and 20–30 nm in case of Ag. Figure 1a presents the time-resolved diffraction patterns for of I–HMDI–II–(Si) samples and, at the right, individual XRD patterns taken at some temperatures. It follows that the combustion process proceeds in the following several stages. First, the green mixture is preheated up to 100°C ahead of oncoming combustion wave, which is accompanied by observation, at 2θ = 33–40°, of a broad halo from a mixture of diffraction-silent starting materials. This is followed by a sharp (in 4–5 s) drop of the halo intensity down to zero level on the background of rapidly growing temperature caused by passing the combustion wave through the zone of registration. There is also a period (of 1–2 s) during which the entire material is present in its diffraction-silent state. The Ni (111) line at 2θ = 44.5° begins to appear and grow at temperatures above 250°C. The Ni line is strongly broadened, which is indicative of a nanosized of the Ni particles. The attained temperature does not exceed 340°C. The intensity of the Ni (111) line levels-off in 10–12 s after its appearance, that is, at the stage of cooling down. In what follows, the diffraction patterns undergo no visible changes.

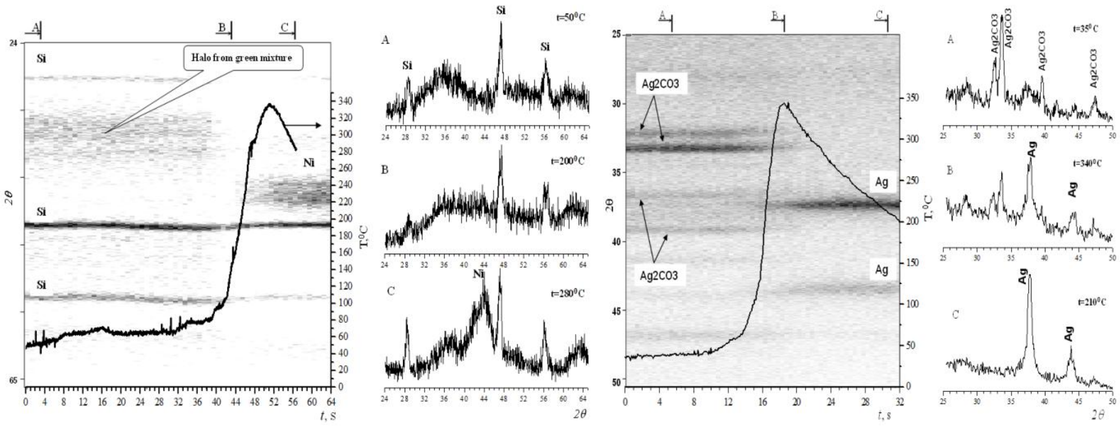

Fig.1 Time-resolved diffraction patterns.
Left: I–HMDI–II–(Si), resolution time τ = 1 s; Right: I– HMDI –III, resolution time τ = 0.5 s

In case for of I– HMDI –III samples, a decrease in the intensity of the Ag_2CO_3 lines gets started at 100°C and lasts for 4–5 s. In contrast to the previous case, there is no a region of diffraction silence. Within a period of *t* = 16–20 s, the phases of precursor and end product coexisted. The lines of Ag (111) became pronounced at temperatures around 150°C and attained a maximum value in 15–17 s, that is, when the reaction front passed a distance of 5–6 mm from the registration zone. The combustion temperature did not exceed 350°C. Complete crystallization of Ag particles is achieved far behind the combustion wave and then the diffraction patterns undergo no noticeable changes.

Flameless combustion of mixtures containing cellulose nitrate and nickel carbonate was found to result in direct (without crystalline intermediates) formation of Ni nanoparticles, although in the course of reaction the material dwelled in its diffraction-silent state for 1–2 s. The formation of Ag nanoparticles did not involve a diffraction-silent intermediate but the phases of precursor and newly formed Ag nanoparticles coexisted for a time period of 3–4 s.

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THERMALLY COUPLED SHS REACTIONS: EXPERIMENTAL STUDY

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Recently [1], one of us has suggested to use the so-called thermally coupled reactions for initiating SHS reactions in low-caloric systems incapable of burning in a self-sustained mode. In this work, we explored combustion in the system (Fig. 1*a*) involving the highly caloric (donor) system Fe_2O_3–Al and low-caloric (acceptor) system Ti–Al under argon. For the donor reaction, the adiabatic combustion temperature (T_{ad}) is 3470 K [2]. In order to avoid the melting of initial components and reduced Fe, the green mixture was diluted with MgO powder. The dilution decreased T_{ad} down to 2345 K and prevented spreading of the donor compact. In order to provide good contact between donor and acceptor layers and hence favorable conditions for heat exchange, it was desirable that there would be no shape change during SHS reaction.

For equimolar Ti–Al mixtures, T_{ad} = 1518 K [2]. However, the thermal effect of this reaction is insufficient for maintaining combustion in a self-sustained mode and the system requires preliminary warm-up [3]. In thermally coupled reactions, the donor system plays a part of external heater for a low-caloric donor reaction.

We measured the temperature profiles in the donor and acceptor layers and at their interface. The results are presented in Fig. 1*b*. Readings of thermocouples T1–T4 clearly show that the combustion front in the acceptor mixture is formed at the donor/acceptor interface and then proceeds to the center (position of thermocouple T1). Simultaneously, the burning donor layers promote propagation of combustion front in acceptor from the sample top to its bottom. Thus burning of the acceptor layer occurred at a slight time lag compared to the donor one, as was evidenced by video record of the process. According to XRD data, the target combustion product was TiAl. In other words, thermally couples SHS reactions proved to be rather efficient and can be recommended for their implementation in SHS practice and technology.

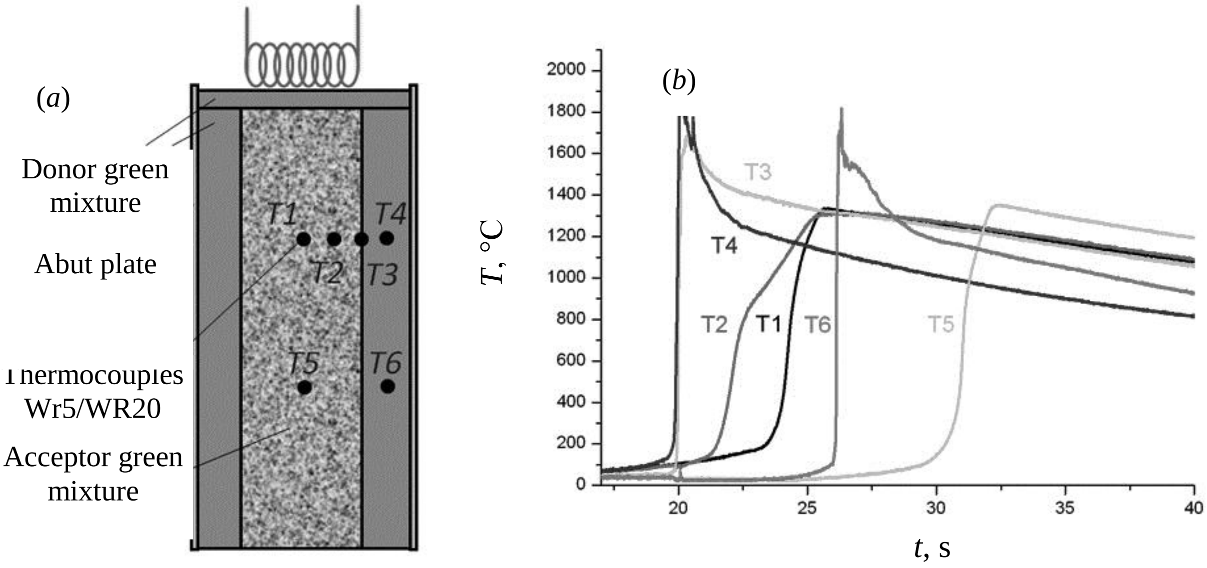

Fig. 1: (*a*) Experimental setup and (*b*) thermocouple readings.

ACKNOWLEDGMENTS

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SHS OF STRUCTURED BIDISPERSED Ni+Al MIXTURES

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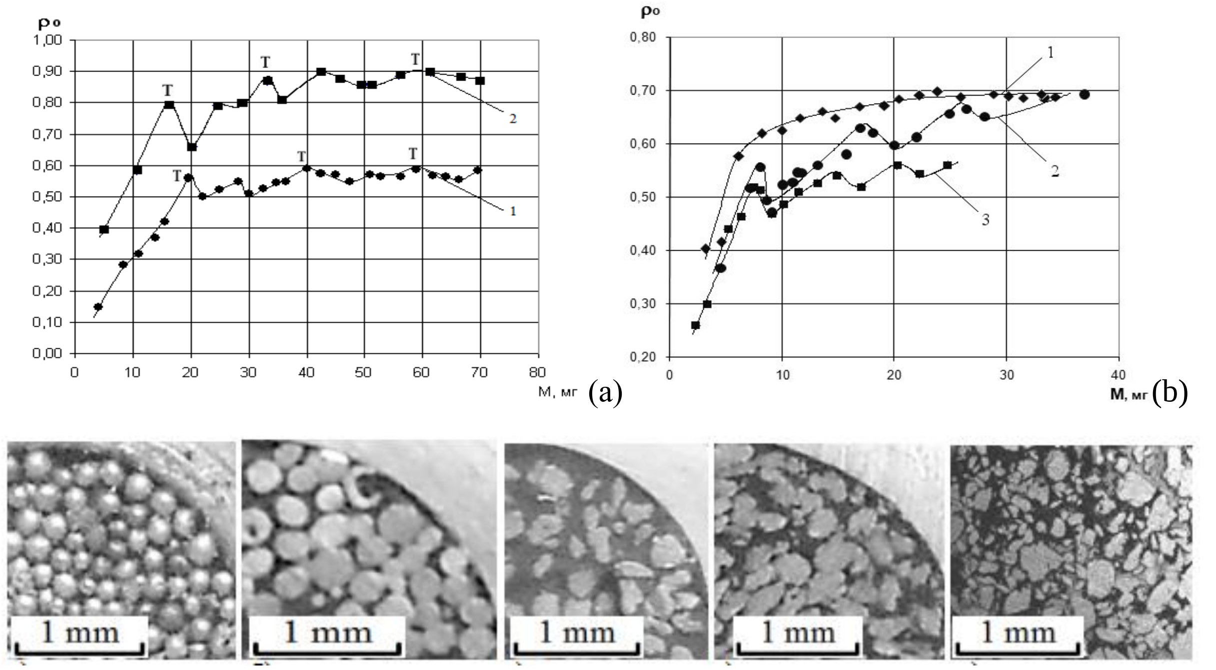
For various practical applications long-sized items ($l/D>>1$) obtained by the SHS method are required [1]. High homogeneity of the items is achieved due to the method of consecutive forcing of powder thin layers into long-sized forms. The method allows obtaining structural ordering of powder particles in the compact volume [2]. The dependence of macro- and microstructure of the final synthesis product on macrostructure of the compact multilayer sample consisting of structurally ordered layers was investigated. Model mixtures were used: mixture 1 – Ni+Al bidispersed mixture with nickel coarse particles of the shape close to spherical (d_1~200 µm) and fine aluminum (d_2<10 µm), as well as Ni+Al bidispersed mixtures including composite particles after mechanical activation – mixture 2 – 50 % of composite particles of Ni-Al of coarse fraction (d_3~300 µm) and 50 % of fine fraction (<125 µm), and mixture 3 – a mixture of Ni-Al composite particles – 50 % of coarse fraction (d_3~300 µm) and 50 % of fine mixture of Ni+Al (d_1<10 µm, d_2<10 µm). During the experiments axial densification in a thin layer of H in the cylindrical mould of D ($D >> H, D > H, D \sim H, D >> d_i$) was simulated. The size of some single powder samples allowed making 1-6 monolayers of the coarse component along the sample height ($H \sim d_i$, $H > d_i$). Structural ordering of the coarse particles is developed due to the non-monotonous dependence of the sample density on its mass $\rho_0 = \rho_0(M)$; some extremes of density are observed in Fig.1 (T – “main” maximums). Such structures are similar to regular packages of monodispersed balls (tetrahedral, etc.) [2, 3].

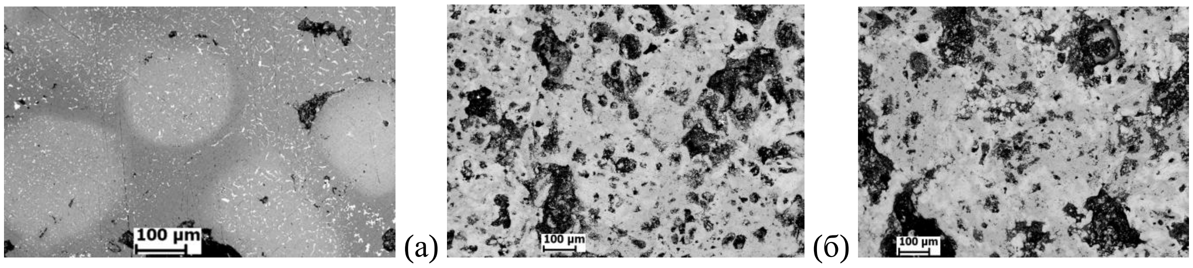
Multilayer samples were synthesized by sintering or by the SHS method with preliminary heating from 500ºC up to 900ºC or under the terms of heat explosion. The product macrostructure corresponds to the initial structure consisting of nickel particles in the compact sample (Fig. 2, a) and that of composite particles Ni-Al in the compact sample (Fig. 2, b).

The work was carried out with the support of the Russian Fund of Fundament Research, Grant № 11-03-00572-a.



(c) (d) (e) (f) (g)

Fig.1. Relative density of the layer depending on its mass M and sample surface structure: (a) “1” – Ni powder (d_1~200 μm), “2” – mixture 1; (b) “1” – mechanically activated Ni-Al particles; “2” – mixture 2, “3” – mixture 3; (c) Ni powder (d_1~200 μm); (d) mixture 1; (e) mechanically activated Ni-Al particles; (f) – mixture 2; (g) –mixture 3.



(a) (б) (в)

Fig.2. Ni-Al product structure: (a) – obtained from mixture 1; (b) – from mixture 2; (c)- from mixture 3.

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SHS OF Ti+2B and Ti+Al STRUCTURIZED MIXTURES

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For various practical applications long-sized items (l/D>>1) obtained by the SHS method are required [1]. High homogeneity of the items is achieved due to the method of consecutive forcing of powder thin layers into long-sized forms. The method allows obtaining structural ordering of powder particles in the compact volume [2]. The dependence of macro- and microstructure of the final synthesis product on macrostructure of the compact multilayer sample consisting of structurally ordered layers was investigated. During the experiments axial densification in a thin layer in the cylindrical mould of D=4 mm ($D/d>>1$ D/d_1 ~14, D/d_2 ~10) was simulated. The size of some single powder samples allowed making 1-6 monolayers of titanium along the thin layer height H ($D >> H$, $D > H$, $D \sim H$). The particle size (d) of the coarse component (Ti) of the narrow fraction (±10%) was 200; 300; 400 μm; and that of the fine component (B, Al) was less than 10 μm. The thin layer was densified by shift and repacking of titanium particles. Structural ordering of coarse particles in the mixture is exhibited by non-monotonous character of the sample density dependence on its mass; it has some density extremes. Thin layers of the bidispersed mixture have some fragments of structurally ordered package consisting of the coarse component particles. Such structures are similar to regular packages of monodispersed balls [2, 3].

The synthesis in the structurized samples of Ti+2B and Ti+Al was carried out at sintering at T=600-1000^{o}C and SHS under the terms of heat explosion or combustion with preliminary heating up to 450-1400ºC. The microstructure of Ti-Al sample (Fig.1, b) illustrates interpenetration of titanium and aluminum. After SHS initiation three phases were detected in the product - TiAl$_3$, Ti$_3$Al, Al, Ti. The structure of Ti-Al samples after short (t=30 min) sintering is shown in Fig. 2, c. There are three phases in the product: TiAl$_3$, Al, Ti. The macrostructure of Ti-Al samples inherits the initial structure of titanium particles in the compact sample. When the synthesis is carried out under the mode of heat explosion most of the titanium particles manage to be dissolved in the surrounding melt. The maximum size of the undissolved titanium particles is 20-200 μm (Fig.2, d), the phases of TiAl, Ti$_3$Al are present in the product.

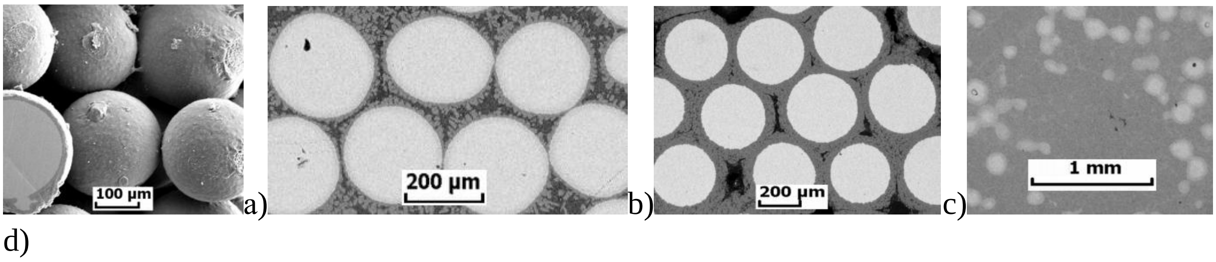

Fig.1. Chip, cut (a) and Ti-Al sample microstructure after: SHS initiation (T$_0$=800^{o}C, T$_m$ = 980^{o}C) (b); sintering (T=1100^{o}C, t=30 min) (c); heat explosion (d).

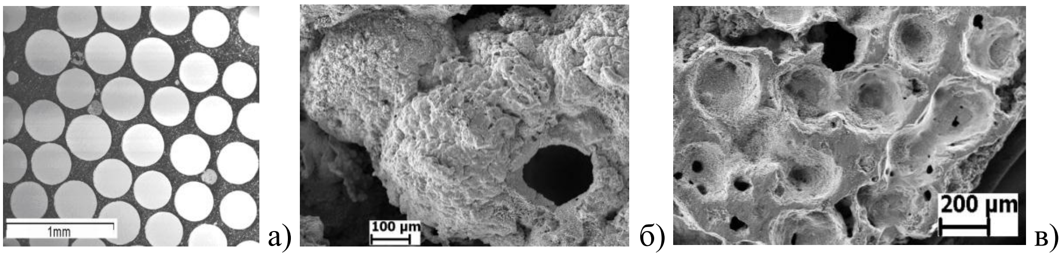

Fig.2. Structure of Ti-B compact sample Ti-B (a) and TiB_2 product after SHS - granules (b) and polished section (c).

The structure of the final TiB_2 consists of sintered hollow granules of ~400 μm in diameter (Fig.2). The product is remarkable due to four types of the pores. The first type – the pores inside the granules (spherical shape, 200-250 μm) and between them (irregular shape, 150-200 μm). The second – the pores connecting granule hollows with each other (20-50 μm). The third – the pores appearing when liquid titanium penetrates into the surrounding boron (5-10 μm). The forth – the pores appearing with the product microstructure formation (<1 μm).

The work was carried out with the support of the Russian Fund of Fundament Research, Grant № 11-03-00572-a.

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EFFECT OF MILL SCALE USAGE ON THE PRODUCTION RATES OF IRON BASED ALLOYS VIA SHS

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SHS (Self propagating high temperature synthesis) technique has several advantages including less synthesis times, high quality of the products, simple operation and generation of fine microstructures for synthesizing a wide variety of materials including intermetallic compounds, alloys and advanced ceramics as well as their composites. Also SHS process has many prominent properties compared to the furnace applications such as low energy requirement and low cost [1, 2]. In a SHS process, the ignition starts the combustion and propagates throughout the reactant mixture to obtain the desired product. However, the disadvantages of the process such as inhomogeneous or unreacted products due to undesirable reaction rates needs to be overcome by changing some parameters such as ignition temperature, particle size, additive, atmosphere etc. [3, 4].

Mill scale is a layer of iron oxide which forms on the surface of ferrous materials during cooling after being processed in hot rolling or continuous casting plants. Mill scale contains iron (II) and iron (III) oxides, which result in a 70% total iron content in oxide form [5].

This study proposed a SHS process to produce iron based alloys using a mixture of mill scale, NiO, Cr_2O_3, MoO_3. Al used as a main reductant, Mg and Si added for better Cr recovery.

Before the SHS experiments, a thermochemical simulation was performed to estimate the effect of precursor compositions on the SHS process. Effect of Al_2O_3 addition to the mixture of mill scale and stoichiometric Al amount on the obtained products under 1 atm pressure were investigated at the adiabatic temperature. With the increase in Al_2O_3 addition into the green mixture (%49 Fe_2O_3 + %25 FeO + %3 Fe + %23 Al), Al contents in the liquid alloy was decreased, Fe contents in the liquid alloy was slightly increased. The advanced thermochemical simulations of the reactions were investigated in detail including different ratios of initial mixtures, heat sinker or reductant additions as well as different initial temperatures in order to reduce the number of experiments.

The mill scale was utilized in this study is formed in a continuous casting plant and is of non-oily nature. Other than iron oxides of different valence states, it contains metallic iron and impurities. In the SHS experiments, a mixture of mill-scale, NiO, Cr_2O_3, MoO_3 and Al powders were used in order to produce metallic Fe, Fe-Ni, Fe-Ni-Cr, and stainless steel alloys. The metal oxide powders had over 96% purity and 200 μm average grain sizes. The reaction mixtures were mixed thoroughly 15 minutes in a turbula mixer and powder mixtures (approximately 150 g) were charged into Cu crucible and were compacted. Tungsten wire was placed at the top of copper crucible and the reaction realized by passing current through the wire. After initiation, a highly exothermic reaction became self-sustaining and propagated throughout the SHS mixture. The obtained SHS products were discharged from the crucible after cooling. Then, SHS products were crushed and grounded.

In the first series of SHS experiments, a mixture of different stoichiometric mill scale and reductant aluminum powders were studied. The highest metal recovery was achieved with using a mixture of 100% stoichiometric mill scale and 100% stoichiometric Al powders. Total metal recovery was decreased with both the increase in stoichiometric mill scale ratio and the decrease in stoichiometric Al ratio. The ratio of the lost part due to the scattering was occurred at higher values when starting with 200 g of mill scale and 57.8 g Al.

In the second series of SHS experiments, heat sinker additives were investigated. Fe scrap was used as heat sinker. The ratio of the lost part due to the scattering was occurred at higher values when starting with 200 g of mill scale. Total iron recovery was higher than the first series of SHS experiment but total metal recovery is reduced.

In the third series of experiment, productions of Fe-Ni and Fe-Cr-Ni alloys were investigated by using a mixture of Mill scale + NiO + Al and Mill scale + NiO + Cr_2O_3 + Al with using Cu crucible. NiO addition into the green mixtures decreased the total metal recovery. On the other hand, Cr_2O_3 addition into the green mixtures decreased the scattered ratio due to the lower exothermicity of Cr_2O_3 reduction.

In the last series, reductant effect has been investigated by adding Mg and Si. 316 and 201 stainless steel standarts selected for this experiments, because 316 series Cr recovery were the worst of third series of experiments and 201 series had the best Cr recoveries in the same series. Various charge mixtures were carried out in the last experimental set such as stoichiometric %5Mg + %95 Al, %5Si + %95 Al, %5 Mg + %100 Al, %5 Si + %100 Al and %2.5 Mg + %2.5 Si + %95 Al. Both Mg and Si additive positive the Cr recovery the best result have been detected in stoichiometric 100% mill scale + 95% Al + 5% Si system. The Cr recovery increased from 61.5% to 69.4% but the same effect was not observed in 201 stainless steel experiment.

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SYNTHESIS OF ZnO NANOPARTICLES BY FLAME SPRAY PYROLYSIS: PARTICLE CHARACTERIZATION AND TOXICOLOGY

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Zinc oxide (ZnO) nanoparticles have been prepared by a flame spray pyrolysis method utilising a self-sustaining flame with zinc naphthenate/toluene as the starting reagents. The processing route is described and a particle characterisation protocol presented. The powders were crystalline, having the wurtzite hexagonal structure. Particles were elongated in the c-crystallographic direction, with average length ~ 23 nm and width ~14 nm. Sources of impurities identified by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy are discussed. Results of an in-vitro study of cytotoxicty and genotoxicity of the ZnO particles in relation to A549 lung epithelial cells are presented; relative contributions of soluble Zn and particle-cell interactions are considered. The presentation concludes by comparing the relative merits of flame spray pyrolysis to other synthesis routes for ZnO.

COMBUSTION JOINING OF CARBON/CARBON COMPOSITES BY A REACTIVE MIXTURE OF TITANIUM AND MECHANICALLY ACTIVATED NI/AL POWDER

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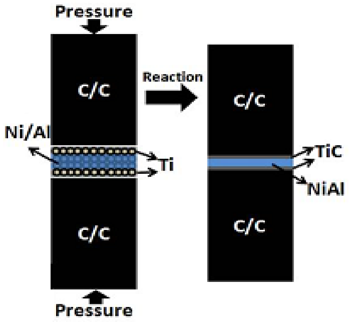
Combinations of properties of carbon/carbon (C/C) composites, such as low density, high strength-to-weight ratio, as well as high thermo-elastic stability at elevated temperatures, make it attractive material for a variety of applications. These characteristics allow using C/C composites for producing rocket nozzles, noses and leading edges of reentry vehicles, as well as gas turbine engine components. In addition, the high thermal-shock and wear resistance that C/C composites possess make them suitable for aircraft brake disks, where temperatures during harsh landing conditions can be as high as 2000 K. As the demand for such materials increases, development of rapid and energy-efficient techniques for joining C/C composites are of great interest.

Combustion joining (CJ) is an attractive method for joining of a variety of materials. Due to short (seconds) processing time, energy efficiency, simple technological equipment and the ability of producing joint layers with functionally-graded properties this method has proved as an effective tool for joining of refractory and dissimilar substances. White et al.[1], reported joining of refractory C/C composites via a class of refractory materials (carbides, borides, etc) by CJ. However, a short-term (~30 sec) but high-temperature (up to 2000 K) preheating of the joint stack was required in order to initiate the chemical reaction in the joint layer, which affected the composite properties.

Here is reported an improved combustion-based technique for bonding of C/C composites by using a CJ approach with a reactive mixture of titanium and mechanically activated Ni/Al powders. The present work focused primarily on validating the concept of low temperature joining of C/C composites with a reactive mixture of Ti powder and Ni/Al mechanically activated composites [2]. The novelty of the technique is that use of a mechanically activated reactive medium enables joining of C/C composites by a rapid and energy-efficient CJ method by preheating the C/C stack to only 630 K, and produces a robust joint layer. The influence of the CJ parameters, including temperature, applied pressure and durations on the quality of the joint layer was investigated. The microstructure, phase and elemental composition of the joint layer were also studied. Finally, tensile-strength testing of joined C/C composites was performed.



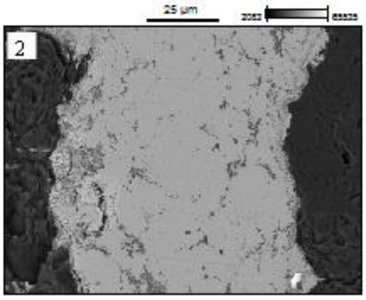


Figure 1. Schematic illustration of the C/C joining method

Figure 2. Cross-sectional image of joined layer

Figure 1 demonstrates a scheme of the C/C joining configuration. The reactive medium stack, i.e. Ti+$(Ni/Al)_{MA}$+Ti is placed between two C/C composites. Once triggered, the heat release and high temperature of the Ni/Al reaction facilitates the interaction between the Ti and the C/C composites, forming a TiC phase and simultaneously bonding the C/C composites. After the joining process, it is expected that a functionally graded joint layer (i.e., C/C-TiC-NiAl-TiC-C/C) will be produced.

Figure 2 shows typical back-scattered electron (BS) SEM images of a joined C/C sample cross-section in the vicinity of the joint layer. First, it can be seen at lower magnification that a crack-free joined layer ~75−100 μm in thickness was produced by the CJ method. Second, it was observed that part of the resulting interlayer infiltrated ~100 μm into the porous skeleton of the C/C composites. Third, compression during the reaction forced the molten reactive medium to bond with the C/C composites, yielding simultaneous formation of a dense, pore- and crack-free interlayer.

Joined samples were machined to a configuration suitable for tensile-strength testing. As expected in brittle C/C materials, the rupture occurred without a pronounced strain difference ($\varepsilon \sim 0.04$) in the course of elongation. In this typical case, the obtained ultimate tensile strength of a joined C/C sample was ~5.8 MPa. More importantly, the rupture occurred through C/C composite, indicating that the joined layer was stronger than the C/C matrix.

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THE JOURNEY FROM MACRO TO NANO VIA SHS

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This study covers information about our previous investigations on production of advanced ceramics powders via SHS, sintering and RF magnetron sputtering PVD processes carried out in our laboratories over 20 years [1].

Boron containing advanced ceramic powders such as B_4C, TiB_2, ZrB_2, W_xB_y were synthesized via self-propagating high-temperature synthesis (SHS) method using a mixture containing B_2O_3 and reducing Mg powders with TiO_2, ZrO_2, $CaWO_4$ and/or C powders followed by acid leaching. It was found that micron and sub-micron sized boron compounds without requiring any industrial milling processes [2 - 7].

Obtained advanced ceramic powders were consolidated by using Spark Plazma Sintering (SPS) technique which is mainly used for obtaining compacts within very short times compared to other sintering techniques. In SPS technique, powders which are in micro or nano scale form sintered bodies without causing grain growth which will lead to high mechanical and physical properties. By that processes, high purity, high density target materials were produced for PVD systems [8 - 10].

In RF magnetron sputtering PVD system, sputtered atoms from target material tend to move within plasma and condense on a substrate which will lead thin film coatings. Thin film coatings would give certain properties to substrate materials such as tribological, optical and electronic. To obtain these properties, B_4C and TiB_2 PVD thin film coatings were successfully applied on silicon, glass and steel substrates by using the targets which were produced via SHS+SPS processes [11]. In this study, the results of conducted researches will be presented.

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PECULIARITIES OF COMBUSTION AND STRUCTURE FORMATION OF MULTICOMPONENT Cr–Al–Si–B CERAMICS

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Development of new multifunctional coatings for use in mechanical engineering, aerospace industry, tool production, etc. is a current trend in modern R & D [1]. Protective coatings [2] combining high hardness, resistance to abrasive wear, heat/corrosion resistance, and low friction coefficient markedly improve service parameters of numerous machine parts. Promising candidates for the above role are multicomponent ceramic coatings formed by the borides, silicides, aliminides, and nitrides of transition metals well-known for their good chemical, mechanical, and tribological properties. Doping protective coatings with Cr, Al, and Si was used to combine high wear resistance with good resistance to high-temperature oxidation [3,4].

The use of multicomponent composite cathodes (targets) made of chromium borides, silicides, and aluminides (which already contain all necessary elements) for PVD of such coatings can be expected to markedly simplify a deposition process, to improve homogeneity of coatings and process reproducibility, and to shorten a deposition time. Required multicomponent compositions can be readily produced by combustion synthesis using the technique of so-called forced SHS pressing. One of the most actual problems in the field of SHS is the investigation of peculiarities and mechanisms of combustion, phase and structure formation processes during the synthesis of composite materials, as knowledge in this area, allows effectively control the structure and properties of synthesized materials.

We explored the combustion synthesis of multicomponent ceramics in the Cr–Al–Si–B system, with special emphasis on the effect of green composition and initial temperature (T_0) on combustion rate (U_c) and combustion temperature (T_c). An increase in T_0 lead to a proportional growth in T_c and U_c. The measured effective activation energies of combustion (E_{eff}) afforded to assume that the combustion mechanism remained the same within the range of T_0 = 293–753 K and to suggest some mechanistic details for combustion of individual green compositions. Experiments on combustion front quenching in a copper wedge and time resolved XRD analyses allows us to establish the mechanisms of phase and structure formation of synthesized products. For green mixtures with low Al content, the combustion proceeds through solid-state and gas-transport reactions of Cr with Si, B, and B_2O_2 [5]

yielding chromium silicides and chromium borides, with reactive diffusion as a limiting stage. So, E_{eff} have a maximum value 290 kJ/mol. In case of high Al content the amount of liquid phase becomes higher, the combustion is controlled by dissolution of Cr particles in melted Al, which markedly diminishes the energy barriers and E_{eff} = 110 kJ/mol.

The synthesized ceramic composites containing CrB, Cr_5Si_3, $(Cr,Al)Si_2$, and Cr_4Al_{11} exhibited good physical-mechanical properties and excellent resistance to high-temperature oxidation.

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SOLUTION COMBUSTION SYNTHESIS OF FERROELECTRIC CERAMIC MATERIALS ON THE BASE OF TITANATES

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Ferroelectric ceramics refers to the category of materials capable to reversible spontaneous polarization. That includes some titanates and zirconates of a number of elements such as barium, lead, bismuth, strontium etc. as well as their solid solutions. Thanks to their unique electrophysical properties ferroelectric materials and items made on their base are used as high-voltage dielectrics, capacitor materials and as materials for manufacturing chemical and physical sensors, memory cells, etc.

This paper describes investigating the possibility of exothermal synthesis of ceramic ferroelectric materials in the BaO – TiO_2, PbO – TiO_2 and Bi_2O_3 – TiO_2 systems. Glycine ($C_2H_5NO_2$), carbamide (CH_4N_2O) and glycerin ($C_3H_5(OH)_3$) were selected as reducing agents capable to provide conditions required for the exothermal oxidation-reduction reaction. Barium, lead, bismuth and titanyl nitrate were used as oxidizers and carriers of metal cations and anions.

The calculation results obtained by thermodynamical modeling have shown that the combustion temperature of mixtures is 1700 to 2500 K (1427 to 2227°C). However, under the real synthesis conditions the combustion temperature does not exceed 1300°C due to high temperature losses with escaping gases and heat transfer to environment. The titanates and zirconates forming during synthesis are precipitated in solid state.

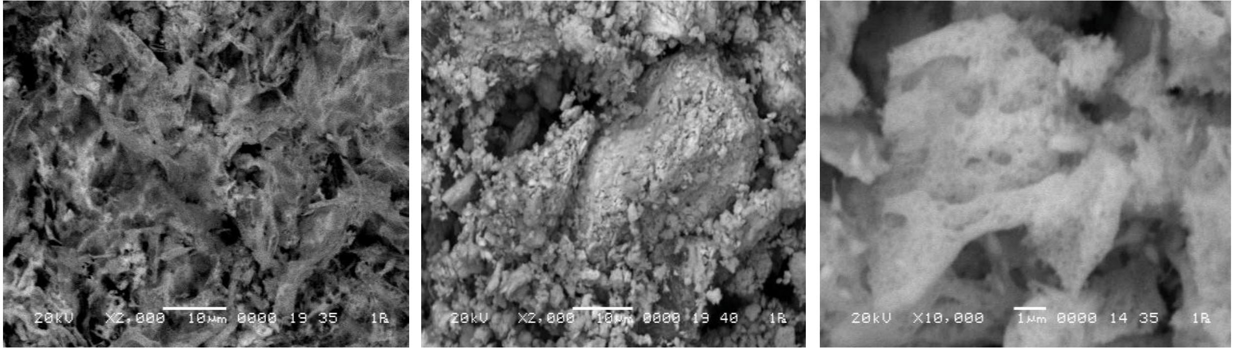
To produce ceramic materials using a high-temperature exothermal synthesis the stoichiometric quantities of raw components were dissolved in distilled water followed by a subsequent mixing with a pre-synthesized solution of titanyl nitrate.

The prepared solutions placed in alumina crucibles and put into a muffle furnace with temperature of 500°C. After water has evaporated exothermic inflammation of the solution components with a sharp increase of temperature started. The synthesis duration was in the range of 4 minutes and up to 10 minutes for glycine and glycerin respectively, which is considerably lower compared with the temperatures observed by conventional methods of high-temperature sintering.

In order to investigate phase composition and microstructure of synthesized materials they were subjected to X-ray phase analysis and microscopic examination. It has been established that a synthesized ceramic material of the BaO-TiO_2 system contains a barium titanate ($BaTiO_3$) of a high-temperature cubic modification as a basic phase in the cases in which glycine was used as a reducing agent. The retention of metastable state at low temperatures can be attributed to the effects of both the synthesis conditions (material quenching during rapid heating cooling) and space-dynamic factors (high mechanical stresses between fine grains prevent crystal rearrangement). The analogues data have been also obtained for materials synthesized in the PbO – TiO_2 and Bi_2O_3 – TiO_2 systems. In both cases the using of glycine allows to obtain ceramic materials ($PbTiO_3$ and $Bi_4Ti_3O_{12}$, respectively) in high-temperature metastable polymorphic modification.

At the same time using carbamide and glycerin as reducing agents results in that the phase composition of synthesized materials contains nitrates of metals and titanium dioxide, while the target product is in the minor quantities. This indicates that the use of these reducing agents with preset synthesis parameters does not result in achievement of the conditions required for proceeding the oxidation-reduction reaction between the components in a reaction system.

The synthesized materials have a fine crystal homogeneous structure that is characterized by a low density. The microstructure of synthesized materials contains some crystal elements aggregated in the form of thin plates, dendritic and filamentary formations (seen in Figure).



a b c

Figure 1. Micrographs of surfaces of synthesized ceramic materials
(a) $BaZrO_3$ (×2000); (b) $PbZrO_3$ (×2000); (c) $Bi_4Zr_3O_{12}$ (×10000)

Thus, in the course of carried out investigations it has been found that ferroelectric ceramic materials can be produced by the method of exothermal interaction in solutions. It is shown that synthesized materials possess high porosity and a high-developed surface.

ELECTRON MICROSCOPY OF NANO-MATERIALS PRODUCED BY COMBUSTION SYNTHESIS

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Development of novel nano-materials as well as new economical methods to synthesize them is of high interest due to fast growing demand for inexpensive nano-structures of high quality for electronics, catalyses, and energy conversion applications. A combustion or self-propagating high temperature synthesis (SHS), which involves the heat generation due to an exothermic chemical reaction, has been shown to be a promising economical method to produce a variety of advanced nano-materials and unique compounds. Because physical properties of nano-materials significantly depend on their atomic structure and composition, nano- and especially atomic-scale analytical techniques such as transmission electron microscopy (TEM) is of high importance. Here we review TEM capabilities in application to several CS synthesized nano-structures.

We developed combustion synthesis (CS) method for a number of high performance nano-materials including Graphene, MoS_2, FeO_x and others. For example, a novel exothermic *self-sustaining* reaction between a refractory silicon carbide (SiC) and polytetrafluoroethylene (PTFE) under the *inert atmosphere allows for synthesis of* hybrid structure of *graphene sheets* and *porous carbon nanoparticles* shown in Figure 1a. During this reaction, the tetrafluoroethylene (C_2F_4) gas, released due to PTFE decomposition in the combustion wave, reduces SiC to tetrafluorosilane (SiF_4) gas resulting in formation of disordered carbon particles with folded “native” graphene layers on their surfaces. The continuous supply of carbon, in the form of C_2F_4, enables further rapid growth of “free-standing” graphene flakes on the surface of those graphene-coated porous particles. The High Resolution Transmission Electron Microscopy (HRTEM) images (Fig. 1, b-c) clearly show that flakes appear to be single layer or few layers of graphene. The formation of graphene is also confirmed by Raman spectroscopy (see insert in Fig. 1a). The hybrid structure of *graphene sheets* and *porous carbon nanoparticles* combine the merits of electrical properties of graphene and large specific surface areas for porous carbon, and is a desirable structure for applications including batteries, super-capacitors, and catalysis. HRTEM images of MoS_2, W_3O_3 and FeO_x nano-structures are shown in Fig. 2.

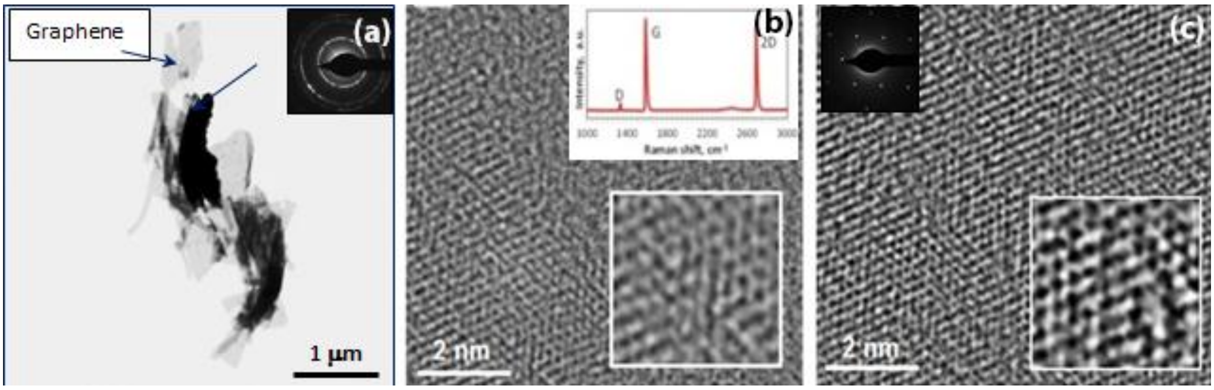

Figure 1 TEM images of graphene – porous carbon nano-structures (a), and graphene flakes (b,c). Inserted are diffraction patterns and Raman spectrum from grapheme flake.

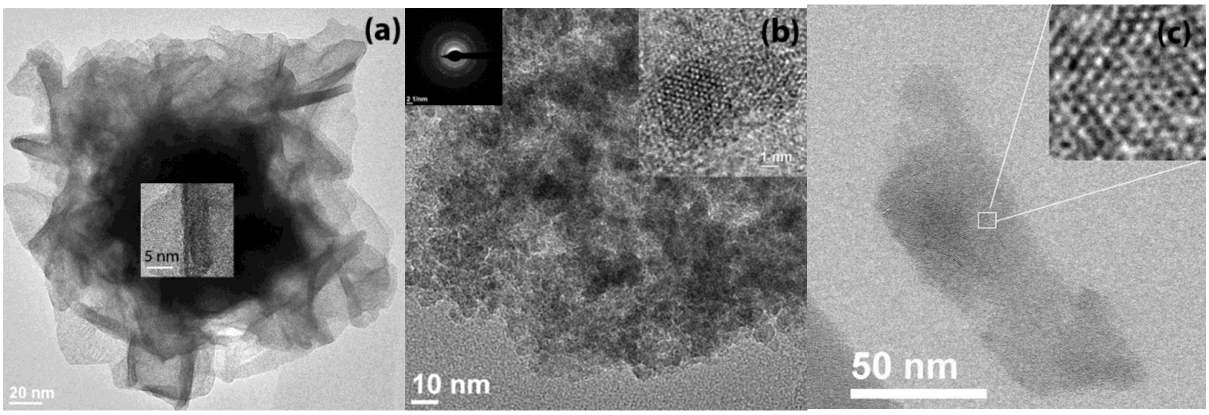

Figure 2 TEM images of W_2O_3 (a), FeO_x (b) and MoS_2 (c) nano-structures

The unique aspect of this method for synthesis of nano-materials does not require external energy source, as it occurs in a self-sustained synergetic manner. This method is flexible in terms of tuning the synthesis conditions, which provide materials with different microstructure and composition. It is also important that the low oxygen content in the reacting system allows synthesis of oxygen-free products.

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SYNTHESIS AND ELECTROCHEMICAL PERFORMANCE OF NANOSTRUCTURED $LiCoO_2$

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Despite increasing research into alternative energy, the llithium cobalt oxide remains the basis cathode electrode material due to the best performance in terms of high specific energy density and excellent cycle life, so that it has already been commercialized as a cathode material in commercial lithium ion cells. The theoretical capacity of $LiCoO_2$ is 300 mAh/g and practical capacity is significantly lower than theoretical value 150 mAh/g since concentration polarization occurs within the particle before the entire capacity can be utilized [1]. In general, reducing the particle size of electrod materials in lithium-ion batteries to nano domain level overcome this problem. Nanoscale dimensions will provide a short path for the ion motion in the ionic solid electrodes. Therefore, reactions become faster and batteries can be charged and discharged rapidly [2].

In this report we describe the behaviour features of the electrochemical performance of lithium ion battery electrod material ($LiCoO_2$) produced by Carbon Combustion Synthesis of Oxide (CCSO) invented by Martirosyan and Luss [3-5]. In CCSO the exothermic oxidation of carbon (393.5 kJ/mol) generates a thermal reaction wave with temperature up to 800 °C that propagates at a velocity of 0.1-3 mm/s through the solid reactant mixture converting it to the desired oxide product by the reaction: $3LiNO_3 + Co_3O_4 + \alpha C$. The major parameters affecting the synthesis and properties of the $LiCoO_2$ are the carbon concentration in the reactant mixture, type of precursors, and density/porosity of sample, which controls the ability of the oxygen infiltration to the reaction zone. The release of carbon dioxide CO_2 generates many pores producing the synthesized powders friable and loosely agglomerated. XRD analysis and electron probe microanalysis of as-synthesized catalysts show that essentially complete conversion to single-phase products was accomplished during the synthesis.

The custom-made pouch-type battery were prepared consisting of the active powder material (93.5 wt %), carbon black (4 wt %) and polyvinylidenefluoride (PVDF, <1 μm) dissolved in N-methyl pyrrolidinone (NMP) as the binder (2,5 wt %). After all components were mixed thoroughly, the cast was coated on an aluminium foil substrate; the coating was followed by pressing and drying at 120 °C for 12 h under a vacuum. The battery was assembled in glove box using separator membrane with special type of polyethylene. $LiPF_6$ was used as electrolyte with conductivity of 10.5 ± 0.5 ms/cm at 25 ^oC. The charge-discharge cycles were carried out in the potential range of 2.7-4.2 V using 8-channel battery analyzer. Fig.1,a illustrated the pounch-type battery consisting the $LiCoO_2$ nano-composite powder producing by CCSO. In the first stage, battery was charged with 150 mA/h constant current mode until the voltage raised to 4.2 V. At this point, the charging mode shifted to 4.2 V constant voltage charging mode and charging continued until the current droped to the 10 % of initial value (15 mA). After charging, the battery was relaxated for 1 min and then the constant current discharge with 50 mA was applied until the voltage dropped to the cutoff value of 2.7 V. The decreasing tendence of charge-dischgarge time of one cycle (Fig. 1,b) is indicating that the battery capacitance is also decreasing because initially more Li ions could pass from cathode to anode and vice versa, but after several cycles not all ions are returning to their initial positions and therefore the capacitance is dropping over many cycles, which is a known factor for the rechargeable batteries. The small deviations around 100 % of efficiency is demonstrated that the cycles showed substantial consistentency over 30 cycles. The specific capacity had initial value of 200 mAh/g and after 30 cycles the capacity dropped to almost 180 mAh/g showing that over 90 % of initial capacity is preserved over continuous charge-discharge series as can see from Fig. 1,b. This result is confirming that CCSO synthesized ultrafine $LiCoO_2$ has stable structure and gives opportunity to extract more than 66 % of theoretical capacitance (200 mAh/g form theoretical value of 300 mAh/g).

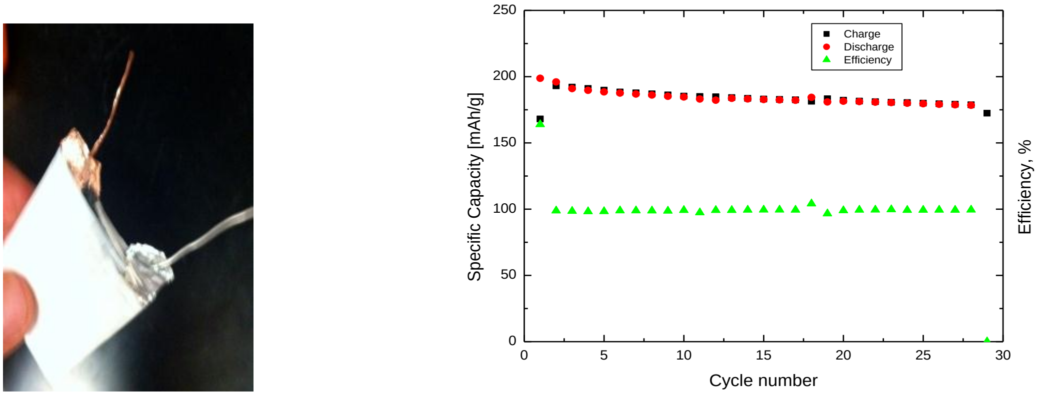

Figure 1. (a) - Laboratory made pounch-type battery; (b) - Galvanostatic cycle life of the Li-ion battery using $LiCoO_2$ powder produced by CCSO.

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FORMATION OF NANOCRYSTALLINE Cu–Cr COMPOSITE DURING MECHANICAL ACTIVATION

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For over the past decades, composites with nano-grained and nano-dispersed structures have been of current interest because of unique properties exhibited by nanoparticles. Cu–Cr matrix composites are a novel kind of advanced materials with high mechanical strength and high electrical conductivity. They are considered to have great potential for their use as electric contact and brush materials.

The material investigated in the present study is a Cu–Cr composite containing 45 wt % Cr. This system was chosen because both the elements show low solubility due to positive heat of mixing. High energy ball milling is an attractive way to increasing the solubility and material properties.

Mechanical activation (MA) was conducted in a high-energy planetary ball mill using stainless steel drums and balls in an argon atmosphere. The ball to mill weight ratio was 20 : 1. The milling times were chosen as 1, 3, 5, 9, 12, 15, 30, 60, 120, and 180 min.

MA leads to deformation and multiple flattening of Cu particles, while the Cr particles are crushed into smaller ones. The initial components intermixed and formed mechanocomposites consisting of alternating layers of Cr and Cu. MA allows us to obtain composite particles composed of intermixed (on micro and nano levels) layers of starting Cu and Cr reagents.

The structural evolution during milling was characterized by XRD (DRON-3 apparatus, Cu-$K_{\alpha 1}$ radiation). The widths of the Bragg reflections from Cr were found to undergo gradual broadening (Fig. 1.), while those from Cu widened much faster. For milling time more than 30 min, the width of the Cr reflections increased to such an extent that this phase became diffraction-silent.

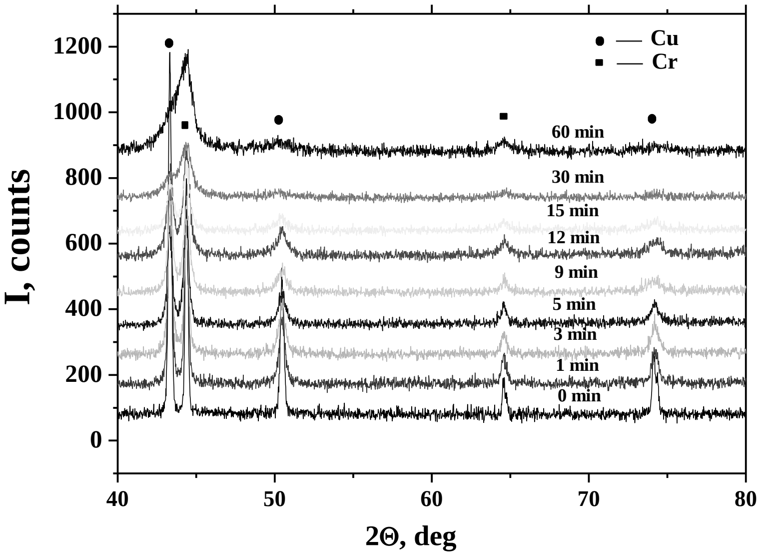

Fig. 1. XRD patterns of Cu–Cr blends activated for different milling times τ (indicated).

Microstructure, crystal structure, and local atom structure were characterized by XRD, high-resolution SEM, and high-resolution TEM. It has been shown that after 60 min of MA the grain size of Cr is in the range of only 3–5 nm. High energy ball-milling leads to the formation of mechanocomposites with small-sized crystallites of C and Cr which can be expected to show their unique properties.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 13-03-01403a) and Russian Academy of Sciences (program *Combustion and Explosion*).

COMBUSTION CHARACTERISTICS OF CONDENSED PHASE REACTIVES IN MICROSCALE METAL CHANNELS

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While the $W/BaCrO_4/KClO_4$ pyrotechnic formulation is widely used for a variety of pyrotechnic applications (e.g., delay fuzes) [1], replacement formulations are needed due to the toxicity and recent environmental regulations on hexavalent chromium (exposure < 5 μg m^{-3}) and perchlorates [2]. Condensed phase reactives (gasless or nearly gasless) may be an attractive alternative for various applications due to their wide range of combustion velocities and potentially low environmental and health impacts. While some of these reactive systems have been previously investigated for the production of intermetallic materials (combustion synthesis), they have not been studied at diameters applicable to those used for delay fuzes. A typical fielded delay fuze is comprised of a metal housing (e.g., aluminum or stainless steel) with a microscale channel as small as 5 mm that houses the pyrotechnic or reactive formulation. At these small diameters, high heat losses can be substantial (particularly for metal channels) and lead to combustion front instabilities (oscillations, pulsating, etc.) or extinction. Therefore, the combustion characteristics of such reactions and their stability at these diameters must be characterized in order to develop fieldable replacement formulations.

In this work, reactive systems such as Ti/C-3Ni/Al and $Si/Bi_2O_3/Sb_2O_3$ were considered as potential replacements for the traditional tungsten based delay fuze formulation. The combustion characteristics were studied in aluminum, stainless steel, and quartz microchannels. For the Ti/C-3Ni/Al system it was observed that by tailoring the stoichiometry a range of combustion velocities (2.1-38.1 $mm \cdot s^{-1}$) was achievable. Likewise, for the $Si/Bi_2O_3/Sb_2O_3$ system a range of combustion velocities (4.4-18.5 $mm \cdot s^{-1}$) was observed. To observe reaction combustion stability within the microchannel slitted stainless steel or aluminum microchannels were used as shown in Figure 1B. Combustion temperatures were also measured in-situ with microthermocouples. Even in the absence of microchannel induced heat losses, measured combustion temperatures were approximately 500 K lower than the predicted adiabatic temperatures due to the small scale of these experiments. As shown in Figure 1A the combined reactive system Ti/C-3Ni/Al can be tailored to propagate at various microchannel diameters by shifting the ratio of Ti/C and 3Ni/Al. This indicates that such systems may have broad applicability as delay formulations depending on system configuration and timing requirements. A predictive model utilizing experimentally determined apparent activation energies and thermal properties of the reactants is developed to complement microchannel combustion experiments. This model may provide an enhanced understanding of how thermal properties, combined system activation energies and heat losses to the delay housing affect the combustion and reliability.

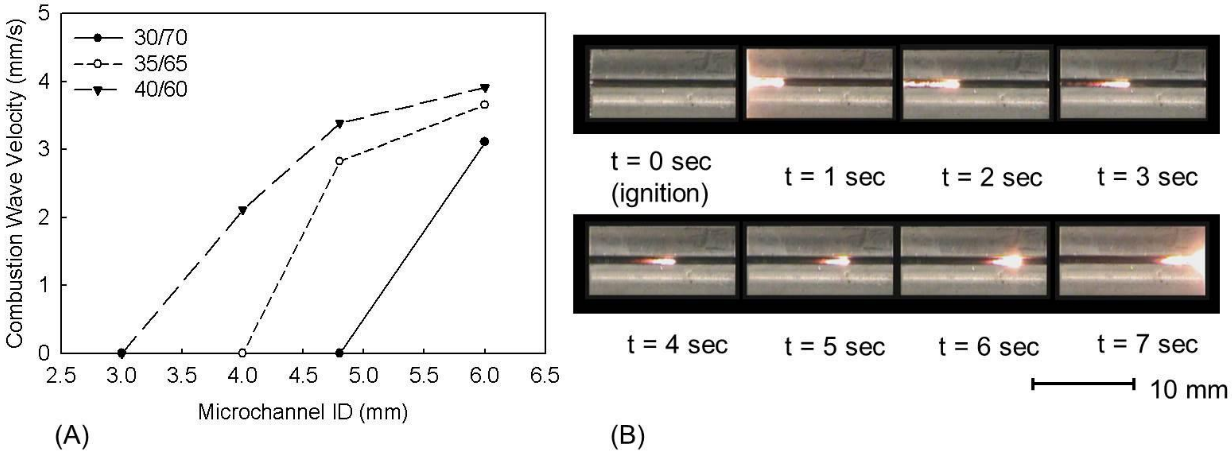

Figure 1 - (A) Combustion wave velocity of Ti/C-3Ni/Al as a function composition ratio at various diameter Al microchannels. (B) Images of the combustion front of a slitted microchannel to assess combustion stability.

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SHS AND SENSORY PROPERTIES OF $BiFe_{1-x}Mn_xO_3/BaZr_{1-x}Y_xO_3$ PEROVSKITES

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The field of (bio-)chemical sensor research represents one of the most interesting and exciting multi-disciplinary topics with a broad range of applications [1, 2]. Y-doped $BaZrO_3$ films are attractive to detection of relative humidity which is essential to accurately measure a large variety of gaseous species and concentrations since the water vapor may have a huge impact on the accuracy of other gas measurements especially at high temperature. These sensors are important for environmental monitoring, industry and human life: food packaging, air conditioning, agriculture, biological technology and medical services. Sensors with $BiFe_{1-x}Mn_xO_3$ are appropriate for continuous controlling composition of hazardous gases (ethane, methane, hydrogen and other hazardous gas sensors): for a threat detection and identification within enclosed spaces. Rapidly and accurately identification of hazardous situations to detect and warn of an occurrence of a chemical incident within enclosed spaces, such as buildings and transportation facilities is of great importance. These gases are associated with fires and mining operations, and it is of the highest importance to warn and protect operators from potential harm caused by overexposure to high concentrations of these gases.

The commercial reagents (from Sigma-Aldrich) with purity more than 99.6% and 1-10 μm of partial size: Bi_2O_3, Fe_2O_3, MnO_2 and Fe powder are used to self-propagating high temperature synthesis (SHS) of $BiFe_{1-x}Mn_xO_3$ (x-0.001, 0.005, 0.01, 0.03); BaO_2, ZrO_2, Y_2O_3 and Zr powder for synthesizing of $BaZr_{1-x}Y_xO_3$ (x-0.05, 0.10, 0.15) [4]. During syntheses of $BiFe_{1-x}Mn_xO_3$, the values of combustion temperature and front propagation velocities are 850…1150 ^{O}C and 0.11…0.20 mm/s, respectively, when the content of combustible (Fe powder) is changed from 6% to 14% [3]. In case of $BaZr_{1-x}Y_xO_3$ they belong to 1600…2000 ^{O}C and 10…55 mm/s, respectively, when the content of Ti powder is changed from 8% to 16% [4]. Each synthesized product was characterized by X-ray diffraction (XRD) employing CuKα radiation (λ = 1.5418 Å).

Mechanical treatment of the SHS products was carried out in a planetary centrifugal mill with acetone as a milling media and the speed of the platform rotation 600 r/min and the speed of rotation of milling vessels 1100 r/min, until to obtain particle sizes of 5 to 8 μm. Samples are sintered in a muffle furnace at the temperature of 760 and 1550 °C, respectively.

Silver or gold ohmic contacts were deposited on BiFe1-xMnxO3 ceramic thin films. The electrical resistance measurements of gas-sensitive elements were carried out under various concentrations of acetone, ethanol, natural gas and petrol in the temperature range 250 to 450 ^{o}C. The gas sensitivity as a function of temperature (up to 450 ^{o}C) and the concentration (up to 10 vol.%) of analyzed gas in the air present in the test chamber is investigated, the sensors show high sensitivity at temperature of 250-400 ^{o}C.

In order to test humidity sensitivity of Y-doped $BaZrO_3$ samples platinum contact was deposited on surface and the electrical conductivity of they was investigated at various partial pressures of water in the temperature range of 200 to 1000 °C. The measurements showed that intensive reaction is performed by samples at 270…300 °C and conductivity is changed up to 2.5 under water vapor.

ACKNOWLEDGMENTS

This work was made possible by a research grants from the Armenian National Science and Education Fund (ANSEF, based in New York, USA), grant # 3171 and National Foundation of Science and Advanced Technologies (NFSAT), State Engineering University of Armenia (SEUA), U.S. Civilian Research and Development Foundation (CRDF), grant # ECSP-12-08.

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SHS OF SILICON CARBIDE NANOPOWDER

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Ceramic materials based on silicon carbide (SiC) have a set of unique properties, such as thermal and chemical stability, refractoriness and high hardness. Due to these properties, SiC has a wide range of applications, including abrasives and cutting materials, structural ceramics and crystals for microelectronics, catalysts, and coatings. The traditional method of manufacturing SiC is the process invented by E. Acheson in the 19th century and is based on the reduction of silica SiO_2 with carbon. The method requires high temperatures (above 2000 K) and long durations (30 - 150 h), which makes difficult a production of nanosized silicon carbide powders. A modern alternative to the Acheson process could be self-propagating high temperature synthesis (SHS), which is based on the use of the heat of an exothermic chemical reaction for production of various advanced compounds. To date, many inorganic materials, including high performance nanomaterials, have been synthesized by this method. However, the problem is that the reaction for the direct synthesis of silicon carbide from elements,

$$Si + C = SiC + 73\ \text{kJ/mol},$$

is an insufficiently exothermic and has a relatively low adiabatic combustion temperature (1173 K), so that self-sustaining combustion cannot be accomplished in this binary system. Therefore, SiC can be produced by SHS only by using different types of “activation” processes, such as, preheating of the initial mixture, addition of chemical activators, or synthesis in nitrogen or air atmospheres.

In the present work, we report SHS of a submicron nanocrystalline SiC powder from elements in an inert atmosphere [1,2]. It is shown that initial micro-scalled mixture of silicon and graphite powders after 15 minutes of high energy ball milling (HEBM) transformers to the nano-size media of composite particles, which consist of amorphous carbon and crystalline silicon. It is also demonstrated that self-sustained reaction can be accomplish in such nano media in argon atmosphere and reaction front propagates with velocity of ~ 5 mm/s and maximum temperature 1800 K. Under optimum conditions, the synthesis of sub-micron (50–200 nm) SiC powder with a specific surface area (BET) ~20 m^2/g can be accomplished in the self-sustained reaction.

The influence of HEBM on the combustibility of the Si/C mixture possesses a critical character: the combustion synthesis becomes feasible when some threshold duration of milling is achieved. Increasing the power of HEBM (acceleration of milling balls) can decrease this critical duration by several times. However, an excess of HEBM duration results in decreasing reactivity of the mixture because of gradually formation of SiC during ball milling.

Comparison of the microstructures for as-milled (Fig1a,b) and as-synthesized powders (Fig.1c,d) reveals that for all investigated conditions the morphologies of the as-milled reactive Si/C media are essentially the same as that for SiC combustion products. The mechanism for direct synthesis of SiC by combustion reaction is also proposed.

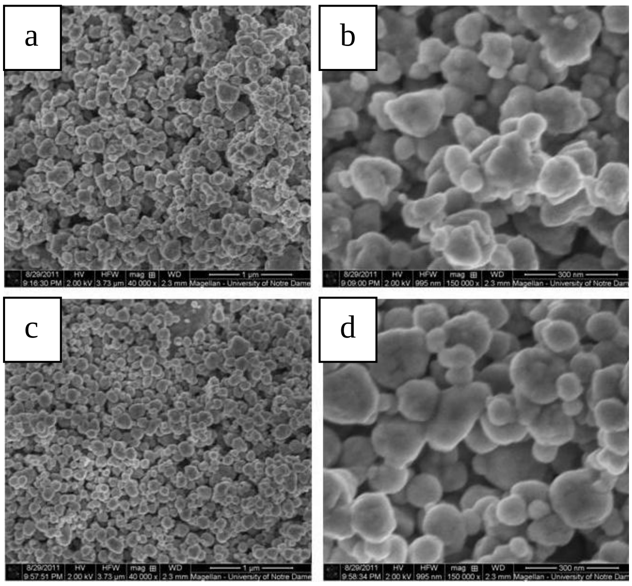

Figure 1: Typical SEM images of initial Si+C powder mixture (a,b); and combustion products (c-d).

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COMBUSTION SYNTHESIS OF TiFe-BASED HYDROGEN STORAGE ALLOY FROM ILMENITE BY UTILIZING HYDROGENATION HEAT OF CALCIUM

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Titanium iron (TiFe) is an attractive hydrogen storage alloy because of abundance in resources, cyclic property, and reversibility of absorption/desorption at room temperature. In this study, we proposed a new process to synthesize the TiFe alloy from ilmenite ($FeTiO_3$) using combustion synthesis (CS). In the experiment, the effects of the purity of ilmenite and the reaction atmosphere on the ignition temperature in CS and the hydrogenation properties of the products were mainly investigated.

Reagent ilmenite, $FeTiO_3$, and natural ilmenite was used as raw materials. Ilmenite was first roasted at 1223 K in air to improve the reactivity with hydrogen. The sample was then reduced to a mixture of Fe and TiO_2 at 1173 K under 50%-H_2 gas flow. The partially-reduced ilmenite and Ca were mixed with a molar ratio of 1:4 and heated in argon and in hydrogen atmospheres until the ignition due to an exothermic reaction. Table 1 lists the experimental condition of CS. The product powders were then washed with an aqueous solution of 10 mass% acetic acid so as to remove the calcium residue and the by-product of calcium oxide and hydride and were finally dried in a desiccator in air at 353 K.

Fig. 1 shows changes in sample temperature with time and its secondary differentiations during CS. The ignition temperature was strongly dependent on the reaction atmosphere. The melting of calcium triggered ignition in the argon atmosphere. In contrast, in the hydrogen atmosphere, the ignition was triggered by hydrogenation of calcium. The ignition point decreased with an increase in hydrogen pressure because the hydrogenation rate of calcium accelerated. As a result, TiFe hydrogen storage alloys were successfully synthesized from both reagent and natural ilmenite. However, the purity of the product was affected by thermal history during CS. The product synthesized in 0.1 MPa hydrogen from reagent ilmenite showed the largest hydrogen capacity of 1.40 mass%, which was almost equal to the commercially available TiFe produced by melting method, as its reaction temperature was suitable for CS of TiFe alloy. The product synthesized from the natural ilmenite showed a lower storage capacity and sloped equilibrium pressure because of impurities, e.g., aluminum and silicon, in the raw material. The results demonstrated that CS

Sample	**Ilmenite**	**Reaction Atmosphere**	**Pressure [MPa]**
R-01A	Reagent (3N)	Argon	0.1
R-01H	Reagent (3N)	Hydrogen	0.1
R-10H	Reagent (3N)	Hydrogen	1.0
N-01H	Natural*	Hydrogen	0.1

* Chemical composition (max.-min. mass%) of natural ilmenite are TiO_2 (49-51), FeO (30-35), Fe_2O_3 (10-14), T.Fe(30-40), SiO_2 (0.5-2), Al_2O_3 (0.5-1.5), P (0.02-0.04), ZrO_2 (0.02-2.0), Cr_2O_3 (0.04-0.07) and U+Th (< 50ppm).

Table 1 Experimental conditions for combustion synthesis of TiFe from calcium grains and ilmenite powder pre-reduced by hydrogen at 1173 K for 3h.

has many advantages for synthesizing TiFe hydrogen storage alloy, such as lower reaction temperature, high product purity, and direct powder production. This method could be applied to develop a new TiFe production process from ilmenite ore.

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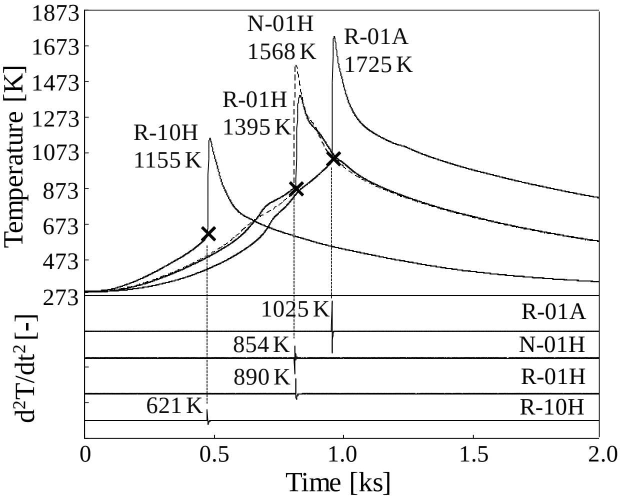

Fig. 1 Changes in sample temperature with time and its secondary differentiations during CS. The samples were heated at the rate of 60 K/min to the ignition points.

$Ca_2Si_5N_8:Eu^{2+}$ PHOSPHORS SYNTHESIZED BY A SHS METHOD AND THEIR LUMINESCENT PROPERTIES

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A combustion synthesis method has been developed for synthesis of Eu^{2+}-doped $Ca_2Si_5N_8$ phosphor and its photoluminescence properties were investigated. Ca, Si, and Eu_2O_3 powders were used as the Ca, Si and Eu sources. NaN_3 and NH_4Cl were found necessary to be added for the formation of the product phase and addition of Si_3N_4 was found to enhance the product yield. These powders were mixed and pressed into a compact which was then wrapped up with an igniting agent ($Mg+Fe_3O_4$). The reactant compact was ignited by electrical heating under a N_2 pressure of 0.7 MPa. Effects of these experimental parameters on the product yield were investigated and a reaction mechanism was proposed. The synthesized $Ca_2Si_5N_8:Eu^{2+}$ phosphor absorbs light in the region of 300-520 nm and shows a broad band emission in the region of 500-670 nm due to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Eu_2O_3 was found partially unreacted and a certain amount of oxygen is believed to be incorporated into the lattice of the product phase. The peak emission intensity (~93% of a commercially available phosphor, $YAG:Ce^{3+}$) and the peak emission wavelength (571-581 nm) were found to be lower and shorter, respectively, than that reported in the literature. These are considered to be mainly due to oxygen incorporation, which not only reduces nephelauxetic effect and crystal field splitting but also causes a lowering of internal quantum efficiency.

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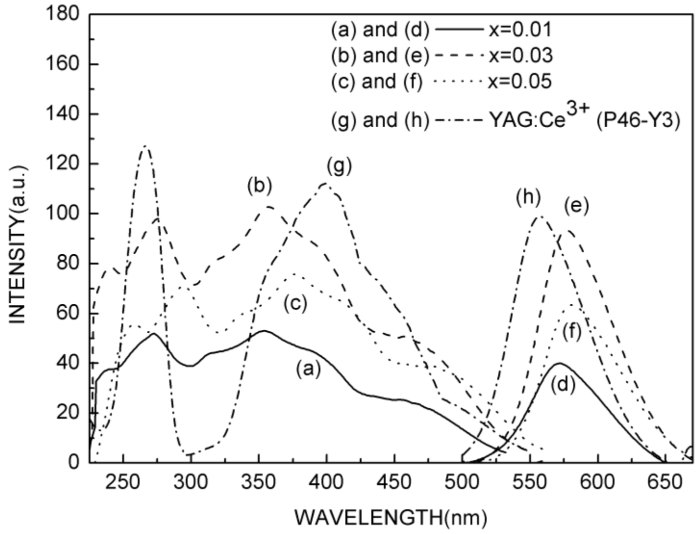

FIG. 1. The excitation (curves (a), (b) and (c)) and (d), (e), and emission (curves (d), (e) and (f)) spectra of the phosphor synthesized in the present study and similar spectra of $YAG:Ce^{3+}$ phosphor (P46-Y3) are also shown ((g) and (h)) for comparison.

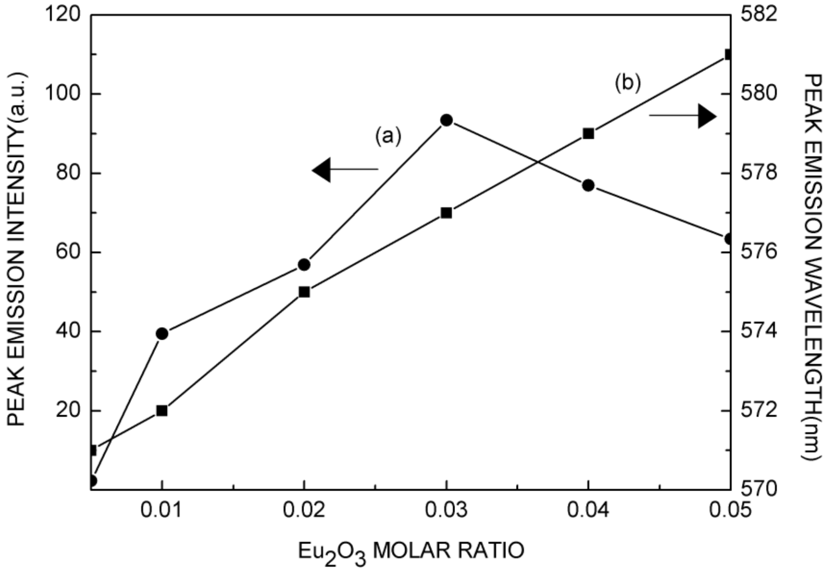

FIG. 2. Dependence of peak emission intensity (a) and wavelength (b) on the Eu_2O_3 molar ratio.

SOLUTION COMBUSTION SYNTHESIS OF HIGHLY POROUS NICKEL: DYNAMICS OF PHASE AND MICROSTRUCTURE FORMATION

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Nanoscale metal powders often possess non-traditional mechanical and physical properties as compared to those for micron sized particles. Such nanopowders found applications in catalysis, electronics, medicine and other fields of science and technology. Different methods are used for synthesis of nanomaterials, such as precipitation from salt solutions, oxide reduction by hydrogen, the gas-phase reactions, etc. A specific class of approaches for synthesis of the nanopowders is based on combustion phenomenon. Indeed, the self-sustaining exothermic combustion reactions offer a variety of methods for nano materials production [1]. One of them is known as solution combustions synthesis (SCS), which e.g. involves self-sustained reaction in a solution of metal nitrates and a fuel [2].

The composition of the solutions is determined according to the main principle of self-propagating high-temperature synthesis (SHS), namely, the rule that the heat released in the process should be sufficient for the self-sustain propagation of a chemical reaction. The main difference between SCS and the classical SHS is in the microstructure of the initial reaction medium. For SHS, mixtures of solid powders are typically used with the scale of the heterogeneity is on the range 1–100 μm. For SCS the reactants in solutions are mixed at a virtually molecular level. The latter simplifies the synthesis of nanomaterials at high temperatures of the combustion wave.

Although many compounds (mainly oxides) have been already produced by solution combustion, the reaction wave structure, and dynamic of phase transformation, which take place during SCS are poorly understood. To investigate these issues, it is rather to use in-situ techniques that allow one to observe the process under operando conditions. Time resolved X-ray diffraction (TRXRD), high speed micro video recording (HSMVR) and IR-recording are among such advanced techniques. In this work, these diagnostics were used to investigate the combustion wave structure and the dynamics of phase formation during SCS of highly porous nickel powder by using the nickel nitrate – glycine reactive solutions.

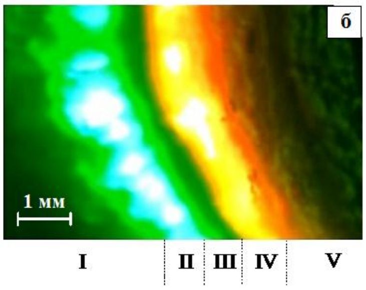

Fig 1: Structure of the SCS wave in the nickel nitrate–glycine system.

Analysis of the HSMVR images and IR-movies allows us to conclude that the combustion wave can be divided into five zones (Fig.1). Zone I is the initial gel. Zones II and III together constitute the preheating region. Zone II is characterized by the intense release of gases and vapors and can be called the fume zone. After completion of the gas release, the gel layer becomes continuous again. The width of the reaction zone (IV) is 0.6–0.8 mm. Then the temperature rapidly decreases, and the zone of solid reaction products (V) begins.

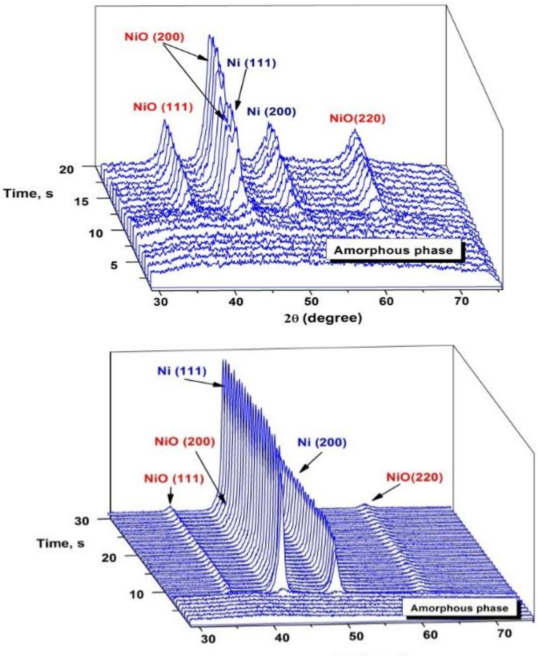

Fig 2: The sequences of X-ray diffraction patterns in the three-dimensional coordinates time–scattering angle–peak intensity

Figure 2 shows the results of TRXRD analysis. The initial gel is amorphous; therefore, diffraction peaks emerge only once the combustion front reaches the analysis region (*t* = 2 s). In the combustion of the stoichiometric (φ = 1.0) mixture, Ni and NiO phases emerge simultaneously and grow at approximately equal rates. For the sample with an excess of glycine (φ = 1.25), an oxide phase is virtually absent, and in the reaction wave front, a phase of pure nickel immediately forms. The combustion products have high porosity, a large specific surface area of 20 m^2/g, and a particle size of ~30 nm.

Based on the obtained results a fundamental conclusion has been made [3] that the mechanism of the phase formation in the system depends on the conditions of heating of the reaction medium. Indeed, under more equilibrium conditions of temperature change (20–100 K/min), the phase that is the first to form in the reaction in the nickel nitrate–glycine system at any compositions (φ = 1.0 and 1.25) is the nickel oxide (NiO) phase, while at a high heating rates (~10^3 K/s) during SCS, a nickel phase forms directly in the combustion wave.

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SYNTHESES AND CHARACTERIZATION OF BFO-BTO MULTIFERROELECTRIC CERAMICS AND THIN FILMS

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Mn doped (1-x)$BiFeO_3$-x$BaTiO_3$ (BFO-BTO) multiferroics attracted considerable interest due to their high dielectric constant, large spontaneous polarization, low losses and good piezoelectric and sensorial properties. Possible applications include tunable microwave components, high-speed non-volatile memory and piezoelectric devices, chemical and biosensors, etc. Electrically tuneable thin Film Bulk Acoustic wave Resonators (FBARs) utilizing electric field induced piezoelectric effect in BFO-BTO enable development of novel reconfigurable/adaptable microwave circuit architectures [1-2].

In this work Self-propagating High-temperature Synthesis (SHS) is developed for the fabrication of $0.99[0.67BiFeO_3–0.33BaTiO_3]$-0.01Mn compound. SHS is attractive for very short syntheses time, low energy consumption, and high productivity. In $0.6633(1/2Bi_2O_3+(1-k)/2Fe_2O_3+kFe)+0.3267(BaO_2+(1-K)TiO_2+KTi)]+0.01MnO_2+O_2$ system (where k and K are the factors controlling the exothermicity) the process of the combustion synthesis (SHS) has been investigated by computer simulation using National System DAQ and LabView programs. It has been established that temperature (900-1350 ^{O}C) and propagation velocity (0.5-5 mm/s) of the combustion front depended on amount of combustible (Fe and/or Ti have been changed from 3.5% to 8%), partial size of the initial components (dispersion was 1-5 μm), relative density (as well as pressure of oxygen) and mechanical activation of green mixture. By controlling these critical parameters powders with the desired/controllable stoichiometry and microstructure are produced. The phase structure investigation shows no other phases when the amount of combustible was about 5.5% (Fe-1.5%, Ti-4%).

Conventional ceramic technology is optimised for fabrication of ceramic targets for thin film deposition. Single-phase BFO-BTO multiferroic thin film FBARs fabricated by pulsed laser deposition reveal resonance at 4.1 GHz, tunabilty of resonant frequency 4.4%, electromechanical coupling coefficient of 10% and unloaded Q-factor 220 [2]. These parameters are highest for the electrically tuneable FBARs reported so far.

Acknowledgments. The authors gratefully acknowledges Dr. Spartak Gevorgian (Chalmers: Microtechnology and Nanoscience) for his assistance with fabrication and investigation of microwave devices.

Acknowledgments

This work was made possible by a research grant from the Armenian National Science and Education Fund (ANSEF) based in New York, USA.

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NiAl SYNTHESIS BY SHS AND MECHANICALLY ACTIVATED SHS

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The synthesis of NiAl intermetallic has been studied as a function of the granulometry and shape factor of the reactants, using large Al spherical particles (<100µm) or Al flakes (ϕ≈11µm, thickness 250nm), and three sizes of Ni spherical particles (44-144µm, 3-7µm, 100nm) or Ni flakes (ϕ≈20µm, thickness 370nm). Using time-resolved infrared imaging, the behavior of the reaction fronts are described as a function of ignition time t_{ig}, ignition temperature T_{ig}, maximum combustion temperature T_{max}, reaction front velocity V_r and maximum heating rate in the combustion front T'. From these experiments, the influence of Al morphology, and of Ni size and morphology is described.

Sample are then analyzed using SEM observations and X-ray diffraction, and using the Williamson-Hall methodology on our x-ray patterns, the size of diffracting domains of the products and the resulting microstrains inside the samples are evaluated.

In a second part, the same material is synthesized either by mechanical alloying (reaction during planetary ball milling) or by mechanical-activated SHS (ball co-milling of the reactants, shaping, followed by SHS reaction). From these experiments, the evolution of the granulometry of the reactants during milling, the reaction delay and the evolution of the granulometry and completeness of the reaction as a function of milling time (up to 9h), ball-to-powder ratio (15:1, 30:1, 45:1), rotation velocity (250, 350 or 500 RPM) of the planetary ball mill and atmosphere (air or argon) will be presented.

Results will be presented as milling maps, depicting for each value of the rotation velocity, showing that the reaction under our experimental conditions, the powder first consist of the milled reactants, then a progressive reaction takes place, with the apparition of non-stoichiometric NiAl together with both reactants, followed by a progressive disappearance of Al then Ni diffraction peaks.

Finally, unreacted milled powders were subjected to SHS reactions, or to global heating at 200, 300 and 450°C, with at first a solid-state diffusion reaction, then a observed thermal explosion.

NANO-TUNGSTEN SYNTHESIS BY BALL MILLING AND BALL-MILLING-INDUCED THERMITIC REACTIONS

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In the ITER tokamak, two different materials are now considered as possible components for the walls of the reaction chamber, namely Beryllium in the upper part, and tungsten in the lower part, known as the divertor. Due to the presence of thermonuclear reactions in this chamber, high energy neutrons (14 MeV) and ions are produced and do induce sputtering of the walls, generating fine dusts, which behavior must be known for safety reasons (e.g. in the case of a Loss Of Vacuum Accident (LOVA), due either to an air leak inside the chamber or a water leak from the wall cooling system). On the other hand, periodical cleaning and dust removal must be performed to minimize such a risk, and at that point, possible tritium intake of these dusts must be taken into consideration.

Our goal is here to consider the worst case scenario, and therefore to study the behavior of the most dangerous particles. In HEPA filters, the bigger particles are stopped by the size of the mesh of the filter, whereas the smaller particles are trapped by a kinetic effect. In between, in the 100-150 nm range, the efficiency of the filter presents a minimum, and these particles have therefore the highest probability to be released in the atmosphere.

Our aim, as presented here is to synthesize with the best yield tungsten particles in this dimension range, through different means, e.g. planetary ball milling, in dry or wet (ethanol) environments, or through a reaction between tungsten trioxide and magnesium ($WO_3 + 3Mg \rightarrow W + 3MgO$), using different salts as diluents. In this later case, salts and MgO are removed using 2M HCl leaching for 2 hours at 50°C under stirring, followed by sonication to de-agglomerate the powders, and by filtration using 3µm, 450 nm, 220 nm and 50 nm filters to evaluate the yield ratio of each dimension range.

Results are then obtained by SEM observations, X-ray diffraction, followed either by Rietveld refinement or using the Williamson-Hall methodology, and SSA measured by the BET method. The different synthesis methods will then be compared, focusing on the grain sizes, the polydispersity of the powders, and the residual microstrain, as the defects present in the lattice may be a sign of an increase of a possible tritium trapping within the metal.

In a later part of this work, our aim will be, in collaboration with toxicologists from the CEA, to study the toxicity of these particles, possibly after marking such particles with gaseous tritium.

COMBUSTION BONDING OF FUNCTIONALLY GRADED W/CU TARGETS FOR NEW ACCELERATORS

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A new generation of accelerators, such as the St. ANA accelerator at the University of Notre Dame and the accelerator in the proposed Dakota Ion Accelerators for Nuclear Astrophysics (DIANA) project at the Sanford Underground Research Facility (SURF), will produce higher intensity beams than ever previously attained. Beam intensities are estimated to be on the order of hundreds of μAmps. These new intensity thresholds introduce significantly higher temperatures at points where the ion beam interacts with the beamline components, the experimental target, and/or the beam slits. These temperatures are high enough to destroy the current generation of solid target backings and slits in the beam-line, traditionally both made from tantalum [1]. Tantalum is traditionally used for targets and slits in the beam-line because it has a high proton number, making it effective for stopping ion beams. However, tantalum is brittle, a poor conductor, and, if produced commercially, often contains impurities (e.g. fluorine) that produce undesirable background and reaction products. Tungsten, despite its brittleness and poor conductivity, has a higher atomic mass and lacks of impurities, which make it a promising target backing. In conjunction with tungsten's properties, copper is robust and a far superior thermal conductor.

In this work we describe a new method for production of the ***functionally graded targets*** that use the advantageous of both tungsten and copper. This method is based on combustion joining approach [2] and involved the following steps: (i) placing a reactive powder mixture (such as Fe_2O_3 + Mg + Fe, Ti + C + Ni or Ti + Si + Ni) in between tungsten and copper plates; (ii) applying an optimum load force on the stack to be joined; (iii) reaction initiation in the exothermic mixture; (iv) which provides extremely high temperature for reactive joining of W to Cu.

Thermodynamic calculations and experiments showed that all reactive mixtures are able to generate the necessary heat to join the materials; however, it became apparent that both thermite Fe_2O_3 + Mg and gasless Ti+C systems introduced defects to the reacted layer that either did not create a stable join or left a low quality join layer. The major issue is related to the fact that combustion of both systems in air leads to the release of a large amount of gas phases (e.g. Mg vapors, CO_2), which causes the material ejection from the reaction zone. The latter does not allow us to produce joint layer of desired properties.

The self-sustained reaction in Ti+Si system does not lead to any gas phase products and thus provides the desirable conditions for combustion joining. The optimal reactive mixture to joining copper and tungsten plates (with thickness of 0.05 – 1 mm) was found to be 5Ti+3Si reactive mixture diluted with 20wt.% Ni. Other experimental parameters, such as force load, geometry of samples, thickness of soldering layer (nickel) are also have been optimized. Targets prepared within the optimized joining conditions results in a join layer that is free of cracks and pores (Figure 1).

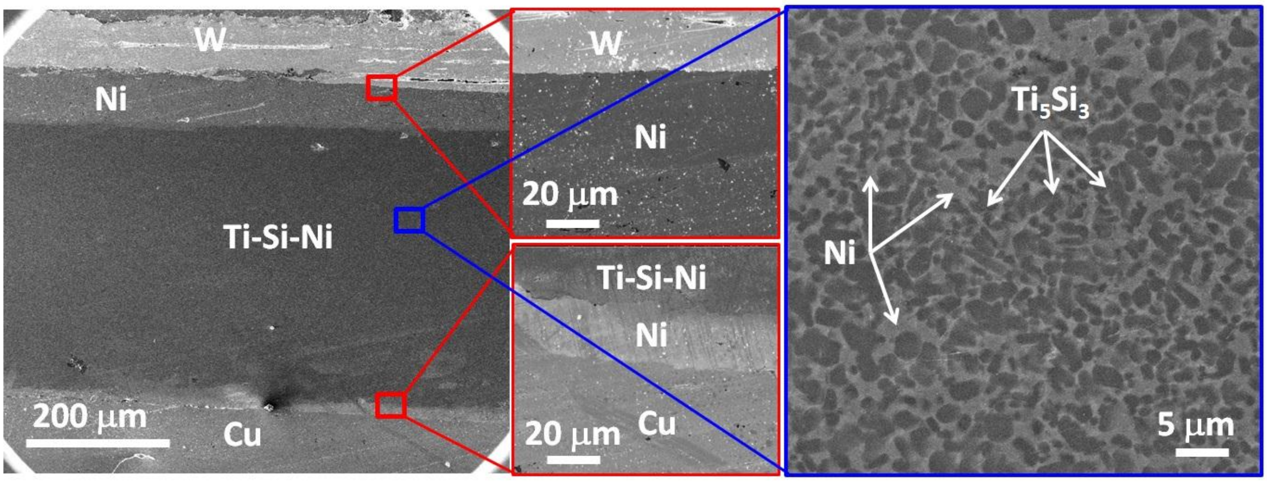

Figure 1: The microstructures of the join layer cross-section

We show that the microstructure of samples does not deteriorate through heating to ~700 °C in inert gas for several hours. Moreover, such treatment even reduces or eliminates small microstructural defects. More details on synthesis conditions, as well as the results of testing of W/Cu backings under an intense ion beam bombardment will be discussed.

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PREPARATION AND CHARACTERIZATION OF YFe_2O_4 BY SOLUTION COMBUSTION SYNTHESIS

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The ternary oxide system Y-Fe-O represents interesting magnetic properties which can be sensitive to the crystalline size of particles. There is a major challenge to receive these particles in nano-crystalline form due to particles conglomeration during the nucleation and synthesis process. In this report we describe self-propagating solution combustion synthesis, which can be used to fabricate nanocrystalline yttrium magnetic ferrites. Yttrium ferrite YFe_2O_4 is a complex oxide compound. Yttrium is considered as rare earth element since it tends to occur in the same ore deposits as the lanthanides and exhibits similar chemical properties. The mineral known as *yttrium-iron garnet* (YIG) contains the rare-earth element yttrium, has the formula $Y_3Fe_5O_{12}$. The rare-earth ferrites similar to YFe_2O_4 are widely used in fuel cells, catalysts, gas sensors, magnetic materials, and environmental monitoring application. Yttrium ferrite exhibits soft magnetic properties which can be used in devices with high frequency applications. Recent studies also show that it has electrical and magnetic coupling, and shows ferroelectricity near the ferrimagnetic transition temperature around 250 K. It is also a multiferroics, and displays more than one primary ferroic order parameter simultaneously.

For the synthesis procedure, we used $Y(NO_3)_3$ x $6H_2O$ (99.9%), $Fe(NO_3)_3$ x $9H_2O$ (99%) and glycine NH_2CH_2COOH, that were dissolved in distilled water. The mixture was gradually vaporized during heating at 250 °C. The produced soft foam then was ignited and a light brown fluffy product was received. The molar ratio of $Y(NO_3)_3$ x $6H_2O$ (99.9%):$Fe(NO_3)_3$ x $9H_2O$ (99%) was 1:2, and the glycine was 3-6 wt. % of the mixture. Yttrium ferrite nanoparticles were fabricated according to the following reaction:

$$2Y(NO_3)_3 \text{ x } 6H_2O + 4Fe(NO_3)_3 \text{ x } 9H_2O + 2.22C_2H_5NO_2 = 2YFe_2O_4 + 53.56H_2O + 18NO_2 + 4.44CO_2 + 1.11N_2$$

We analyzed the solution combustion of ferrite by thermo-gravimetric analysis to understand the mechanism of interaction, as well as characterized the combustion products by XRD and measured magnetic properties over the temperature range from 1.8K to 300K with PPMS.

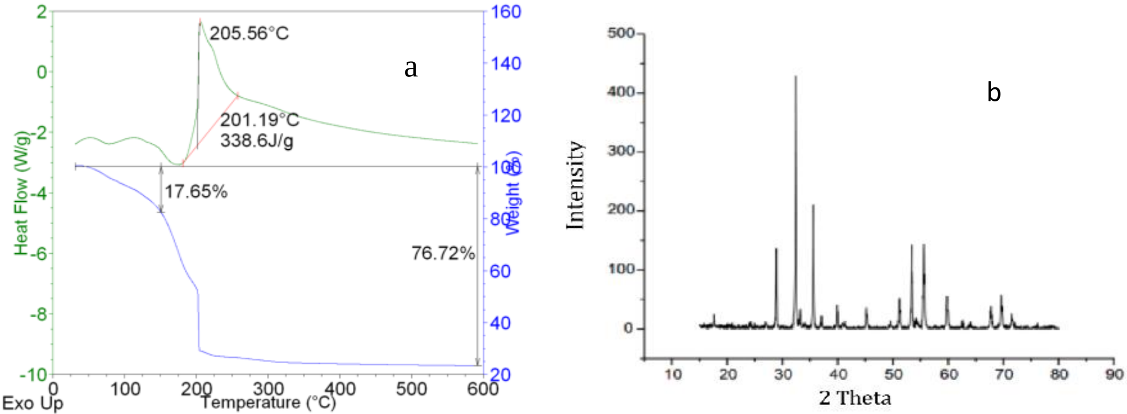

Figure 1. (a) DSC of the system $Y(NO_3)_3 \times 6H_2O$ - $Fe(NO_3)_3 \times 9H_2O$ - 6 wt. % NH_2CH_2COOH, (b) - X-ray diffraction patterns of fabricated yttrium ferrite obtained at 6 wt. % NH_2CH_2COOH.

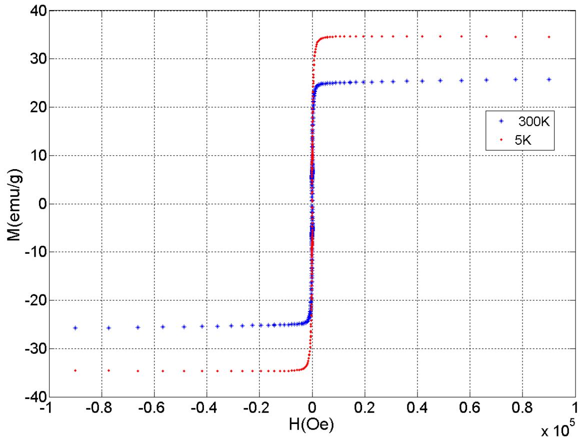

Figure 2. Magnetic hysteresis of the yttrium ferrite at 5K and 300 K.

According to Fig. 1a, the decomposition of the nitrides starts at around 150 °C. Before 200 °C, the 18 % weight decrease is corresponding to the loss of some water molecules. The exothermic interaction begins at 200 °C. The overall 77 % weight loss is due to nitrogen, nitric oxide, carbon dioxide and water are leaving the reaction zone. The resulting product has sharp XRD peaks (Fig. 1b). This is an indication that after the 600 °C heating a highly crystalline final product can be obtained. Fig. 2 is presenting the magnetic properties of the combustion product. At 5K, the remnant magnetization was 9 emu/g and the coercivity was at a magnetic force of -74 Oe. The saturation magnetization began at a magnetic force of 3100 Oe, and a magnetic moment of 34 emu/g. At 300 K, the remnant magnetization was 6 emu/g and the coercivity was at a magnetic force of -47 Oe. Saturation began at a magnetic force of 7767 Oe, and at a magnetic moment of 25 emu/g. At a magnetic force of 1000 Oe, the magnetic moment is 24 emu/g.

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COBALT CATALYSTS SYNTHESIZED BY SHS AND SOLUTION COMBUSTION FOR REFORMING GREENHOUSE GASES TO SYNTHESIS GAS

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The mitigation and utilization of the greenhouse gases CO_2 and CH_4, are among the most important challenges in the area of energy research. CO_2 reforming of CH_4 has received much attention from both an environmental and an industrial perspective because the reaction can convert these greenhouse gases into synthesis gas with a low H_2/CO ratio.

This paper presents the results of an investigation of cobalt-based catalysts produced by both SHS and solution combustion synthesis (SCS) for the above reforming reaction. SHS catalysts were produced from Al, Co_3O_4, Al_2O_3, H_3BO_3. In the case of SCS, the catalysts were synthesised from cobalt, zinc, barium nitrates and urea or glycine as reducers at the pre-heating temperature of 500°C. Properties studied include microstructural morphology (SEM, EDAX), atomic structure and phase distribution (XRD), porosity and specific surface area.

The catalytic reaction was carried out at 750, 800, 850 and 900°C using a feed gas of CO_2:CH_4:N_2 in the ratio 1:1:1 and the reaction products were analyzed by gas chromatography. The basic reaction of CO_2 reforming of CH_4 is: $CO_2 + CH_4 \rightarrow 2CO + 2H_2$. It was found (Fig.2) that maximum conversion of methane and CO_2 was given by the SHS catalyst that contained 5% Co_3O_4. The ratio of H_2/CO in the products changed from 0.88 to 1.12 and was found to depend on both the catalyst composition and the temperature of reaction, as shown in Figure 3. Best results were obtained on SHS catalysts (Fig.3) where conversion of methane reached 84% and conversion of CO_2 reached 92%, double that of SCS catalysts. According to the results, Figure 4, the ratio of H_2/CO of 0.98-1.02 was obtained on the SHS Co-Al-B-O catalysts. The results also show that SHS catalysts are more active, even when the surface area is 2 orders of magnitude lower that SCS catalysts. This confirms that the specific activity of SHS catalysts is very high which may in fact increase even more if their surface area can be increased.

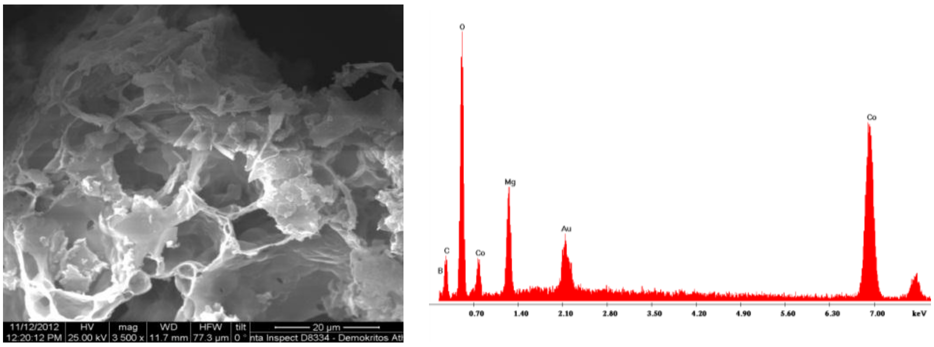


Figure 1:SEM analysis of Co-Mg-B-O based catalyst.

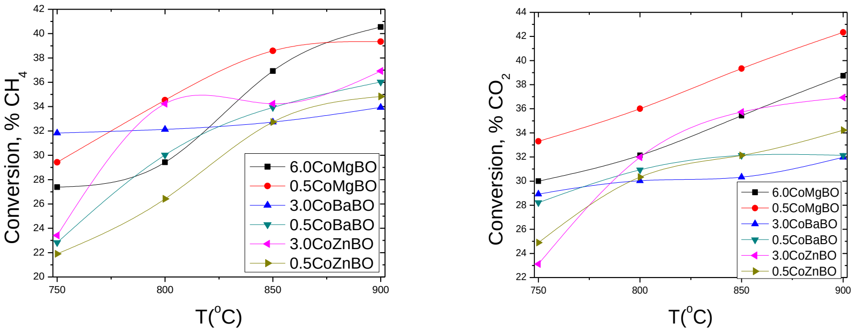


Figure 2: Conversion of CH_4 and CO_2 by SCS cobalt catalysts

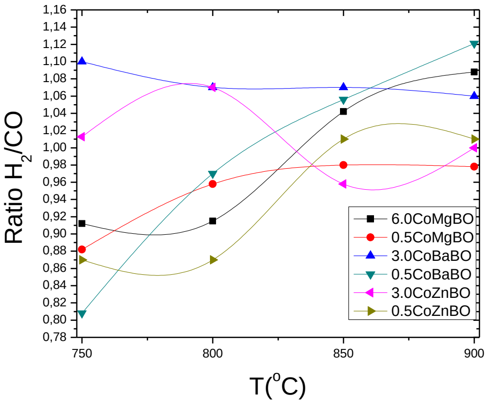
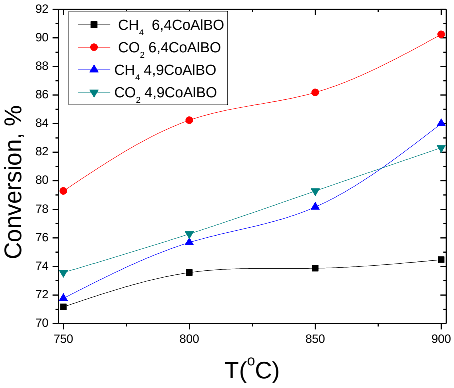


Figure 3: Ratio H_2/CO by SCS catalysts in the systems Co-Al-B-O and Co-Zn-B-O



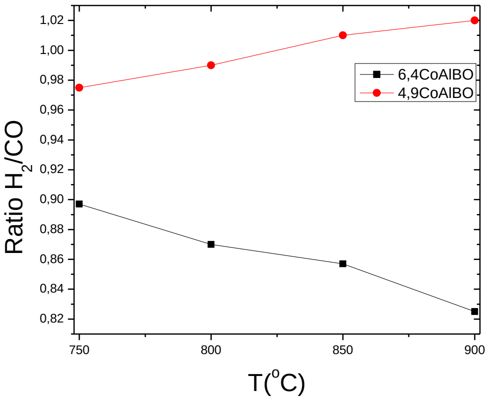


Figure 4: Conversion of CH_4 and CO_2, Ratio H_2/CO by the best SHS Co-Al-B-O catalyst.

CATALYSTS FOR DIESEL SOOT OXIDATION PREPARED BY SOLUTION COMBUSTION SYNTHESIS

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The number of diesel vehicles is continuously increasing due to both the good performance of modern diesel engine and their low fuel consumption. However, diesel emissions – in particular soot- are a known danger and various solutions have been proposed to reduce soot emissions. The most promising is soot capture and subsequent removal by catalytic oxidation [1]. In the first stage, the carbonaceous particles are separated from the gas phase by mechanical filtration using a diesel particulate filter, followed by their combustion inside the filter. However, diesel soot combustion is known to be difficult to achieve satisfactorily, since this material burns at about 550–600 °C in oxygen, while diesel exhaust gases are generally at 200 to 400 °C. Therefore, catalytic soot oxidation is necessary [2].

A soot oxidation catalyst usually combines highly active metals or metal oxides with supports, including zeolites and metal oxides. A variety of catalysts have been examined for diesel soot oxidation including Pt, molten salts [3], perovskites [4], zeolites [5] and different metal oxides [6-8] including PbO_x/CoO_x [9], $CsNO_3/ZrO_2$ [10], Mo/Al_2O_3 [11], MnO_x [12] and CeO_2 [13]. However, most of the commercial oxidation catalysts are based on the very expensive Pt or Pd. In many cases, the catalytic activity of the support is crucial [14]. Van Doorn et al. [15] studied several metal oxides on various supports and concluded that Al_2O_3 and SiO_2 had no catalytic effect, while TiO_2 and ZrO_2 had moderate activity, and CeO_2, La_2O_3, and V_2O_5 exhibited substantial activity for soot combustion. Peralta et al. [16] suggested that K in K/CeO_2 catalyst may act to form a carbonate-type intermediate with partially oxidized soot. These studies indicated that catalysts containing alkali metals, such as K, show considerable activity for diesel soot combustion [17-20] which is also important in view of economic and environmental concerns [21].

In the present work, a range of catalysts was synthesised by Solution Combustion (SCS) from manganese, cerium and copper nitrates, potassium dichromate, chromium (VI) oxide and urea as reducer at pre-heating temperatures 500°C. Properties measured include microstructural morphology (SEM, EDAX), atomic structure (XRD), porosity and surface area. Catalytic oxidation of diesel soot was studied in air in a reactor using a mixture of 25wt% soot + and 75wt% powdered catalyst (<20μm) with air flow of about 1l/min and a heating rate of about 10°C/min. The results show that the temperature at which combustion initiates depends on composition of catalyst. Catalysts based on $Cu(NO_3)_2$ - $K_2Cr_2O_7$ (or CrO_3) in urea gave very promising results (figure.1). Remarkably, the system containing 10% CrO_3 gave catalytic oxidation at a temperature of only 415°C which is as much as 215°C lower than the combustion temperature of the same diesel without any catalysts (640°C).

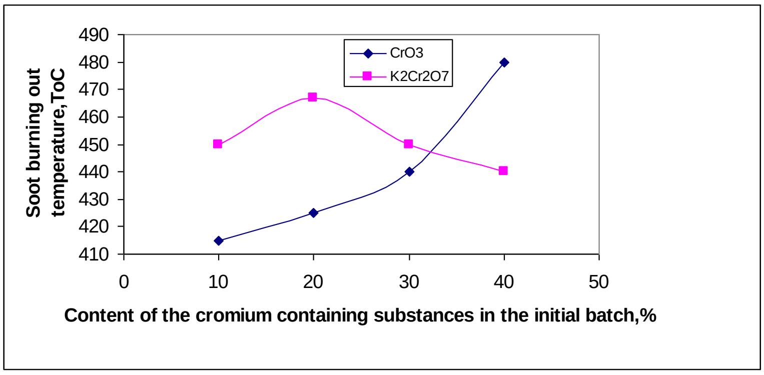

Fig.1 Dependence of soot burning out temperature from the chromium content in the initial batch $Cu(NO_3)_2$ - $K_2Cr_2O_7$ (or CrO_3) in urea

Catalysts on the basis of Mn-Ce-O also were studied and were found to display reduced activity than the Cu-Cr-O catalysts. The work is continuing with other types of diesel soot.

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REGULARITY OF COLOUR FORMATION IN COBALT PIGMENTS PRODUCED BY SOLUTION COMBUSTION SYNTHESIS

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Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nano-structured materials. The process involves a self-sustaining reaction in a homogeneous aqueous solution of oxidizers and fuels [1]. Depending on the type of the precursors and on the process conditions used, SCS occurs either in volume or in the layer-by-layer propagating combustion mode. SCS not only yields nano-structured materials of high purity, but also allows uniform doping of trace amounts of rare-earth ions in a single step, something particularly well suited for the synthesis of oxide pigments such as alumina, aluminates, silicates, borates, zirconia and zircons doped with transition metal or rare-earth ions [2]. Cobalt pigments are of significant importance in ceramic industry due to their large variety of colours, their unique properties and their stability under chemical, thermal, and reducing conditions. Colours range from blue, green to pink depending upon the host lattice and co-ordination geometry. Tetrahedral compounds are blue while octahedral ones are pink to violet.

Cobalt pigments on the basis of nano-structured oxides and spinels were synthesized by the combustion of aqueous solutions of stoichiometric and non-stoichiometric amounts of the metal nitrates $Co(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$, $Zn(NO_3)_2$, $Bi(NO_3)_2$, $Ba(NO_3)_2$, $Ca(NO_3)_2$ using urea as a reducer. The synthesis was carried out in a preheated furnace at 350^oC – 600^oC and the products were homogeneously coloured pigments. Figure 1 shows a typical SEM of a SCS pigment of initial batch $Ba(NO_3)_2$, $Co(NO_3)_2$, H_3BO_3 and urea. EDX analysis confirms the presence of Ba, Co and O, supported by XRD where $BaCoO_2$ and CoB_2O_4 were identified. Various ratios of those phases in the products gave many shades of blue, red, purple and violet.

One way of characterising the pigment colour is by assigning the characteristic “a” meaning “more red” and “b” meaning “more blue”. The mixture of those 2 characteristics gives purple of violet. Interestingly, these two parameters were found to correlate well with the shift in atomic lattice spacing, as measured by XRD, as shown in Figure 2.

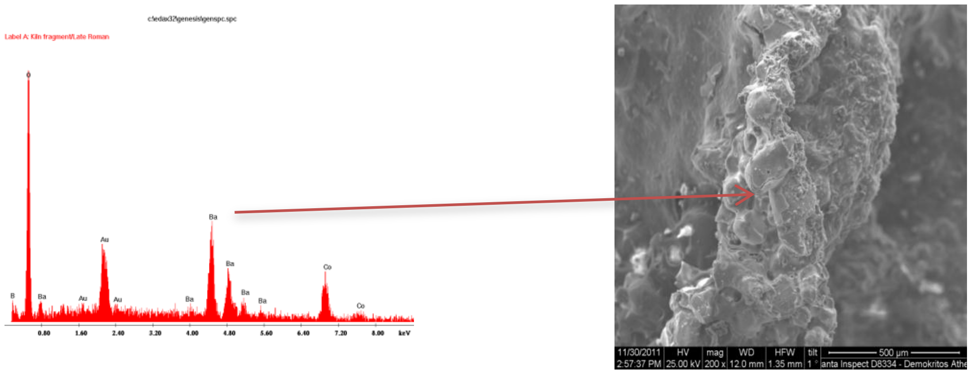

Figure 1. Typical microstructure of a SCS pigment in the system Ba-Co-O

Colour spectrum measurements show that there exists a minimum (figure 3) on the curve of crystal lattice spacing vs concentration of cobalt nitrate composition of the initial SHS charge which can be explained by the fact that at low concentrations (up to about 20%, the stoichiometric ratio of H3BO3 and cobalt nitrate for the spinel) B^{3+} (ionic radius 0.23) replaces Co^{2+} (ionic radius 0.72) which leads to a decrease in crystal lattice of spinel CoB_2O_4. On the other hand, at 20-70% of cobalt nitrate in the SHS charge, Co^{2+} replace B^{3+} and this leads to increasing of crystal lattice spacing.

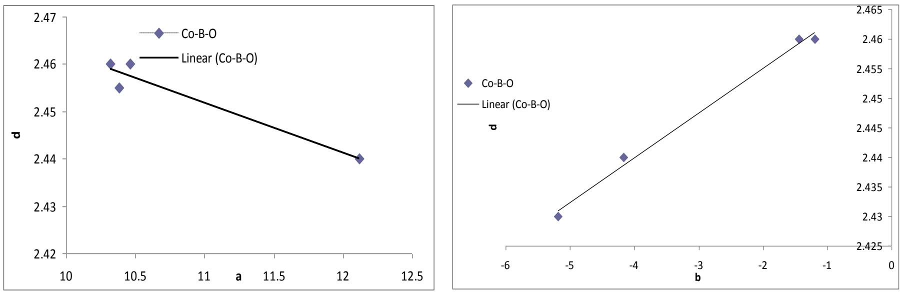

Fig.2 Dependence of a and b colour characteristics upon crystal lattice spacing in the CoB_2O_4 spinel pigment

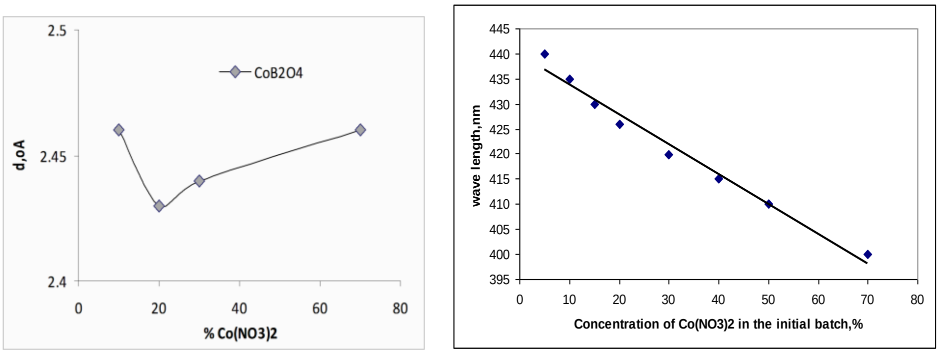

Fig.3. Dependence of crystal lattice spacing and dominant colour wavelength on the concentration of $Co(NO_3)_2$ in the initial SHS charge.

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OBTAINING OF MINERAL-LIKE CERAMICS BY SHS COMPACTION FOR HLWs IMMOBILIZATION.

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Neutralization of high-level radioactive wastes (HLWs), their safe storage, and burial is a serious task of modern science and technology. Normally, HLWs are being immobilized by vitrification into various phosphate and borosilicate glasses. However the above glasses suffer from their low thermodynamic stability and hydrolytic resistance, especially at elevated temperatures. Alternative approach is the use of synthetic mineral-like ceramics exhibiting high chemical, thermal, and radiation resistance. Previously, we suggested producing mineral-like ceramics based on perovskite, zirconolite, and pollucite for immobilization of the entire set of HLWs by forced SHS compaction [1, 2]. Thus prepared host materials exhibited low porosity, reliable immobilization of HLWs, and good mechanical strength.

Earlier it was suggested incorporating actinoides into mineral-like $Y_2Ti_20_7$ matrices with a pyrochlore-type structure. SHS-produced $Y_2Ti_2O_7$ matrices showed good immobilization behavior, but insufficient radiation stability. The radiation and hydrolytic stabilities of pyrochlore-type matrices were found to grow sufficiently in the presence of embedded zirconium. In some cases when pyrochlore is obtained by the SHS method, metal zirconium is proposed to be used. This paper offers another solution to enrich pyrochlore structure with zirconium.

Since actinides can also be incorporated into other mineral-like structures such as zirconolite $CaZrTi_2O_7$, we attempted to synthesize the ceramics containing both $Y_2Ti_2O_7$ and $CaZrTi_2O_7$. With an increasing amount of embedded Zr, such mixed pyrochlore-rich ceramics could be expected to exhibit good hydrolytic stability, high radiation resistance, and a higher amount of incorporated Ca^{2+} ions. Due to Ca^{2+} the number of incorporated tetravalent actinides can be increased. The balance by the main matrix components is achieved automatically. We used cheap zirconium dioxide ZrO_2 in our work.

This work was aimed at SHS production of ceramic matrices for immobilization of high-level actinide wastes formed at fractionation of HLW and in exhausted weapons-grade plutonium.

Low-porosity compacts of mineral-like ceramics were prepared by forced SHS compaction. Cold-pressed cylindrical compacts about 100 g in weight and 48 mm in diameter were placed into a container filled with sand and ignited from the bottom. A still hot combustion product was squeezed with an applied force of 2.4 tons.

Synthesis of $Y_2Ti_2O_7$ and $CaZrTi_2O_7$ ceramics was carried out by the reactions:

$$6Ti + 4MoO_3 + 3Y_2O_3 \rightarrow 3Y_2Ti_2O_7 + 4Mo. \qquad (1)$$

$$6Ti + 4MoO_3 + 3ZrO_2 + 3CaO \rightarrow 3CaZrTi_2O_7 + 4Mo. \qquad (2)$$

The mixture modeling real HLWs contained the following oxides (wt %): CeO_2 25, La_2O_3 46.1, Gd_2O_3 4.6, ZrO_2 19.6, MnO_2 3.8, and Fe_2O_3 0.9. The amount of the added mixture was 11 wt %.

We prepared three different green mixtures by taking starting reagents of reactions (1) and (2). When (reaction1):(reaction2) = 2:1, the combustion resulted in obtaining good ceramics based on $Y_2Ti_2O_7$ and Mo. Soldered large $Y_2Ti_2O_7$ fragments are seen to be nearly nonporous in their bulk; the porosity is seen to grow at the interface between the crystallites. Matrix blocks of cast $Y_2Ti_2O_7$ crystallites contained Mo inclusions. Pyrochlore is seen to form rounded crystals with circular structure. Brighter areas may have the following composition: $Ca_{1,1}Gd_{0,1}La_{0,5}Ce_{0,4}Y_{15,8}Ti_{12,3}Zr_{4,0}Mo_{1,1}Mn_{0,1}Fe_{0,0}O_{64,6,}$ while darker ones - $Ca_{2,0}Gd_{0,3}La_{1,0}Ce_{0,5}Y_{12,5}Ti_{14,5}Zr_{3,6}Mo_{1,0}Mn_{0,2}Fe_{0,2}O_{64,2}$. Therefore we managed to synthesize ceramics based on pyrochlore of $Y_2Ti_2O_7$ composition in which Zr was substituted for 25 % of Ti atoms.

Dense cylindrical samples based on $Y_2Ti_2O_7$ ceramics with a pyrochlore-type structure were produced by forced SHS compaction. Synthesized materials were found to exhibit high hydrolytic stability ($R_n^{\mathbf{Y, La, Ce}} < 10^{-8} g \cdot cm^{-2} d^{-1}$; [Ca], [Ti] - below the detection limit**)** and mechanical strength (above 250 MPa). The open porosity was 2–4 %.

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OBTAINING OF COMPOSITE POWDERS BASED ON Si_3N_4 AT SILICON COMBUSTION IN NITROGEN

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Synthesis of silicon nitride Si_3N_4 by combustion of silicon powder in nitrogen is known to require dilution of starting Si powder with a refractory compound. Otherwise, the yield of Si_3N_4 is normally low. Due to a high combustion temperature Tc attained in the rapidly propagating combustion wave, Si undergoes melting and thus forms an obstacle for penetration of nitrogen gas into the reaction zone. In order to suppress the coagulation of melted Si particles, a starting Si powder is diluted, up to 30–70wt%, with the end product (Si_3N_4). Analysis of the literature and preliminary experiments allowed us to suppose that there exists an alternative approach to the SHS of Si_3N_4: instead of strong dilution with final product, we are going to suggest low dilution with organic compounds. It was shown previously [1, 2] that introduction of organic dopants to Si powders intensified their combustion in nitrogen gas without any significant influence on the combustion temperature. Addition of organic compounds improved the extent of conversion. Two types of crystals of SiC and α-Si_3N_4 were formed in the combustion wave at the temperature lower than the melting point of silicon; they created a protective coating preventing their coagulation.

The paper investigates the terms for obtaining submicron and nano-sized composite powders based on Si_3N_4.

The interest to interaction in the system Si-N-organic compound is explained by some non-metals contained in the system and with which silicon can form refractory compounds under the terms of SHS. So there exists the possibility of one-stage obtaining of composite powders based Si_3N_4 and containing SiC and Si_2N_2O. Si_3N_4-based composites are widely used due to their excellent mechanical and chemical characteristics and high corrosion resistance to aggressive metal melts.

Combustion of silicon powders containing organic additives in nitrogen was performed under nitrogen pressures $P(N_2)$ ranging between 20 and 150 atm. Si powders of d<50μm were used in the experiments. Organic and inorganic additives (D) of different composition were introduced. Powders were mixed in a porcelain mortar and then charged (in the amount of 40–50 g) into a quartz tube of 35 mm in diameter. Combustion of thus prepared samples of bulk density was carried out in a constant-pressure bomb preliminary purged with nitrogen gas. Vertically placed samples were ignited from the top with a tungsten coil via a thin layer of Ti powder (about 1 g in weight). The combustion temperature was determined (with an accuracy of ±50 K) by thermoelectric method using W–Re thermocouples (VR-5/20) of 100 or 200 μm in diameter placed at the sample center.

Combustion of silicon powders containing organic dopants in nitrogen gas under pressure was found to yield a mixture of α-Si_3N_4, β-Si_3N_4, SiC and Si_2N_2O. The ratio of phases depends on composition and concentration of the additive and synthesis terms. Introduction of organic compounds into the green mixture enables silicon migration into the gas phase where some reactions take place and form nuclei of crystal phases which are condensed and result in a solid product as ultradispersed and nano-sized particles forming slightly bound agglomerates. The additive type was also found to affect the morphology and final particle size.

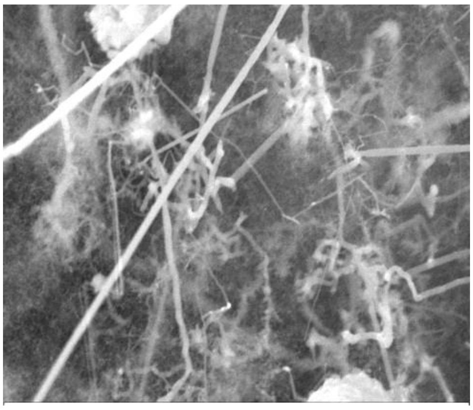

Fig.1

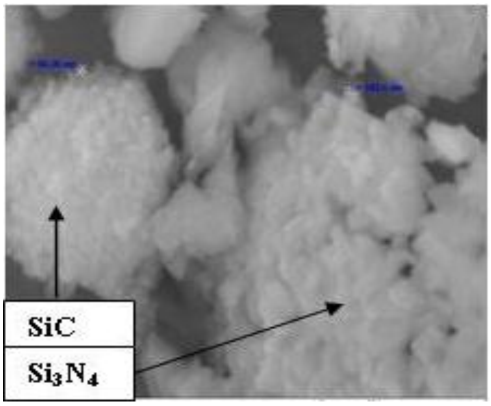

Fig.2

Fig.1 shows SiC crystals as long cobweb-like threads gathered in a ball. In Fig.2 a spherical globule is shown; it consists of SiC crystals as rounded grains of 90 nm in diameter. In Fig.2 slightly drawn Si_3N_4 of 200 nm in size are seen. The crystals were obtained with introduction of $C_{24}H_{20}Si$ (Fig.1) and C_8H_{10} (Fig.2) into the initial mixture.

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SYNTHESIS OF SILICON OXYNITRIDE BY COMBUSTION OF SILICON-CONTAINING COMPOUNDS IN THE COMPRESSED AIR

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Due to its excellent mechanical and dielectric properties at elevated temperatures, silicon oxynitride Si_2N_2O is highly promising for use as a structural ceramic material. Compared to silicon nitride, oxynitride exhibits higher heat resistance in oxidative media [1]. Si_2N_2O-based ceramics can be produced by the methods of powder metallurgy, such as reactive sintering [2], hot isostatic pressing [3, 4], and spark plasma sintering [5]. Silicon oxynitride (in combination with MgO, Al_2O_3, Y_2O_3) is also known as a good sintering agent for silicon nitride and silicon carbide.

Refractory inorganic compounds (including silicon nitride, silicon carbide, and SiAlON) can also be produced by SHS. The synthesis of silicon oxynitride from a mixture of Si, SiO_2, and Si_2N_2O (as an additive) by combustion in nitrogen gas at $P(N_2) = 3$ MPa was reported in [5] while that from a mixture of Si and SiO_2 (crystalline, amorphous) at $P(N_2) = 10$ MPa, in [6]. In work [7] was investigated the synthesis of silicon oxynitride Si_2N_2O from a mixture of Si, SiO_2, and Si_3N_4 by infiltration-mediated combustion in nitrogen gas for $P(N_2) = 4$–14 MPa.

In this work, we investigated the synthesis of silicon oxynitride Si_2N_2O from silicon-containing mixtures by infiltration-mediated combustion in air atmosphere under pressure 4 MPa. In this case, during the burning process silicon interacts with components of the air with the formation of SiO_2 and Si_3N_4, which then react with each other to form Si_2N_2O. Silicon containing mixtures were prepared from powders of Si to SiO_2, Si_3N_4, Si_2N_2O (the powder of silicon oxynitride was prepared as described in work [7]). The chemical/phase compositions of product and process parameters (temperature and burning velocity) were studied upon variation in charge composition.

It was shown:

- to increase the amount of target oxynitride in the combustion products it is necessary to introduce the silicon oxide as an additional source of oxygen in the green mixture;
- to prevent coagulation of melted silicon and silicon oxide particles in the combustion wave it is necessary to introduce a refractory diluents in the initial mixture, for this purpose silicon oxynitride is the best candidate;

- besides the role of anticoagulant the added oxynitride acted as crystallization centers for the newly formed phase Si_2N_2O, as the result the more homogeneous product with a high content of oxynitride phase was obtained.

ACKNOWLEDGMENTS

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THERMAL CONDUCTIVITY OF AlN SHS-DERIVED POLYCRYSTALS

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Aluminum nitride is considered as versatile but challenging material for structural and functional application because very high thermal conductivity and piezoelectric feature. In the form of monocrystal or polycrystals AlN is used in electronic devices thus squeeze out conventional materials like SiO_2, Al_2O_3 or BeO which is harmful for human body. Aluminium nitride is applied for sensors and heat exchanger to improve their sensitivity and efficiency. Due to the thermal properties, it is also used in the arms industry as the parts of a high-power and high resolution radars. The thermal conductivity (λ) of polycrystalline AlN mainly depends on the level of oxygen content dissolved in crystallographic structure, microstructure appearance and nature of points and linear defects. These factors can radically reduced λ factor from 320 W/mK to 70 W/mK unless they are controlled well at every stage of procedure.

Preparation of dense AlN polycrystals requires addition of liquid phases for sintering. Commercially, MgO, CaO, or rear earth metal oxides are used but most promising addition is Y_2O_3 resulting the highest values of thermal conductivity. The AlN grains are usually covered by thin layer of aluminum oxide therefore during sintering yttria forms with alumina several compounds e.g. YAP ($YAlO_3$), YAG ($Y_3Al_5O_{12}$), and YAM ($Y_4Al_2O_9$). The garnets formation promotes densification process but additionally leads to the removal of oxygen from AlN structure at temperatures above 1750^oC. This is related to improving thermal conductivity and density of polycrystals [1,2].

The aluminum nitride polycrystals were prepared from SHS derived powders. Starting mixtures were composed with addition of 3,0 wt. %.; 5,0 wt. % and 10 wt. % of yttrium oxide and next sintered. Relative density of each polycrystals was measured by hydrostatic method and estimated at higher than 97%. The XRD method was used for phase detection of samples after heat treatment. Two phases were detected in X-ray diffraction patterns namely: AlN and yttria garnets located at grains boundaries. All samples were polished and next mechano-chemically etched to reveal microstructure details. Microstructure examination supported by computer add analysis was performed by scanning electron microscope SEM - Nova NANOSEM 200 and energy dispersive spectrometry EDS. The grain size of the sintered material was estimated by computer add analysis - Aphelion Image Processing programme. The results were correlated with thermal conductivity of the samples carried out by the laser pulse method - LFA 427 apparatus. The influence of the sintering conditions and yttria additive content on thermal conductivity and microstructure appearance of aluminum nitride polycrystals was clearly showed.

The LFA measured values of specific heat, thermal diffusivity and thermal conductivity of polycrystals were collected carefully. The highest λ factor was achieved for samples with addition of 5,0 wt. % of yttria. All polycrystals posed rather good thermal conductivity ranging from 125[W/mK] to 240[W/mK] at 25^{o}C.

For the obtained sinters thermal expansion coefficients (CTE) were measured. The CTE values, for the temperature range 40°C-600°C, are estimated to $5{,}72\bullet10^{-6}$ [1/^{o}C], $5.41\bullet10^{-6}$ [1/^{o}C] and 5.54•10-6 [1/^{o}C] with addition of 3,0 wt. %, 5,0% wt. and 10 wt. % Y_2O_3 respectively. The various addition of sintering aids did not influence significantly on thermal expansion of aluminum nitride.

The microstructure appearance of AlN polycrystals showed very similar shapes of grains for each content of yttria. To calculate grain size distribution the images were binarized and next examined by computer add analysis. The 40% of grain population had an average grain size estimated to 1.0 um. The difference in thermal conductivity of the samples was explained by specific YAG, YAM or YAP formation. This reaction can reduce the oxygen content inside AlN grains and this mechanism was showed in details.

ACKNOWLEDGMENT

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FORMATION OF ALUMINUM-BASED INTERMETALLIC COMPOUNDS WITH EARLY TRANSITION METALS

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Equiatomic mixtures of Al and the early transition metal powders in Groups IV and V (i.e., Ti, Zr, and Hf; and V, Nb, and Ta) were subjected to high energy mechanical alloying. Blends were subjected to microscopy and differential thermal analysis to systematically investigate the efficiency of conversion from reactants to products. Each of the Al-X blends was created by mechanically milling pure elemental powders with 1.5 weight-percent stearic acid to prevent cold welding to the milling vial's internal walls during the blending process. The as-milled powders were analyzed via scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction analysis (XRD), and differential scanning calorimetry (DSC) to determine the effect of milling time on the total heat released. The DSC analysis was performed to measure and determine the total energy released from the mixtures while being heated to 1000 °C at 10 K/min. The analyses were performed prior and after DSC to compare the morphologies of the reactants and products, as well as to determine the bulk phases present in the product as they relate to the equilibrium phase diagram for that particular mixture.

Results showed that with increasing milling time the as-milled microstructure was refined. Scanning electron microscopy of powders milled at 3 and 15 minutes, respectively, showed the breakdown and evolution of characteristic microstructures in the various binary mixtures. As determined by the relative hardness of the elemental constituents in each binary mixture, the microstructures changed from and initially equiaxed to an equiaxed or laminar morphology. The decrease in grain size was also reflected in the broadening and shifting of the Bragg x-ray peaks and the appearance of intermetallic phases. Differential scanning calorimetry of the powders, milled to increasing times, also indicated a shift in the onset and end temperatures, as well as the shape of the exo- or endothermic events. Particularly, the milling was found to affect the spatial distribution and interspacing of the constituent elements, which, in turn, resulted in a significant change of the nature of the formation of the intermetallic species. The specific and general characteristics of these mixtures are discussed.

LARGE SCALE SYNTHESIS OF SiC NANOSTRUCTURE BY COMBUSTION

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SiC Nanostructures with a size of about 50 nm in the form of nanofibers whiskers and amorphous nanofilament were synthesized from Si/polytetrafluoroethylene (PTFE) mixtures. The obtained products were characterized by FESEM, HRTEM (together with electron diffraction) and XRD.

SiC nanofibers (as the filler for polymer, ceramic, metallic and intermetallic nanocomposites) synthesis and purification has been optimized using boiling in KOH to remove un-reacted Si removaland thermal treatment in air to burn the residual elemental amorphous carbon and graphite.

The possible applications of nanocomposites based on such nanofibers would be directly linked to the remarkable mechanical, thermal and chemical properties of these (1-D) nanoparticles and, specifically, as fillers in composites.

Keywords: Nanocomposites, Nanofibers, Nanomaterials, SHS, SiC, Whiskers, Amorphous, Nanofilament, Purification.

SYNTHESIS OF METALLIC MATRIX NANOCOMPOSITES REINFORCED WITH NANOCARBON BY COMBUSTION

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Combustion synthesis in the electrothermal explosion mode can be regarded as an efficient method to obtain new nanomaterials. Different starting mixtures of magnesium powder with various carbonates (e.g. Na_2CO_3) were tried and the self-propagating reactions were carried out under both reactive (air) and neutral atmosphere (argon) with an initial pressure of 10 atm to yield novel nanomaterials. Fe, Co, Ni, Pd, Nd, Ta, Ti, Nb, W and NiO powders were used as catalysts and their synthesis and purification have been optimized. To increase the yield of the catalytic combustion, reactions in SHS mode were carried out using NaN_3, Teflon and Ferrocene $Fe(CO)_5$ as a source of catalytic metal nanoparticles. Under the applied conditions the presence of nanocrystalline MgO, NaF and NaO_2 in products, confirmed by XRD analysis even for the reaction under neutral atmosphere, points to the deep conversion of carbonates. To produce fibrous products the Na_2CO_3 system proved to be the most promising one (in other tested carbonate systems, except Li_2CO_3, the content of fibrous phase was insignificantly small). SEM images show the morphology of the products with some 1-D nanostructures resembling carbon nanotubes and with core-shell structures made of iron-based nanoparticles encapsulated in carbon, yielding a nanocomposite with interesting magnetic properties. Different magnetic metals (Fe, Ni, and Co) can be encapsulated in the carbon shell, graphite layers and nanofibers. After the purification procedure, we obtain core-shell or graphite layers encapsulated by metal magnetic nanoparticles without impurity (e.g. noncoated iron or carbides, amorphous carbon). The characterization techniques include the chemical analysis, HRTEM, XRD and FESEM. The VSM and Mössbauer Spectroscopy (in the case of Fe-containing samples) will be performed in the near future. A kinetic model of the formation of pharmacological systembased on a carbon ferromagnet nanocontainer is given. The obtained novel pharmacological molecular nanostructure could be injected in cancer tumor cell (prostate) after sterilization. In the near future, the nanocontainer will be heated by microwave technique at the Laboratoire Central d'Anatomie and Cytology Pathology of the CHU Annaba. The reaction will be observed in HRTEM.

Keywords: Electrothermal explosion reaction, 1-D nanostructures, Core-shell, Graphite layers; Nano container carbon ferromagnet, nanofibers, Kinetic model, Purification.

PRODUCTION TECHNOLOGY AND PROPERTIES OF PERSPECTIVE OF POWDER NANOMATERIALS

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The purpose of the consolidation of nanopowders is to achieve full density material with minimal grain growth. In addition, provision must be large enough to measure the properties of the resulting material and workmanship of a useful product. Among the main problems in the consolidation of nanopowders can distinguish agglomeration of nanopowders, their high activity (pyrophoric metal powders), the presence of impurities, grain growth, difficulties in the manufacture of long workpieces.

The purpose of pressing nanopowders is forming a high-density workpiece with small and uniform in size pores, because the density inhomogeneity pressing leads to defects in the sintered sample. In the diagrams of cold pressing of nanopowders can distinguish the stage of intense and weak seals, the first stage of slippage and rearrangement of particles, and the second - the elastic compression of the particles at the contact, plastic deformation and fracture of brittle plastic particles. Due to high friction, sliding and rearrangement of nanoparticles is limited and nanopowders are more prone to defects in pressing than conventional powders. In addition, the nanoparticles are free of dislocations, which hinders their plastic deformation, so the reduction in particle size leads to a decrease in the density of compacts with the same compaction pressure.

There is an increase in the sintering density of the porous body, caused by the transfer agent in the contact area of the particles. In addition to these mechanisms of growth of the isthmus between the large particles as the volume and grain-boundary diffusion of the interface between the particles, volume and surface diffusion from the surface of the particles, the mass transfer through the gas phase have been proposed for nanoparticles and other mechanisms: viscous flow, rotation of grains and interparticle slip.

PECULIARITIES OF COMBUSTION AND CHEMICAL REACTIONS IN SYSTEM Mo-Si-B ADVANCED FOR HEAT RESISTANCE MATERIALS PRODUCTION

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Regularities of combustion process in system Mo-Si-B and mechanism of phase and structure formation of synthesized products have been investigated. It was found the follow unusual phenomenon in the case of charge composition Mo-10at%Si-30%B. Linear rise of combustion temperature T_c (T_0) and combustion rate U_c (T_0) was observed when the initial temperature before the ignition (T_0) be limits in the range of 500-650 K. Combustion rate function U_c (T_0) decreases abrupt but combustion temperature T_c (T_0) keep increasing character when $T_0 > 650$ K. Authors proposed explanation of this phenomenon assuming that leading chemical reaction changes: parallel chemical reactions of molybdenum silicide and molybdenum boride formation at T_0 = 500-650 K becomes sequential. Main phases in a final product are Mo_5SiB_2 and MoB.

T_c и U_c rise in the range T_0 = 298 - 550 K in the case of charge composition Mo-40at%Si-20%B. U_c rise continuously, but T_c about 2190 K practically do not changes when T_0 =550-770 K. This effect can be attributed by $MoSi_2$ -MoB eutectic melting (T_{melt} ~ 2100 K), this eutectic forms at the some elements and phases concentration. Main phases in a final product are $MoSi_2$ and MoB. Experiments on combustion front quenching in a copper wedge and dynamic XRD analyses allows to establish the follow stages of chemical transformations in combustion wave of this composition. First, molybdenum silicide appears as a result of Mo and Si interaction according to the mechanism proposed in [1]: melting Si; spreading the melt on Mo particles; interaction with forming Mo_3Si as film on the particle; reaction diffusion through the product layer and appearance of $MoSi_2$ phase. Second stage, appearance of MoB phase as a result of Mo and B interaction, was fixed through 2 sec after the first stage. This interaction proceeds at the presence of oxygen impurity in green mixture according to the mechanism proposed in [2, 3]: mass transport of molybdenum to boron surface via the gas phase due to the presence of some amount of MoO_3, adsorption and chemical reaction $3B(s) + MoO_3(g) \rightarrow MoB(s) + B_2O_3$ (melt) in parallel with gasless Mo(s) + B(s) reaction; or the mechanism proposed in [4]: chemical reaction $2B_2O_3$ (melt) + $2B \rightarrow 3B_2O_2$ (g) due to the presence of some amount B_2O_3, further mass transport of boron to molybdenum surface via the gas phase, adsorption and chemical reaction $2Mo(s) + 3B_2O_2(g) \rightarrow 2MoB(s) + 2B_2O_3$ (melt) in parallel with gasless Mo(s) + B(s) reaction. Probably both mechanisms work simultaneously. Only two phases ($MoSi_2$ and MoB) were observed on the final product, intensities of these lines increase during the cooling.

Classical linear dependences of $T_c(T_0)$ and $U_c(T_0)$ in the range T_0=540-760 K for case of initial mixture composition calculated on 100% Mo_5SiB_2 (T_2-phase) were plotted, showing that there are no changing the mechanism and stages of chemical reactions of molybdenum silicide and boride formation.

Mechanical activation (MA) of charges Mo-10at%Si-30%B, Mo-40at%Si-20%B and calculated on 100% Mo_5SiB_2 was applied and optimal regimes were found with purpose to obtain an ignition temperature before 293 K. Classical linear character of T_c, $U_c(T_0)$ dependences in range T_0=293-650 K was established. Combustion mechanism do not changed for all this range of T_0. But transformation from layer by layer mode to thermal explosion was fixed in the case of MA mixtures when $T_0 > 650$ K.

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NOVEL SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) OF β-SiAlON FINE POWDERS

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β-SiAlON, with the general formula $Si_{6-z}Al_zO_zN_{8-z}$ ($0 < z \leq 4.2$) has a hexagonal crystal structure that is derived from the β-Si_3N_4 structure by the equivalent substitution of Si–N with Al–O. β-SiAlON is an attractive material for applications in high-temperature engineering systems due to its excellent properties such as high strength, good thermal and chemical stability. [1–3] In conventional SHS for preparing β-SiAlON, the purity of the product is always low due to the existence of unreacted Si, which is caused by its melting and subsequent agglomeration with high reaction temperature. To obtain single-phase β-SiAlON products, a large amount of β-SiAlON diluent was required. [4–6] In this work, we aimed to synthesize β-SiAlONs with high purity by using a small amount of NaCl as a diluent, which can effectively absorb the reaction heat by its latent heat of melting and evaporation.

The raw materials of Si, Al, and SiO_2 were mixed according to a stoichiometric ratio to synthesize β-$Si_{6-z}Al_zO_zN_{8-z}$ with z-values that varied from 0.25 to 1 with different amounts of NaCl as the diluent. The reaction can be expressed by the following equation:

$$(6-1.5z)\mathrm{Si} + z\mathrm{Al} + 0.5z\mathrm{SiO}_2 + (4-0.5z)\mathrm{N}_2 \rightarrow \beta-\mathrm{Si}_{6\text{-}z}\mathrm{Al}_z\mathrm{O}_z\mathrm{N}_{8\text{-}z} \qquad (1)$$

The starting materials were mechanically activated by a planetary ball milling for 15 min. The activated mixture was charged into a cylindrical carbon crucible with vents, through which the nitrogen gas was introduced. The ignition agent of the Al powders was placed on top of the mixture. The combustion reaction was carried out at a nitrogen pressure of 1 MPa by passing a current of 60 A for 10 s through a carbon foil. XRD, SEM were used for the analysis of phase composition and microscopic morphology, respectively.

β-SiAlONs were successfully synthesized with different content of NaCl as the diluent. Fig. 1 shows the XRD patterns of the synthesized β-SiAlONs. Single-phase product is obtained at all z values. Additionally, the amount of NaCl added is dependent on z-value; higher z-values requires more NaCl due to more amount of heat released from Al in the raw materials. The effect of NaCl during CS can be explained as follows: because of melting or evaporation, it absorbs the heat released during the reaction and lowers the combustion temperature. As a result, the melting and agglomeration of Si particles in the raw materials are greatly reduced, that enhanced the infiltration of N_2. However, when greater amounts of NaCl were added, the combustion reaction could not be maintained due to the insufficient heat released from the raw materials; with a lesser amount of NaCl and a higher reaction temperature, Si particles were fused and subsequently hardened under the fast reaction, which caused Si to remain in the product.

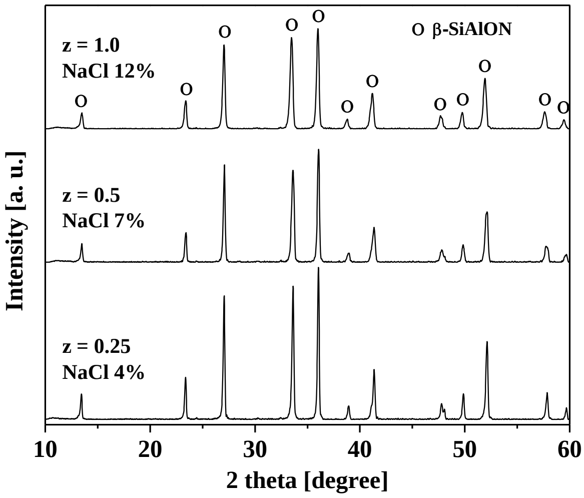

Fig. 1 XRD patterns for the combustion-synthesized β -SiAlON

SEM images indicate the grain shapes of the β-SiAlON varied with the z-value: from rod-like particles tended to become rounder as z value increasing, when the z-value increased to 1, the particles were quite uniform in size and shape, and they appeared round and equiaxed with diameters of approximately 0.6 μm. These changes in morphology and grain size were attributed to the variation in the composition of β-SiAlONs and the addition of NaCl. During the reaction, the liquid NaCl acted as a diffusion barrier between the β-SiAlON particles, which restricted the crystal growth and agglomeration of β-SiAlON. Therefore, the products exhibit well-dispersed fine particles.

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INNOVATIVE COMBINED METHOD FOR OBTAINING NANO STRUCTURE POWDERS AND COMPACTED MANUFACTURES

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Scientific level of modern high-technologies should provide maximal economy of energy-carriers, labor and material resources. At the same time, beyond materials science researchers` technological abilities remains a group of ceramic and metal-ceramic (nano structural, among them) compositions, the synthesis of which is unavailable by means of standard, so-called "ceramic" technologies, or it is too expensive, while to obtain them by modern technology like Self-propagating High-temperature Synthesis (SHS) is an expensive process due to low exothermicity of these systems. To resolve this problem the authors of the study present a two-step energy- and resource-saving innovation technology for obtaining nano powders and composites. The first step is electric-resonance irradiation (ERI) and the second component is the Self-propagating High-temperature Synthesis (SHS).

By the proposed innovative technology, with practically zero energy inputs, only by maximal realization of the system chemical energy is implemented the synthesis of new, high-quality nano powders and composites.

To obtain them by standard ceramic technologies is practically impossible or is related to high material expenses. This considerably broadens the materials nomenclature of composite nano powders and massive/solid composites (among them, low-exothermal) obtained hitherto by standard ceramic technologies.

For solving the problem basic innovative approach is creation and construction of electric-resonance beam synthesizer, original device “ER-1-S”, which is main novelty of scientific work, i.e. original technical and technological approach, which against the background of practically zero expenses provides possibility for obtaining high-quality nano materials.

The priority of ERD/SHS combined technology against currently existing technological level can comprise following components:

ERD/SHS technology allows reduction of manufactured produce prime cost by 30-50% and increase of its competitiveness in such an energy-holding sphere of so-called “high technologies” as manufacturing of ceramic and inter-metal nano powders is. Correspondingly, possibility of obtaining high-quality and significantly lower-cost, in comparison with the analogues, nano materials (B_4C; TiB_2; WC; TiC, etc., SHS-compacted compositions: $B_4C{\cdot}NiAl$; $B_4C{\cdot}TiB_2{\cdot}Al_2O_3$, TiB_2-Al, etc.) sharply increase investment attractiveness of the technology.

Together with energy-efficiency the technology:

- allows to promptly alter the composition of nano powders and massive composites in accord with the market state, which is imposible in case of other technologies;
- does not demand expensive high-temperature equipment, large labor and material resources and area.

High quality and technical level of the produce are due to high purity of the synthesized nano powders.

- In the combined technological scheme the SHS function is a sharp decrease of power consumption (40-100 times) and ahigh quality guarantee characteristic for the SHS-produce;

- ERI function is heating of initial SHS-mixture up to 3000°C with practically zero power consumption and provision of possibilities for obtaining unique-combination materials and manufactures. By means of electric-resonance irradiation sharply is increased the heat-capacity of the reaction mixtures and removed are the limits of energetic and technical character of obtaining SHS-thermal combustión regime of low-energy systems.

The objective of the project is to organize the synthesis of a low-efficiency, but high-cost produce, which is imposible to manufacture due to serious problems of ceramic technologies, despite current demand for nano composites. Considerable part of these problems is removed by means of the ERD/SHS technology developed by our team and the construed original equipment “ER-1-S” based on aforementioned technological approach.

The equipment “ER-1-S” provides obtaining of nano powders, as well as the massive composites synthesis.

Magnetic/resonance irradiator is a low energy consumer and does not require any auxiliary power supplier. The process is controlled. Analyses of the capacity, resistance, magnetic tensión are carried out. The cost of “ER-1-S” system is several thousands of USD, while its manufacturing floor does not exceed 1m^2.

PREPARATION OF W-Cu FUNCTIONALLY-GRADED MATERIALS BY COMBUSTION SYNTHESIS AND CENTRIFUGAL INFILTRATION

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Tungsten-cooper (W-Cu) composites combine high thermal conductivity and high electrical conductivity of copper with low thermal expansion coefficient and high erosion resistance of tungsten, which have been widely used in many fields as structural, electrical and thermal management materials [1]. W-Cu composites with various copper contents have been fabricated by different methods, such as powder metallurgy, pressure-less infiltration, plasma spray and cold spray etc [2].

In general, W-Cu composites with copper contents less than $20_{wt.}$% have been produced by the infiltration of a tungsten skeleton with copper melt.While W-Cu composites containing higher copper contents usually have been manufactured by liquid phase sintering. To reduce the mismatch in mechanical and thermal properties functionally graded material was introduced with a gradual transition of compositions and properties from one side to the other. W-Cu functionally graded material have been fabricated by methods like chemical vapor deposition, vacuum plasma spraying and multi-billet extrusion, and applied in some extreme environmental conditions, such as high voltage arc contact materials and high heat flux components for the future nuclear fusion reactor where homogeneous W-Cu composites are not suitable. However, it remains difficult to prepare full-densified and structure designed W-Cu composites because of the poor solubility of W in molten Cu at thermodynamic equilibrium. Therefore, it is still attractive to develop fast, inexpensive and simple synthetic methods for the preparation of W-Cu composite with increased density and controlled structures.

A novel method by combining combustion synthesis with centrifugal infiltration was developed for the preparation of W-Cu/Cu composite. In this technique, highly exothermic aluminothermy reactions are utilized to realize high temperature and produce molten products. At the same time a high gravity field introduced by centrifugation is applied to accelerate the separation of metallic and ceramic melts and removal of pores from the melts. Meanwhile, the separated high temperature copper melt is rapidly infiltrated into the tungsten loosen powder placed under it at the drive of high gravity. Combustion synthesis and centrifugal infiltration can offer a fast and economical way to prepare W-Cu/Cu composite in one step.

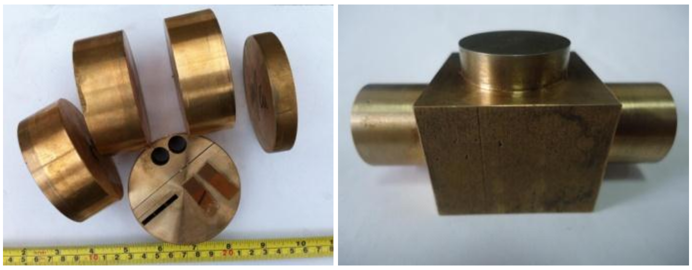

Figure 1. W-Cu materials prepared by combustion synthesis and centrifugal infiltration

This paper reports the fabrication of W-Cu/Cu composites by combustion synthesis and centrifugal infiltration. Effect of high gravity on the compositions and microstructures of W-

Cu/Cu composite are discussed. The evolution of thermal conductivity and hardness along high-gravity direction are investigated.

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COMBUSTION SYNTHESIS IN THE Ni–Al–W SYSTEM

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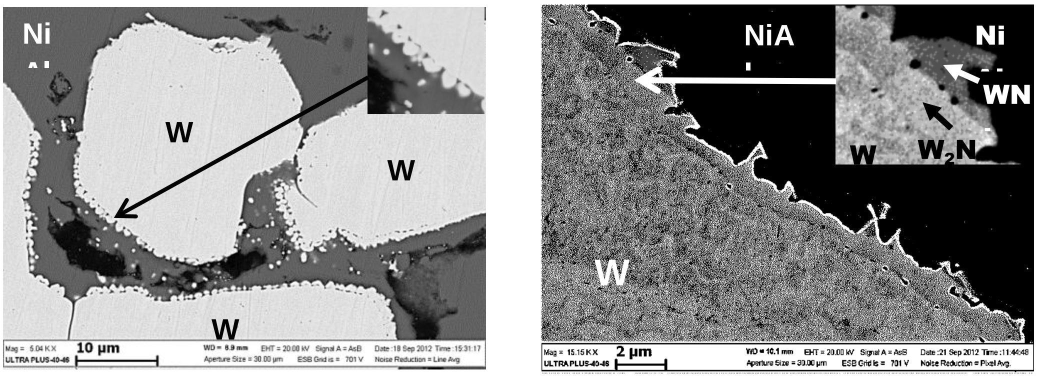
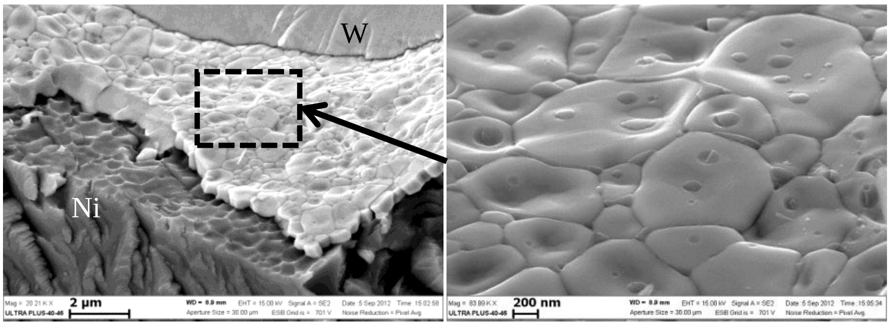
As is known, the Ni–Al–W system, eutectic NiAl–W alloys are being used to fabricate porous foils, nanofiber matrices and wires, turbine blades and similar machine parts. We report on combustion synthesis in the Ni–Al–W system with special emphasis on structural features of the process. The main phases of the combustion products are NiAl and W. The Ni_4W phase is present in trace amounts. The low content of Ni–W intermetallics can be associated with transient character of combustion due to which the duration of W contact with the Al–Ni melt. The lifetime of Ni–Al melt during combustion synthesis in the Ni–Al system is about 1–2 s. Another reason can be a relatively low combustion temperature (1700°C, or $0.43T_{\mathrm{mp}}$, where T_{mp} is the melting point of W), which imposes serious kinetic and diffusion hindrances for formation of W-rich intermetallics.



(a) (b)

Fig. 1. SEM images of SHS-produced NiAl–W composite.

SEM analysis have revealed (Fig. 1) the formation of W and NiAl phases at the intergrain boundaries by the mechanism of reactive diffusion. The reactive diffusion is seen to proceed in two stages: (a) formation of the globular seeds of a new phase (Fig. 1a) and (b) build-up of planar intermetallics layer (Fig. 1b). Judging from the shape of the intermetallics seeds, it can be assumed that the growth of Ni–W intermetallics proceeds toward NiAl alloy. As is seen in Fig. 2, the formation of intermetallics seeds takes place at the sites of W particles (Fig. 2b).



(a) (b)

Fig. 2. Fracture surface of combustion product.

The W content of the intermetallics precipitates attains a value of 70–88 wt %. The W_2Ni phase is off-stoichiometric with a narrow homogeneity range [1,2]. The mutual interdiffusion (in between 800 and 1040°C) at the interphase boundary results in formation of an intermetallics interlayer comprising of WNi and W_2Ni. This well agrees with our observations (see Fig. 2b): reactive diffusion is seen to yield an interlayer formed by one or two intermetallics, W_2Ni and WNi. For the diffusivity of W in Ni, the literature data [1,2] suggest the value of 2.5×10^{-13} m^2/s at 1500°C. This magnitude corresponds to a penetration depth of 2–3 µm at a diffusion time of 5–10 s, which is close to our experimental conditions.

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HIGH-GRAVITY COMBUSTION SYNTHESIS: A FAST WAY TO PREPARE BULK CERAMIC MATERIALS

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Bulk ceramic materials are usually fabricated by sintering from powders in contrast to metals and alloys that are generally produced by melt-casting. For the melt-casting of ceramics, two problems are involved. At first, it is difficult to prepare stable and homogeneous ceramic melts because most ceramic materials have extremely high melting points. For melting the refractory ceramic materials, conventional resistance heating is often insufficient and more powerful heating media are required, such as high-frequency induction, lamp mirror furnaces, and lasers. Another problem in the melt-casting of ceramics is exaggerated grain growth during solidification from hot melts, which will impair the mechanical strength. The grain growth can be limited by higher cooling rates, secondary phases, or multiphase eutectic ceramics.

The melt-solidification of ceramic materials can be realized by unidirectional solidification approaches, such as the Bridgman method, Czochralski method, and floating-zone method [1]. All these methods require an external heating source and complex facilities despite their difference in technical details. Recently, a furnace-free technique for melt-casting of ceramic materials has been developed, which is called high-gravity combustion synthesis [2]. In high-gravity combustion synthesis, combustion synthesis is combined with a high-gravity field, where highly-exothermic combustion reactions are used to produce ceramic melts and a high-gravity field is applied to promote the phase separation (Figure 1). In high-gravity combustion synthesis, the heat energy for melting ceramic materials is provided by combustion reactions, and external heating source is not necessary. At the same time, combustion reactions proceed very quickly and usually finish in several seconds, which is helpful to reduce the total processing time. In this way, high-gravity combustion synthesis offers an efficient way to produce bulk ceramics with a short processing time and low energy consumption. Up to now, a large variety of inorganic materials have been prepared by high-gravity combustion synthesis, including ceramics, glasses, glass-ceramics, alloys, intermetallics, and cermets.

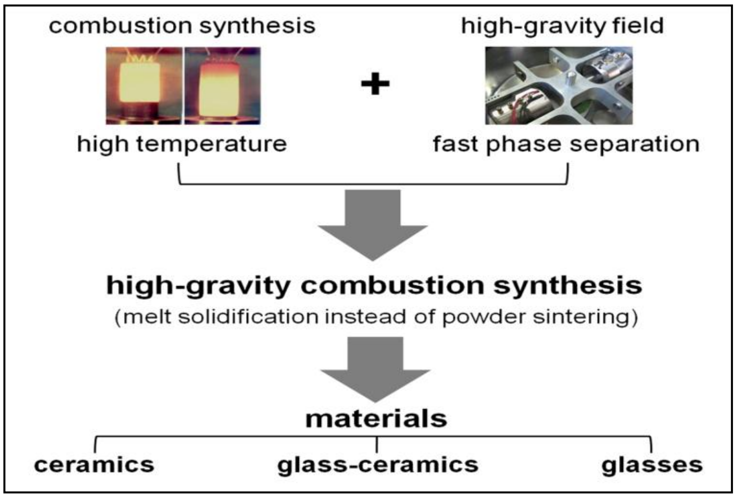

Figure 1. A schematic illustration of high-gravity combustion synthesis

In this presentation, we will give a brief review on melt-casting of ceramic materials by high-gravity combustion synthesis. Several examples of ceramic materials prepared by high-gravity combustion synthesis will be presented. The reaction mechanism in high-gravity combustion synthesis will be discussed, with an emphasis on the phase separation and microstructure evolution.

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FORMATION OF THE STRUCTURE OF SOLID PHASE PIPERAZINE MEDICINAL SALTS PRODUCED AT ORGANIC SHS

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Derivatives of organic diamine - piperazine are widely known as pharmacologically active compounds. In particular, some piperazine salts (for example, adipinate, malonate, citrate etc) display an antiparasite activity and are used as the effective and cheap medicaments for men and animal treatment [1].

On the other hand, just a solid phase medicinal forms lately become interesting for specialists, in connection with possibility of their pharmacokinetics management on the organism by purposeful formation of their microstructure [2].

In this connection, it is interesting to use a method of organic self-propagating high temperature synthesis (OSHS) proposed by us, that classified as “solid phase combustion” in the mixture of dispersed solid phase organic compounds.

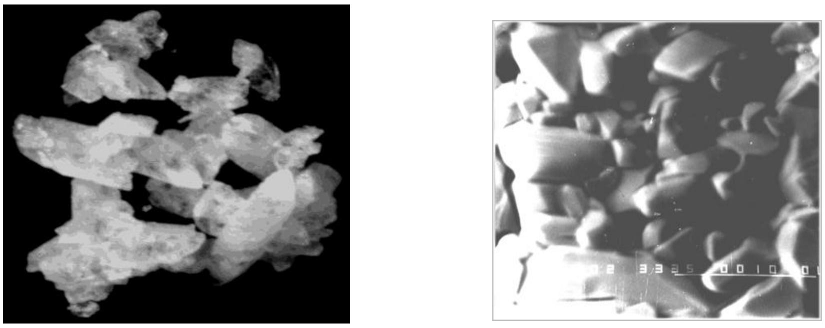
Unlike numerous traditional analogs the OSHS method is technologically simpler and is carried out without any solvents. It is energy- and resources saving method corresponding to principles of “green chemistry”. It has some other advantages and technical applications [3, 4].

For the first time we had shown that the piperazine solid phase salt with malonic acid (piperazine malonate) can be produced in an OSHS mode. Later macrokinetic features and parameters of the process were studied, as well as unique microstructure of the target product [5, 6]. However, the salt had not practical application until now.

In the present work methodology of OSHS is developed for the production of other solid phase piperazine salts (citrate, adipinate etc) having practical application. The proposed methodology includes introduction of the various modifying additives that allows produce the target compounds of appropriate quality.

The peculiarities of the salts microstructure formation were studied in connection with their synthesis conditions. It was shown that the microstructure can be regulated using the conventional SHS parameters, such as the initial temperature, composition of the green mixture, porosity, particle sizes etc.

At the figure the piperazine salt samples are presented having various structures depending on the synthesis conditions. Some important pharmacokinetical parameters of the products were determined.



a) b)

Fig 1 a) piperazine citrat, from solvent, x7; b) piperazine malonat, by OSHS, x4000.

The simplest mathematical description of the OSHS is presented, reflecting its specific features of the mass and heat transferee during the process, namely low initiation temperature (75 – 140 ^{o}C), low maximal temperature of the process (120 – 150 ^{o}C) as well as the solid- and gas-phase transport mechanisms domination in some temperature intervals.

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OPTIMIZING NANO-SCALE METAL LAMINATES FOR HEAT GENERATION

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The primary goal of this study is to fabricate nanolaminate metal particles that produce a large quantity of heat through the combination of a rapid, self-propagating formation reaction and then subsequent oxidation of the intermetallic product. The heat that is generated will be used in our final application to decompose iodine oxide and water-containing compounds for the purpose of bioagent defeat.

Our approach is to first fabricate foils by physical vapor deposition (PVD), in which chemistry and bilayer size can be finely tuned. We primarily use two-color pyrometry and bomb calorimetry to determine which chemistry produces the most heat during the combined formation and oxidation reactions in air. Al(8 at% Mg): Zr was found to be the best, producing around 8.1 kJ/g in a pure oxygen environment. Bilayer thickness does not play an important role in heat generation, though it is an important parameter for propagation velocity and ignition temperature, both of which are used for modeling purposes.

The heat released during the subsequent, slower oxidation reaction results in an extended time at elevated temperature. In Figure 1 below, we compare different foil chemistries based on reaction temperatures measured by two-color pyrometry.

From this comparison, it would appear Al:Zr experiences the greatest oxidation, and therefore would be expected to produce the most heat. However, a cloud of vapor is released from the Al-8Mg:Zr as it reacts. We used spectroscopy to determine the nature of this vapor, and Figure 2 shows that Mg is subliming or vaporizing from the foil early in the reaction, then oxidizing as a vapor. Thus, oxidation is also occurring outside the reactive foil, and this heat generation is not captured by the pyrometer measurements. Also, the loss of Mg appears to generate pores that span the thickness of the foil, therefore allowing increased oxygen diffusion throughout the thickness and leading to more complete oxidation of the foil.

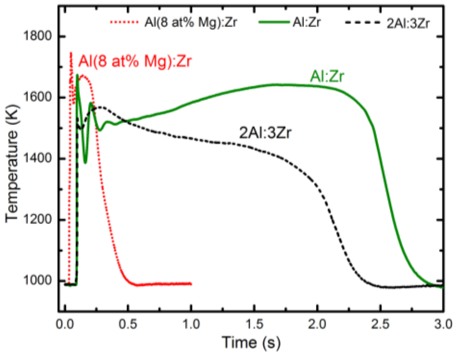

Figure 1: Two-color pyrometry comparison of three chemistries

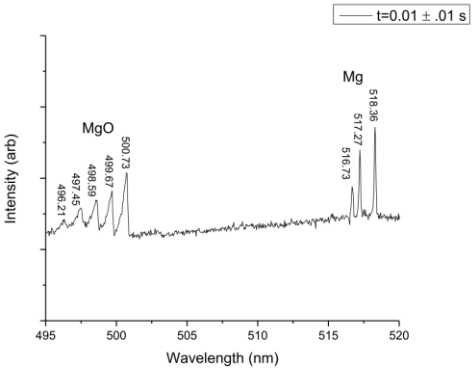

Figure 2: Emission spectroscopy confirming the vapor is Mg, rapidly oxidizing to MgO

To quantify the total heat released through vapor phase *and* condensed phase oxidation, we designed a very low heat capacity bomb calorimeter specifically for the ignition of these foils. Reactions inside the bomb are performed in air, oxygen, and argon environments, and the calorimeter was calibrated using Al:Ni foils with well-known heats of reaction [1].

Preliminary bomb calorimeter measurements show that Al-8Mg:Zr generates about 8.1 kJ/g of heat when reacted in oxygen, in comparison to about 6.2 kJ/g generated by Al:Zr. This confirms that the presence of magnesium is beneficial in increasing total heat output, and so we also measured heat release from a foil of higher magnesium content: Al-38.5Mg:Zr. A smaller heat of reaction (7.5 kJ/g) was observed, however, indicating that increasing the magnesium content further is not advantageous. The optimal chemistry seems to lie closer to Al-8Mg:Zr, and so we selected this system for future work.

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COMBUSTION BONDING OF FUNCTIONALLY GRADED W/CU TARGETS FOR NEW ACCELERATORS

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A new generation of accelerators, such as the St. ANA accelerator at the University of Notre Dame and the accelerator in the proposed Dakota Ion Accelerators for Nuclear Astrophysics (DIANA) project at the Sanford Underground Research Facility (SURF), will produce higher intensity beams than ever previously attained. Beam intensities are estimated to be on the order of hundreds of μAmps. These new intensity thresholds introduce significantly higher temperatures at points where the ion beam interacts with the beamline components, the experimental target, and/or the beam slits. These temperatures are high enough to destroy the current generation of solid target backings and slits in the beam-line, traditionally both made from tantalum [1]. Tantalum is traditionally used for targets and slits in the beam-line because it has a high proton number, making it effective for stopping ion beams. However, tantalum is brittle, a poor conductor, and, if produced commercially, often contains impurities (e.g. fluorine) that produce undesirable background and reaction products. Tungsten, despite its brittleness and poor conductivity, has a higher atomic mass and lacks of impurities, which make it a promising target backing. In conjunction with tungsten's properties, copper is robust and a far superior thermal conductor.

In this work we describe a new method for production of the *functionally graded targets* that use the advantageous of both tungsten and copper. This method is based on combustion joining approach [2] and involved the following steps: (i) placing a reactive powder mixture (such as Fe_2O_3 + Mg + Fe, Ti + C + Ni or Ti + Si + Ni) in between tungsten and copper plates; (ii) applying an optimum load force on the stack to be joined; (iii) reaction initiation in the exothermic mixture; (iv) which provides extremely high temperature for reactive joining of W to Cu.

Thermodynamic calculations and experiments showed that all reactive mixtures are able to generate the necessary heat to join the materials; however, it became apparent that both thermite Fe_2O_3 + Mg and gasless Ti+C systems introduced defects to the reacted layer that either did not create a stable join or left a low quality join layer. The major issue is related to the fact that combustion of both systems in air leads to the release of a large amount of gas phases (e.g. Mg vapors, CO_2), which causes the material ejection from the reaction zone. The latter does not allow us to produce joint layer of desired properties.

The self-sustained reaction in Ti+Si system does not lead to any gas phase products and thus provides the desirable conditions for combustion joining. The optimal reactive mixture to joining copper and tungsten plates (with thickness of 0.05 – 1 mm) was found to be 5Ti+3Si reactive mixture diluted with 20wt.% Ni. Other experimental parameters, such as force load, geometry of samples, thickness of soldering layer (nickel) are also have been optimized. Targets prepared within the optimized joining conditions results in a join layer that is free of cracks and pores (Figure 1).

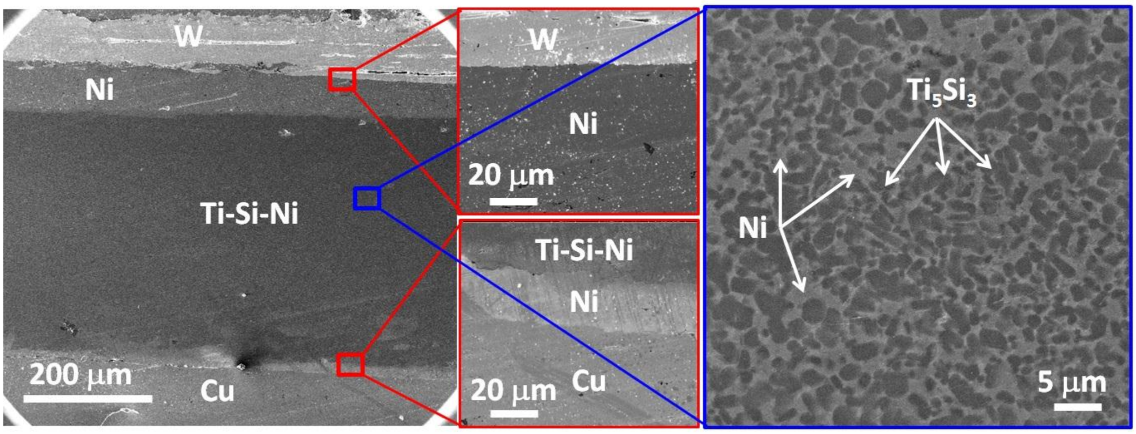

Figure 1: The microstructures of the join layer cross-section

We show that the microstructure of samples does not deteriorate through heating to ~700 ^{o}C in inert gas for several hours. Moreover, such treatment even reduces or eliminates small microstructural defects. More details on synthesis conditions, as well as the results of testing of W/Cu backings under an intense ion beam bombardment will be discussed.

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3. COMBUSTION OF MULTILAYERED NANO-STRUCTURES

MOLECULAR DYNAMICS STUDIES OF NANOMETRIC METALLIC MULTILAYERS: REACTIVITY OF THE Ni-Al SYSTEM

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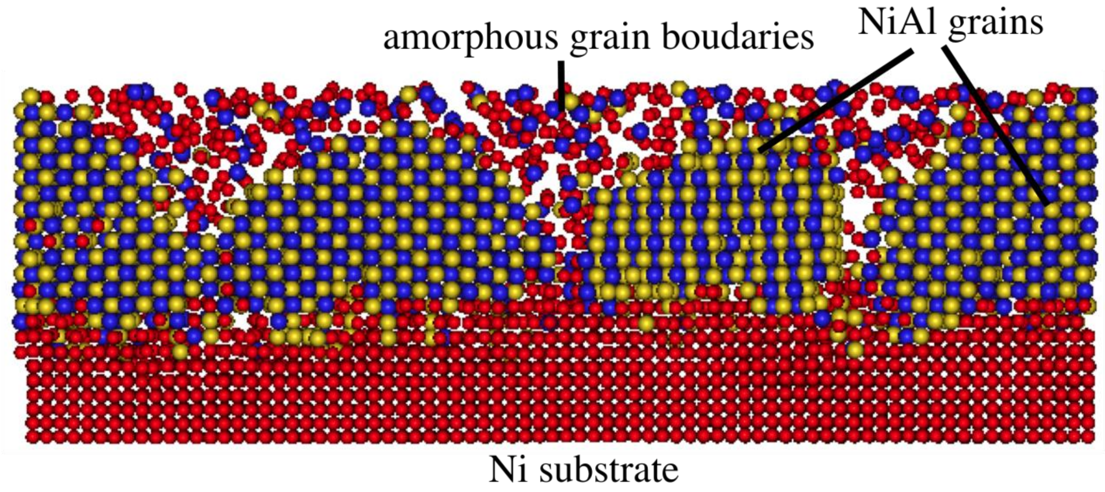
Research on metallic nanomaterials attracts more and more attention since the last decade. Amongst them nanometric metallic multilayers (N2M), also called *nanofoils* or *reactive multilayer foils* are of particular interest [1]. N2M are obtained by the superposition of very thin A-B films, where A and B are pure metals. During the alloying of elements and the formation of intermetallic compounds, a very high density of energy is release. The highly reactive properties of N2M give them many technological applications (joining, ignition, localized heating, hyperthermia for medical applications, …). As Ni-Al nanofoils are intensively studied and well documented, Ni-Al nanofoils was used as the system of interest.

The control of exothermic properties of these nano-systems requires a better understanding of their specific behavior. Molecular dynamics simulations (MD) appear as a valuable tool for the nanoscale investigation of these materials for the following reasons. One is that the time scale of the reaction and the length scales of the multilayer period match the capabilities of MD quite well. The second is that we now have experimental techniques such as DTEM that can probe the reactions in situ at these time (10 ns) and lengths scales (10 nm) and be compared with MD simulations.

During this talk, we will show how MD can be used to study the development of interfacial reactions between Nickel and Aluminum in nanofoils [2]. For instance, the microstructure of the system across a frozen reactive front can be observed. It reveals the formation of rounded shaped grains as observed by the TEM analysis of experimental samples [3]. MD simulations allows to detect the elementary mechanisms on an atomic basis and shed some light on the phase competition during the process. We will underline how amorphization phase plays a crucial role in the kinetics and we will decompose the nucleation and growth process of seeds of intermetallic compounds step by step to understand their development.



Snapshot of the system near the interface after 20 ns at T = 1000 K. Al and Ni are shown by blue and yellow spheres, respectively. For visualization purposes, atoms with non-bcc environment are represented by small red bullets. The rounded shaped grains are formed by the NiAl compound.

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EVIDENCE FOR AN AMORPHOUS INTERMEDIATE PHASE IN THE RAPID SOLID-STATE FORMATION OF NiAl

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Our study is focused on exploring how the sequence of phase transformations in Ni/Al reactive multilayered foils varies depending on the rate at which the foil is heated. Previous work has shown that at low heating rates (1 K/s), NiAl forms through a sequence of solid-state, intermetallic phase transformations [1-4] beginning with $NiAl_3$ or Ni_2Al_9 and proceeding through progressively more Ni-rich phases until the equilibrium NiAl is reached. In contrast, at very high heating rates (10^6 K/s – 10^7 K/s), the Al layer melts before any intermetallic phases form and the NiAl phase precipitates directly from the melt [5-7], skipping all other intermetallic phases.

The present work makes use of nanocalorimetry, a novel thermal analysis technique capable of delivering very high heating rates. This technique has been integrated with the dynamic transmission electron microscope (DTEM) developed at Lawrence Livermore National Laboratory. This system gives us tunable access to a wide-range of heating rates coupled with *in situ* time-resolved electron diffraction on the nanosecond time scale. Together, these allow us to identify the phase transformation sequence in the rapid reaction of Ni and Al at heating rates from 100 K/s to 100,000 K/s.

Typical results from an experiment conducted at 1800 K/s are shown in Fig. 1. The temperature vs. time data shown in Fig. 1a show the presence of an irreversible, exothermic reaction in the first scan only. Extracting the reaction power as in Fig. 1b shows that there are two distinct exothermic peaks associated with the reaction at this heating rate. The electron diffraction patterns in Fig. 1c clearly identify the initial phases as elemental Ni and Al and the final phase as B2 NiAl, but offer no conclusive evidence for the presence of any Al/Ni intermetallics at any point in the reaction.

As this talk will describe, the only explanation for this result is that rather than a Ni/Al intermetallic phase the system is forming an Al-rich amorphous phase in the first exotherm. The presence of an amorphous phase is supported by *ex situ* quenching experiments and cross-sectional TEM. This result is a departure from all previous investigations of reactions in Ni/Al foils and should open the door for a new discussion of how kinetics and thermodynamics interact to determine the first phase to form in reactive systems.

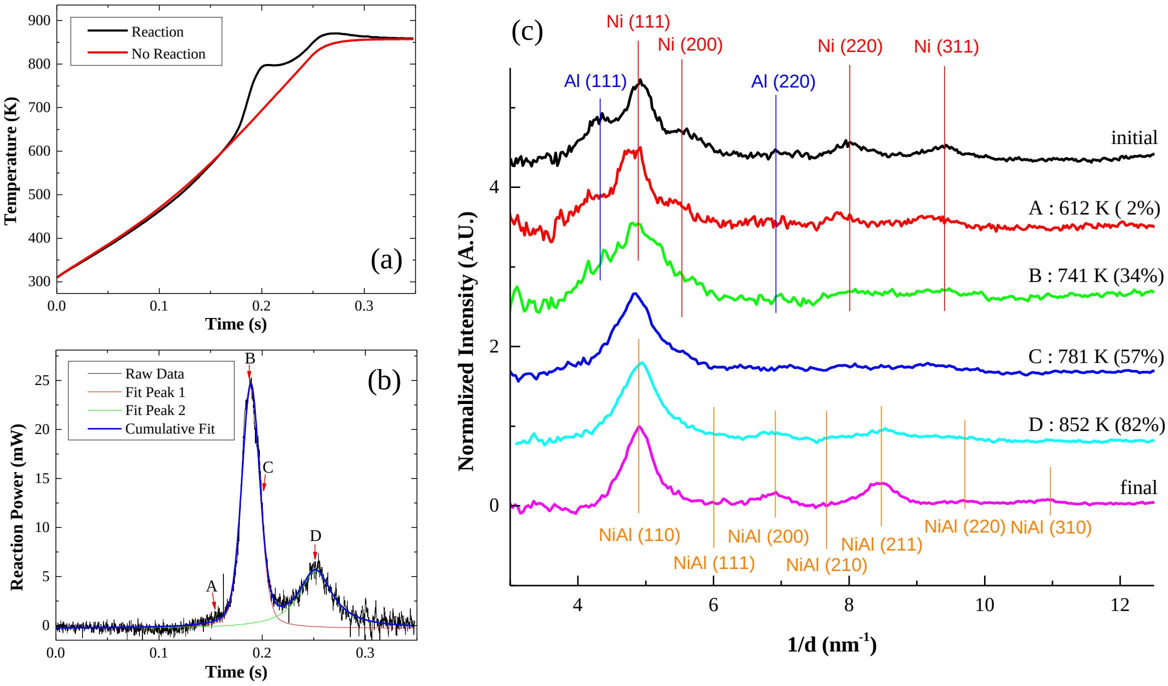

Figure 1: Experimental data compiled for a 100 nm bilayer heated at 1800 K/s. (a) Temperature as a function of time for two sequential heatings, (b) extracted reaction power and fitted peaks, and (c) time-resolved electron diffraction scans at the points indicated in (b). The additional numbers are the chip temperature and the % reaction completion at the time of the scan.

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STRUCTURES OF THE COMBUSTION WAVES IN MULTILAYER NANO-SYSTEMS

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Lamellar reactive nano-materials possess extraordinary parameters of the ignition and combustion, such as low temperature of the reaction initiation and very high velocity of the combustion wave propagation. Here we report some new results of the experimental investigation of the macro-, micro- and nano-structure of the combustion waves in the reactive nano-systems. The temperature-time profiles and propagating velocities were measured by means of high frequency photo sensors and high speed video recording. Quenching of the reaction waves allowed detailed study of the structural transformations from initial reactive media to the intermediate and final products.

Various macroscopic modes of the combustion propagation have been found in the multilayer Ni/Al, Ti/Al and Ti/Ni nanofoils, including steady state propagation, oscillating, spinning and oscillating-spinning regimes. The latter is illustrated in Figure 1. The reaction is localized in the hot spot, and the trajectory of the spot propagation is clearly visible on the surface of the foil. The distance between the trajectories is about 60-80 micron, while the space period of oscillations is 50 – 70 micron. The theory of this combustion mode does not exist yet.

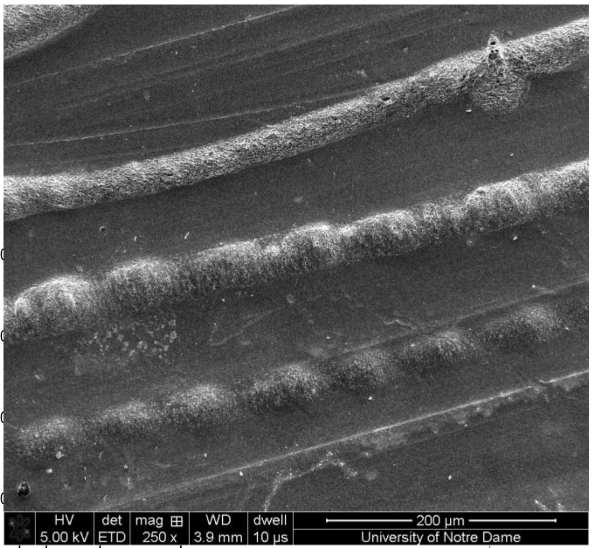
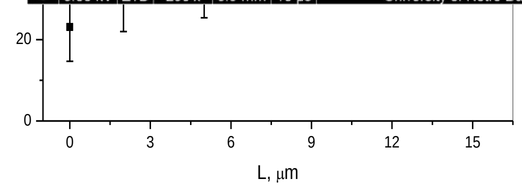


Figure 1. Oscillating-spinning combustion of the Ti/Ni multilayer nanofoil.

High-frequency recording of the brightness temperature profiles reveals complex structure of the combustion waves. For example, the first reaction stage in the Ni/Al with extremely rapid (~3000000 K/s) temperature rise takes place during 0.5 ms, and followed by slower second stage with duration of ~ 10 ms [1]. It was shown that the first stage is a direct dissolution of Ni into Al melt, without formation of the solid product.



The second stage relates to the nucleation of nano-grains NiAl (B2 structure) The final third stage can continues ~100 ms. Fast grain growth takes place during this stage, as shown in the Figure 2.

Figure 2. Average NiAl grains diameter (d) vs distance behind the combustion front in the Ni/Al multilayer nanofoil.

The complex multi-stage structures of the SHS-waves were found also in the other nano-lamellar systems.

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INFLUENCE OF PRECURSORS STOICHIOMETRY ON SHS SYNTHESIS OF POWDERS OF MULTILAYERED MATERIALS IN THE Ti-Al-C-N SYSTEM

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Among many covalent materials such as carbides or nitrides in the Ti-Al-C-N system exists group of interesting ternary and quaternary materials called MAX-phases, H-phases, Hägg-phases, Novotny-phases or thermodynamically stable nanolaminates. These materials are characterised by heterodesmic layer structure and have a $M_{n+1}AX_n$ stoichiometry, where M is an early transition metal, A is an element of A groups (mostly IIIA or IVA) and X is carbon and/or nitrogen. Their specific structure consisting of covalent and metallic chemical bonds strongly influence their semi-ductile features locating them on the boundary between metals and ceramics [1]. This fact may lead to many potential applications, for example as a part of a ceramic armour.

For obtaining sinterable powders of these materials in Ti-Al-C-N system Self-propagating High-temperature Synthesis (SHS) with local ignition system was applied. Synthesized compounds were Ti_2AlC, Ti_3AlC_2, Ti_2AlN and Ti_4AlN_3. Basing on the previous researches on synthesis of Ti_3SiC_2 as well as on earlier studies on Ti-Al-C-N system it is known that stoichiometry of precursors may be crucial for synthesis of ternary materials, therefore the influence of stoichiometry of particular precursors on phase composition of a final product was carefully studied [2, 3, 4, 5]. As a precursors for synthesis of ternary materials SHS derived intermetallic compounds, namely TiAl and Ti_3Al as well as elemental powders and carbides and nitrides, graphite as a source of carbon and pure nitrogen gas were used.

Products of synthesis were ground and the XRD analysis method was used to determine phase composition of the synthesised materials. The basis of quantitative and qualitative phase analysis were data from ICCD [6] . Amounts of the respective phases were calculated by the Rietveld analysis [7]. Observations of the powders morphology were done by FEI Europe Company Nova Nano SEM 200 scanning electron microscope.

The best results of the synthesis giving as a final products powders containing highest amount of the desired MAX phases are presented in the Table 1. Results for of Ti_4AlN_3 were not included due to relatively low amounts of these compound in the final product.

Table 1.

Assumed result of a SHS synthesis	Stoichiometry of chemical reaction	Phase composition of final product [wt.%]

Ti_2AlC	1.05TiAl + Ti + C → Ti_2AlC	84% Ti_2AlC, 5.9 Ti_3AlC_2, 8.7 TiC, 1.4 Ti_3Al
Ti_3AlC	1.1TiAl + 2Ti + 2C → Ti_3AlC_2	76.4 Ti_3AlC_2, 18.9 TiC, 4.7 Al_4C_3
Ti_2AlN	TiAl + TiN → Ti_2AlN	21.2 Ti_2AlN, 44.2 TiN, 0.9 Ti_3Al, 15.9 AlN, 7.9 Al_3N, 9.8 $Ti_3Al_2N_2$

The SHS synthesis seems to be suitable for manufacturing of sinterable powders of nanolaminate MAX phases materials. The best results were achieved for Ti_3AlC_2 and Ti_2AlC, but also basing on previous studies results obtained for Ti_2AlN are promising in case of further sintering processes.

The best powders were destined for further pressureless sintering and hot pressing process to manufacture dense, single phase polycrystalline materials, the mechanical properties of obtained materials will be examined.

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IN-SITU TRANSMISSION ELECTRON MICROSCOPY AND ELECTRON DIFFRACTION INVESTIGATIONS OF SOLID-STATE REACTIONS IN THIN-FILM NANOSYSTEMS

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Transmission electron microscopy (TEM) and electron diffraction (ED) allows one to conduct *in situ* heating experiments and to study phase transformations such as solid-solid transitions or chemical solid-state reactions [1, 2]. A specimen can be heated up to 1200ºC in vacuum of 10^{-5} Pa. Dynamic events at the atomic level can thus be recorded in real time. It is possible to study the change of the sample morphology by obtaining TEM images, or the change of the phase composition by obtaining electron diffraction patterns during heating. A cross-section of a multilayer sample can be prepared making it possible to investigate interfacial solid-state reactions.

In situ heating experiments were conducted with a JEOL JEM-2100 (LaB_6) transmission electron microscope at an accelerating voltage of 200 keV. For the heating experiments a Gatan 652 double tilt heating holder was used. The holder allows heating of a specimen from room temperature up to 1000ºC with a controllable heating rate from 0.02 up to 20ºC/s. The TEM is equipped by a Gatan UltraScan 1000 CCD Camera (4 Mpx) which allows acquiring high-resolution images, and, a Gatan ES500W Erlangshen CCD Camera (1.4 Mpx) which allows acquiring up to 15 frames/s, so that the time resolution of the video recording is ~0.06 s.

The processes of solid-state synthesis in thin bilayer (Cu/Au, Al/Au, Fe/Si, et al.) and multilayer (Fe/Si) films were studied by *in situ* transmission electron microscopy and electron diffraction. The total thickness of a film was from 40 to 100 nm. The goals of the investigation were to study: the structural phase transformations; dynamics of solid-state reactions; change of the morphology during the interfacial reactions; in thin bilayer (or multilayer) films with different composition.

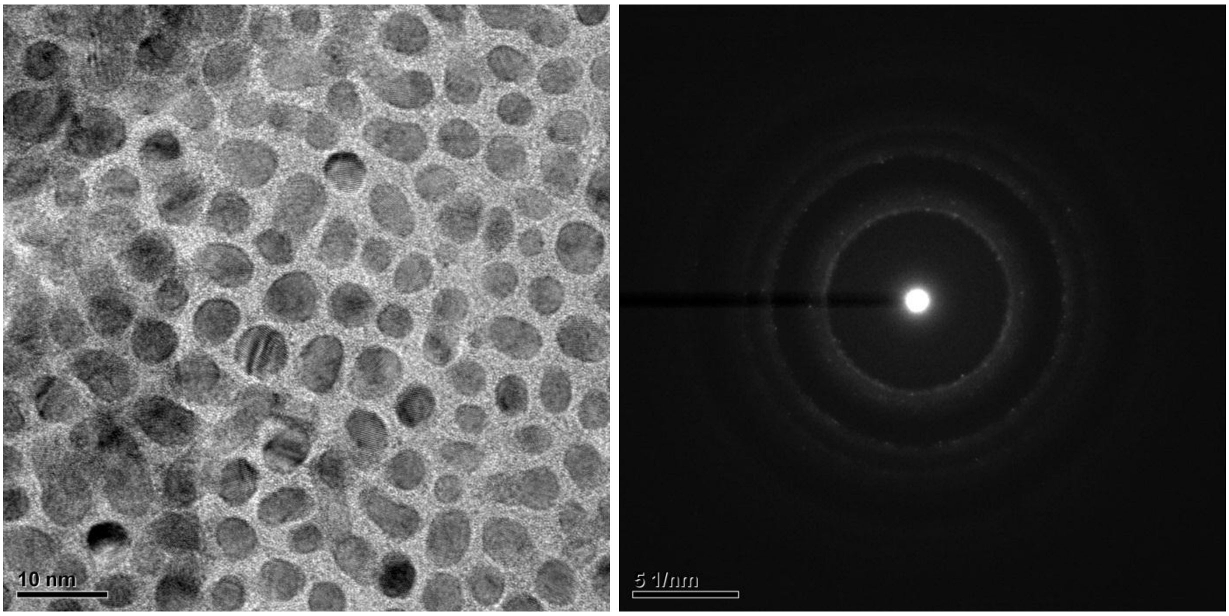

Fig.1 TEM image (left) and selected area electron diffraction pattern (right) of the Cu-Au film at the initial state of solid-state reaction at 240ºC.

As an example, the result of *in situ* TEM and electron diffraction investigations of solid-state reactions in a Cu/Au bilayer film is demonstrated in Fig.1. The Cu/Au film was annealed at 240ºC for 60 min. As a result of the interaction between the Cu and Au layers nanoparticles with a CuAu crystal lattice were formed. Some of the observed nanoparticles had an atomic-ordered CuAuI structure.

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SHOCK-COMPRESSION RESPONSE OF MULTILAYERED Ni-Al COMPOSITES

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Meso-scale heterogeneities arising from structural variations generated from processing or due to differing physical/mechanical properties of constituents can strongly influence the shock compression response of composite or multi-constituent materials. Multilayered Ni-Al composites made by co-evaporation or cold-rolling of Ni and Al foils provide a unique system for studying the effects of material heterogeneities on a propagating shock wave, due to their full density, periodic layering, and intimate contacts between constituents. The response of shock-wave propagation through cold-rolled multi-layered Ni-Al laminates and co-evaporated nano-layered composites is investigated using meso-scale simulations performed employing real microstructures and using the Eulerian hydrocode CTH. In the case of the cold-rolled composites, the orientation of the layers is varied at 0^o, 45^o, and 90^o to the direction of shock-front propagation, to determine the differences in the bulk shock-compression response and the effects of strain localization due to the mismatch in elastic and plastic properties across the interface. Evidence of reaction and validation for the computational results is obtained through time-resolved measurements (VISAR, PDV, and PVDF stress gauges) performed using uniaxial strain plate-on-plate impact experiments using gas gun and laser-accelerated thin-foil impact system. Correlation of the experimental results with those obtained from meso-scale simulations demonstrate that the computations provide an accurate representation of the systems, thereby validating the conclusions and extracted trends.

The meso-scale simulations reveal noticeable differences in the pressure, temperature, and strain response, as a function of the layer orientation of cold-rolled composites. Geometric dispersion is seen to alter the shape of the resulting pressure pulse and inhibit the development of a steady-state shock wave in the laminated geometry. Strain-localization at the interfaces causes shock-wave dissipation through interfacial heating and shearing, resulting in high levels of viscosity and attenuation. The dissipative effects also alter the dependence of shock velocity on particle velocity, making it a major contributor to the bulk response of multilayered composites under shock compression. In the case of the co-evaporated laminate structures, the wavy morphology of the nano-scale layers is observed to promote dispersion and mixing of reactants, leading to self-sustained reaction initiation.

The shock compression response of multilayered systems is contrasted with that of particulate based Ni+Al composites to generate a comprehensive understanding of Ni/Al reactive materials under conditions of high pressure and high strain rate loading.

4. NANOENERGETIC MATERIALS AND PROCESSES

REACTION INTERFACE FOR HETEROGENEOUS REACTIONS OF METAL POWDERS

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Heterogeneous reactions of metals, such as oxidation, are often rate limited by diffusion through a growing layer of oxide or other product. Depending on specific diffusion rates, the reaction may occur at either inner or outer surface of this layer; alternatively, it can occur inside the layer if diffusion rates of both reacting species are comparable to each other. This study offers a simple experimental methodology enabling one to determine where the reaction actually takes place. Once the reaction location is identified, a detailed reaction mechanism can be developed.

The location of heterogeneous reaction is identified processing results of thermo-analytical measurements for at least two reacting spherical powders with different but overlapping particle size distribution. For each experiment, the measured reaction progress, e.g., weight gain for thermo-gravimetric measurements, or heat flow rate for calorimetry, is distributed among particles of different sizes assuming that the rate of reaction is proportional to the reactive interface area. Different models are considered to determine the interface area, assuming that this interface is either on the inside or outside of the growing product layer. Depending on the reacting model, the interface area evolves differently for each powder. Reaction progress dynamics for the same size particles present in different powders are expected to be identical to each other when the calculated reactive interface area reflects the true reaction mechanism.

In this talk, reaction interfaces for reactions of aluminum with gaseous oxygen, liquid water, and steam will be identified. It is concluded that for aluminum oxidation in oxygen, the reaction occurs at the outer surface of the growing oxide shell. Furthermore, it is concluded that this shell becomes rigid after reaching a specific thickness, so that hollow particles are formed. Conversely, for oxidation of aluminum in liquid water, results suggest that the reaction occurs at the surface of the shrinking aluminum core, inside the growing aluminum hydroxide layer. For reactions of aluminum with steam at elevated temperatures, the results are less conclusive, but indicate that the reaction is most likely occurring at the outer surface of the growing alumina shell. The growing alumina shell is rigid and is fractured multiple times during its growth. After a shell is fractured, a new shell begins to grow around the oxidizing aluminum core.

REACTION MECHANISM OF NANOCOMPOSITE THERMITES: PROBING PHENOMENA AT VARIOUS LENGTH AND TIME SCALES

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Understanding the reaction mechanism in nanocomposite thermites has proven to be quite challenging, due to the very rapid heating and reaction time scales occurring on very fine length scales. Aluminum is the most commonly used fuel, and a variety of metal oxides have been investigated. While one might imagine that simply mixing the fuel and oxidizer on finer and finer length scales would enhance the reactivity, the reality is that the mechanism is highly multi-scale and complex. On the finest length scale, aluminum is passivated by a several nanometer thick oxide layer, and this core-shell interaction needs to be understood to predict how aluminum is exposed to the oxidizer during a reaction. On the particle length scale (~20-100 nm), we must understand how a fuel and oxidizer particle can undergo a redox reaction. On a slightly larger length scale, we must consider particle aggregates and the resulting heat and mass transport within the aggregates. Going one step larger to the micron scale, we must understand gas trapping and local pressure buildup / unloading. On the macroscopic level, bulk energy transport must be understood. The multi-scale nature of the problem opens up many other length scales and mechanisms to consider for tuning the reactivity, besides simply shrinking the particle size. If the end goal is for a faster reactivity, we must critically evaluate what the rate limiting processes are and focus our efforts on these limitations.

This work is a compilation of experimental results which have been used to investigate the reaction mechanism at various length scales. Rapid heating microscopy is used to heat particles inside an electron microscope and visualize morphological changes occurring on the particle and aggregate length scales. The sintering time and temperature threshold was measured using dynamic transmission electron microscopy (DTEM), and was observed to occur on a time scale of 10's of nanoseconds, starting at an intermediate temperature between the melting point of aluminum and its oxide. On the micron length scale, we have used phase-contrast imaging to visualize the formation of clusters and the unloading phenomena which occurs under rapid heating conditions. Combining these results with those of the rapid heating microscopy, we have suggested that at least part of the reaction between the fuel and oxidizer proceeds very rapidly in the condensed phase via reactive sintering. Thin films of thermite, from ~10-200 μm in thickness, were deposited using a technique called electrophoretic deposition (EPD). The results show that the reactivity exhibits a two-plateau behavior in flame velocity, with approximately an order of magnitude difference, separated by a linear transition region. We have attributed this behavior to a non-dimensional parameter which is the ratio of the gas generation rate to the rate of gas escape, and is proportional to the film thickness for a given system. For thin films, gases rapidly escape upon generation, and the internal pressure does not build up to cause pressure unloading. However, for larger thickness, more and more of the gases are trapped during the reaction until some critical thickness in which gases are entirely trapped.

This induces enhanced energy transport (and thus a faster velocity) from gases and particles undergoing pressure-driven transport. We have also looked at the effect of microstructure by using direct-ink writing (DIW) to print silver electrodes with controlled height and spacing, followed by the deposition of thermite films onto these electrodes to define the microstructure. We find that a significant enhancement in reactivity occurs when an open channel is present between two reacting filaments, and this is likely due to the pressure-driven expansion of material into the channel where the intermediate and/or products can interact to increase the forward energy flux.

On the macro scale, we will attempt to piece together some of the results to suggest what can be occurring in burn tubes or pressure cells; techniques which are commonly used to investigate reactivity. We have performed some burn tube experiments, and will discuss some of the recent results and limitations of such measurements. Evaluating the body of literature, one can find several general observations for nanocomposite thermites including, but not limited to; gas generation is very important, low packing densities react faster than high, open pathways or channels result in higher flame speeds, fuel-rich formulations almost always outperform stoichiometric, gases which are evolved are likely intermediate species, microstructure matters, the flame zone is very wide, fuel particle size is less important than oxidizer. This collection of results suggests that energy transport is likely the rate limiting step, and is what we need to focus our efforts on to improve the reactivity in the short term. The heating times of aluminum particles were calculated as a function of particle size and ambient heating rate. Specifically, we find that the ignition delay of aluminum is likely the rate limiting step and, depending on the heating rate, there may be no real advantage to using particles below a critical size. Several suggestions for methods to improve the energy transport include; 1) Use engineered microstructures to direct energy transport 2) Alter the aluminum in some way to reduce ignition temperature and/or delay 3) Promote the formation of low molecular weight gases.

ACKNOWLEDGMENT

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NANOCOMPOSITE AND MECHANICALLY ALLOYED REACTIVE MATERIALS AS ENERGETIC ADDITIVES IN OXYGEN GENERATORS

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Chemical oxygen generators are widely used for aircraft, spacecraft, submarines, and other applications [1]. The solid compositions used include a source of oxygen, such as sodium chlorate ($NaClO_3$), which decomposes at high temperatures, and an energetic additive that provides heat for self-sustained combustion. Since energetic additives may lead to deterioration in the generator's effectiveness and to safety problems, such as combustion instabilities and risk of fire, it is important to minimize their amounts. The present paper investigates the feasibility of replacing iron and tin, currently used in oxygen generators, with reactive materials, produced by arrested reactive milling (ARM) [2, 3] and by mechanical alloying. The nanocomposite materials obtained by ARM contain fully-dense, micron scale particles in which components are mixed on the scale of about 100 nm, but are not chemically bound. These materials include compositions combining metal and oxidizer as well as compositions that take advantage of uniform mixing on the nano-scale between components reacting exothermically and not requiring oxygen (e.g., intermetallic or metal-metalloid composites). Mechanically alloyed powders were shown to be more reactive fuels compared to regular alloys or pure metals. Their developed surface area accelerates ignition, while combustion is optimized by finely tuned elemental compositions. The nanocomposite and mechanically alloyed reactive materials have the potential to improve the process stability and fire safety of chemical gas generators. Because of a higher gas yield, more controlled heat release, and a smaller amount of energetic additives, both efficiency and safety of gas generators can be improved.

Thermodynamic calculations of the adiabatic flame temperatures and combustion product compositions were conducted for mixtures of sodium chlorate with various reactive materials. using THERMO software [4]. The formation enthalpy of $NaClO_3$, –365.77 kJ/mol [5], was added to the software. The calculations showed that many of the reactive materials fabricated by ARM are promising substitutes for currently used iron and tin. For example, the best metal/metal (metalloid) system are B/Ti and Al/Ti, while among the metal/salt and metal/oxide systems, the best are $Al/NaNO_3$ and $Mg/NaNO_3$, followed by Al/MoO_3 and Mg/MoO_3. Based on the calculations, alloys of Al and Mg are even more attractive, while they are less reactive than the aforementioned nanocomposite materials. Thermodynamically, all these additives are more efficient than iron or tin. More specifically, a lower concentration of the additive provides the same adiabatic combustion temperature and simultaneously a higher oxygen yield.

The experiments were conducted with the following energetic additives: Fe, Ti/B, $Al/NaNO_3$, and Al/Mg. The Ti/B mixture ratio corresponded to the stoichiometry for producing TiB_2, while for other pairs of compounds, different mixture ratios were tested. All tested compositions included 3 wt% Co_3O_4, which is a catalyst for $NaClO_3$ decomposition [6]. Sodium chlorate, cobalt oxide, and the tested additive were mixed in a three-dimension inversion kinematics tumbler mixer (Inversina 2L) and compacted to pellets by a hydraulic press. The pellets were ignited at the top by an infrared beam of a CO_2 laser (Synrad Firestar ti-60) in a windowed reaction chamber filled with argon. The combustion wave propagation was studied using a high-resolution camera (Sony XSD-SX90CR) and an infrared camera (FLIR SC7650). The results have shown that, among the tested compositions, Al/Mg (70 wt% Al) is the most promising substitute for iron in chemical oxygen generators based on sodium chlorate.

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REACTIVE NANO-COMPOSITES: STRUCTURE – REACTIVITY RELATIONSHIP

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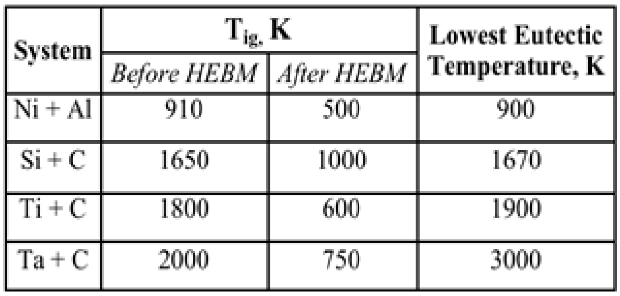
It is well known that initiation of self-sustained exothermic reaction in micrometer-scale reactive mixtures (e.g. Ti+C, Ni+Al) is primarily correlated to the formation of a liquid phase (lowest the eutectic temperature). In some systems (e.g. Ta+C) adsorbed impurity gases on the surface of initial powders may also significantly accelerate mass transport. In our recent studies [1-3] we have shown that short-term (minutes) high energy ball milling (HEBM) leads to decreases the self-ignition temperatures (Tig) by hundreds or even thousands of degrees (Table 1).



System	T_{ig}, K		Lowest Eutectic Temperature, K
	Before HEBM	*After HEBM*	
Ni + Al	910	500	900
Si + C	1650	1000	1670
Ti + C	1800	600	1900
Ta + C	2000	750	3000

Table 1 Self-ignition temperatures (T_{ig}) of different binary reactive systems

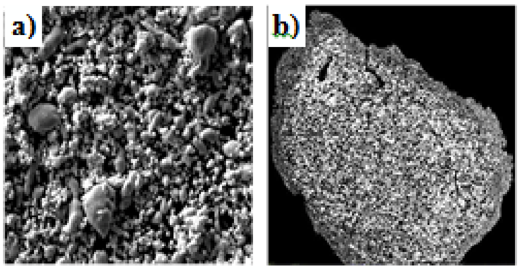


Fig. 1 Transformation of conventional media (a) into nanostructured composite particles (b) in Ni+Al system

Such decrease of Tig well below melting points (eutectic temperature) of the reagents, indicate that the solid-sate mass transport processes become solely responsible for the self-initiation of the reactions. We have performed comprehensive analysis of microstructure for HEBMed materials in order to understand the influence of mechanical treatment on reactivity enhancement. In current talk we discuss important phenomenon, which take place during energetic milling of binary reactive systems with different mechanical properties, such as Ni-Al, Ti-C, Si-C, Ta-C. The relationship between microstructure and reactivity of resulting materials will be outlined to understand the mechanisms which involved in enactment of reactivity.

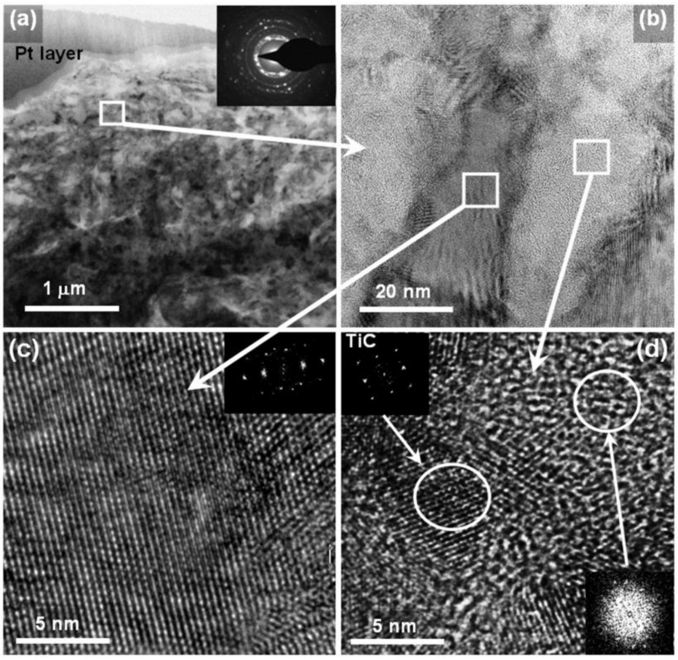


Fig. 2 TEM analysis of Ti/C composite particles: a cross sectional TEM image and a SAD pattern (a), HRTEM image of a selected area (b), and enlarged images of Ti (c) and TiCx (d) nano- crystallites

Our results show that in most systems heterogeneous micrometer-scale media of initial reactants transforms into nanostructured composite particles in early stages of HEBM. For example, Fig.1 shows that in Ni+Al system (ductile-ductile) Ni/Al composite particles are forming by so-called cold welding within first two minutes of milling. Farther mechanical treatment leads to some decrease in composite particle sizes. However, continuous refinement of microstructure inside particles leads to the formation of an intermixed Ni/Al layered nanostructure with average layer seizes of ~50nm. It is shown that this nano-laminated microstructure is responsible for self-ignition of HEBM Ni/Al composite particles. In Ti+C and Ta+C mixtures (ductile-brittle) similar composite particles are formed followed by rapid milling of crystalline graphite flakes to amorphous carbon due to the intensive high energy impact. Microstructural refinement in Me/C composite particles leads to nano-mixing of amorphous carbon and metals (Fig. 2). It is important that some amounts of tiny (2- 5 nm) nucleus of TiCx (TaC) are also formed in this stage (Fig. 2). Compered to abobe metal-based systems the HEBM in Si+C mixture (brittle-brittle) leads to the formation of nano-scaled composite particles, which consist of amorphous carbon and crystalline silicon. Such microstructures allow direct synthesis of SiC nanopowders in the combustion wave. Analysis of the microstructures and reaction kinetics suggests depending on the system and HEBM conditions following factors are responsible for reactivity enhancement: - formation of oxygen-free high surface area contacts between the reagents; - formation of sold solution or products nucleus; - mixing of the reactants on the nano-scale level; - amorphyzation of the reagents

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A SELF-SIMILAR MODEL OF GAS DYNAMICS BEHAVIOUR IN NANOTHERMITE REACTIONS

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Nanostructured highly exothermic reactive mixtures, referred to as nanoenergetic materials or metastable intermolecular composites, may release energy much greater than conventional energetic materials [1]. Recent studies revealed that Al/Bi_2O_3 and Al/I_2O_5 nano mixtures can generate a transient pressure pulse up to seven times larger than that during the explosion of traditional thermite reactive mixtures [2]. Moreover, the combustion of such nano mixtures demonstrated four times higher gas release than molecular explosives such as conventional trinitrotoluene (TNT). During the explosion, various physical processes such as thermal heating and expansion, vaporization, complex gas, and particles motions behind shock waves can occur. The theory of explosions includes two main topics: the propagation of blast waves in unbounded media and the interaction of blast waves with different obstacles and shocks. The goal of this report is to model and predict the pressurization behaviour of explosion of nanoenergetic materials by using equations of gas dynamics. The experimental data were used for the illustration of the theoretical conclusions.

We assume that the explosions of nanothermites are very quick and all the explosion energy is released into the gas instantaneously in a thin cross-section of the cylinder. We also assume that the pressure in the shock wave, which forms after the explosion, is much greater than the pressure of the ambient gas (strong explosion). An explicit self-similar solution for a strong instantaneous explosion was first obtained in the spherical symmetric case by Neumann and Taylor and for the spherical, plane, and cylindrical case by Sedov. Detailed analysis of a self-similar solution reveals that if the gas pressure as well as the contribution of the drag force per unit area, are taken into account, a good match with nanothermite mixtures experiments is achieved [3].

We consider here gas dynamics in one spatial dimension (along the axis of a cylindrical reactor). For adiabatic flow, equations of gas dynamics can be presented as the conservation of momentum, entropy, and mass.

In Figure 1, (a, and b) we plot the time dependence of the pressure which can be observed at detector at distance L from the explosion along the reactor axes, in accordance with our self-similar solution, for drag coefficient $\alpha = 0$ and $\alpha = 2$. We note that contribution of the drag is significant, and when the drag is taken into account, the result of computation is in good match with the experiment. In Figure 1, (c) we plot the experimental results for the peak pressure at the detector times the detector volume, as a function of mass of the explosive Al/Bi_2O_3 mixture in grams. The theoretical prediction of the peak pressure is a linear dependence on the explosive mass, since the peak pressure is proportional to the total energy released into the gas, which in turn is proportional to the mass of the explosive mixture.

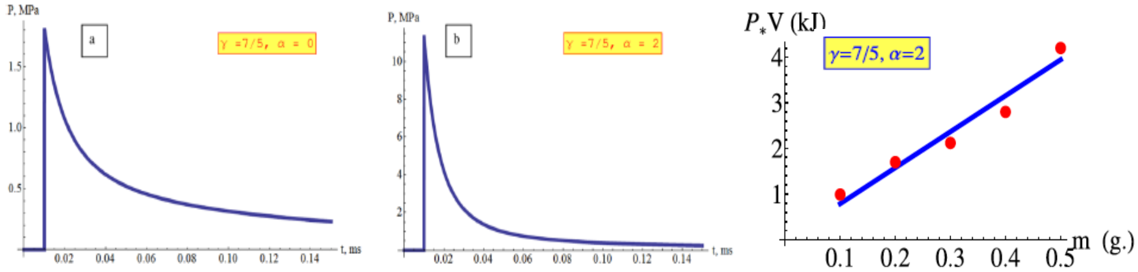

Figure 1: Results of modeling of the force per unit area, including gas pressure and the contribution of the drag. Explosion of 0.5 grams of Al/Bi_2O_3 mixture occurs at an end of a cylindrical reactor (a) $\gamma = 7/5$, $\alpha = 0$; (b) $\gamma = 7/5$, $\alpha = 2$. (c) PV dependence on mass of Al/Bi2O3 mixture, where P_* is the peak pressure at a detector, and V is the reactor volume in front of the detector. Blue: the theoretical prediction for γ=7/5, and the drag coefficient α=2: Red dots: the experimental data.

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SELF-HEATING MODEL OF SPHERICAL ALUMINUM PARTICLE OXIDATION

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Aluminum-oxygen reaction is important in highly energetic and high pressure generating systems. Nanoenergetic thermites include mixtures of Al and metal oxides in nanoscale. Several studies have been directed to understand the mechanism and kinetics of aluminum particle oxidation. [1-4]. The main distinguishing features of these reactive systems are their significant enthalpy release and tunable rate of energy discharge, which gives rise to a wide range of combustion rates, energy release, and ignition sensitivity. Aluminum oxidation exhibits high enthalpy and has been extensively used for propulsion, pyrotechnics and explosion reactions [5]. Nanoenergetic materials (NM) based on aluminum thermites may store two times more energy per volume than conventional monomolecular energetic materials [6,7]. The research problem we consider is oxidation in spherically symmetric case. We use the Cabrera Mott oxidation model to describe the kinetics of oxide growth of an aluminum nanoparticle and to predict reaction temperature, thermal front velocity and oxidation time.

We attempt a more accurate self-heating model of particle oxidation based on balance of enthalpy released as a result of chemical reaction and lost principally due to convection. To estimate the reaction times, we assume that aluminum sphere (radius 25 nm, with thin oxide layer of 2 nm) is surrounded by oxygen. The sphere is rapidly heated to ignition temperature, sufficient to initiate oxidation reaction, further boosted by self-heating as a result of oxidation. To find the temperature distribution of the nanostructured particle throughout rapid oxidation process, we have used detailed modeling of the heat loss, which is mainly due to convection. We have used the COMSOL software in this study for detailed air convection dynamics, and found the overall oxidation time scale using self-heating modeling in COMSOL.

Our set-up for this computation was as follows. We have placed a solid aluminum ball of radius $R_{in} = 25nm$ at the origin, surrounded by a concentric control sphere of radius $R_{out} = 1500$ nm filled with air. Initial temperature of the aluminum ball was taken to be $T_{in} = 800K$. Slip condition for the air velocity was used at the air-metal boundary. The boundary condition at the outer sphere was the open boundary condition with zero normal stress, but otherwise allowing air to move through the outer sphere, and with the outside temperature taken to be $T_{out} = T_{in} = 800K$. Nonstationary 3d solver was used in our modeling. To model chemical reaction itself, we used data for oxidation power release $P\left(\frac{m}{m_0}, T\right)$ as a function of the remaining metal mass and temperature computed in [7]. In our COMSOL self-heating model, we added a surface heat source with power surface density $\frac{P(\frac{m}{m_0},T)}{4\pi r_0^2}$ on the air-metal boundary. We introduced an extra boundary ODE on the air -metal boundary to compute the total energy Q escaped from the metal into the surrounding air, by integrating instantaneous energy flow $w_Q \equiv \dot{Q}$ through a sphere surrounding the metal particle, and used it to compute $\frac{m}{m_0}$. The energy flow w_Q could be readily computed in COMSOL using an instantaneous surface integration of the flow density. In Figure 1, we plot (a) temperature dynamics (b) the total energy released as a function of time, using detailed convection and self-heating modeling in COMSOL. Overall oxidation time scale is compatible with the simpler self-heating mechanism considered in [7]. Also we plot the velocity magnitude at different times.

(a)

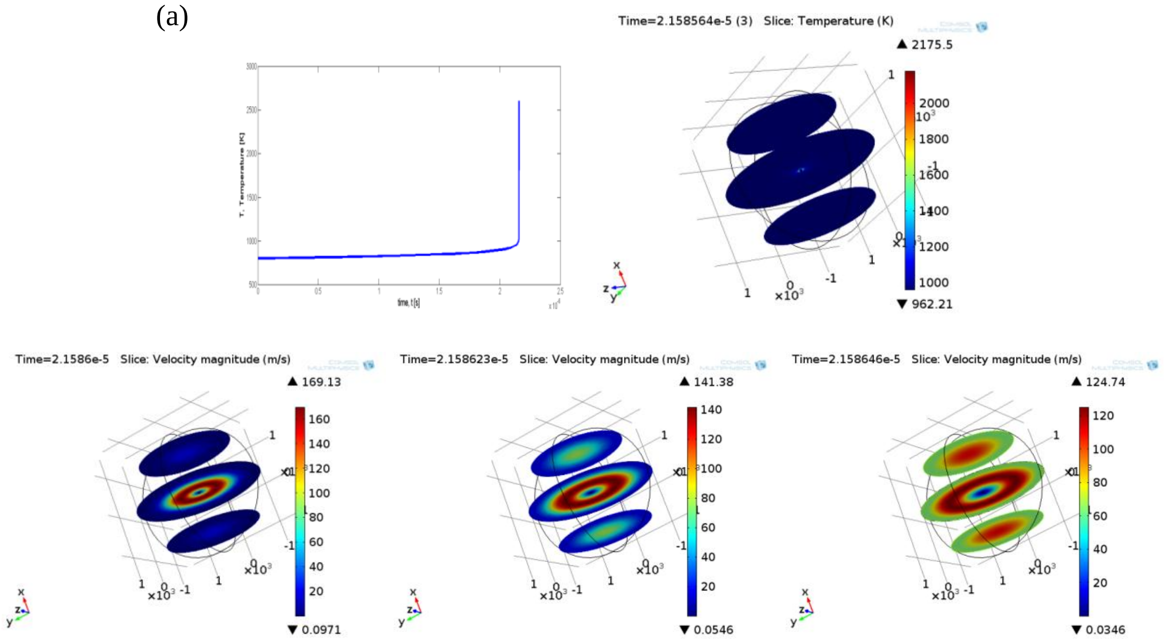

Figure 1. (a) Temperature as a function of time, for the case of spherical aluminum particle of radius r_0= 23 nm, with initial oxide thickness d = 2 nm. Initial temperature and the outside temperature are taken to be 800 K; (b) the velocity magnitude at different times.

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REACTION DYNAMICS OF PTFE/AL_2O_3 SYSTEM AT VARIOUS HEATING RATES

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Introduction

The well known energetic system polytetrafluoroethylene (PTFE, Teflon^{TM}) - aluminum should be always considered in conjunction with the system PTFE-Al_2O_3 due to the strong oxide layer that naturally forms on the aluminum surface. The PTFE can potentially remove the oxide layer from aluminum and increase the direct contact area between oxygen and aluminum [1], which increases the reaction velocity and improves the energy release abilities of the nanoenergetic system [2]. The reaction behavior of alumina with PTFE has been investigated by several research groups [3, 4]. However, all investigations were made at slow heating rates <20 °C/min, while in the thermite reactions the heating rates are significantly higher, which can alter the entire reaction mechanism between PTFE and Al_2O_3.

In this work we attempt to study PTFE-Al_2O_3 system at high heating rates up to 3200 °C/min and show that there is a transformation from endothermic to the exothermic mode.

Experimental Results and Discussion

The Differential Scanning Calorimetry (DSC) technique was used to characterize dynamic features of interaction between polytetrafluoroethylene (PTFE) and calcinated Al_2O_3 under different heating rates. The thermodynamic analysis by using the thermochemical code HSC-7 confirmed exothermic behavior of reaction and predicted maximum adiabatic temperature of 1425 K for the stoichiometric ratio of PTFE/Al_2O_3 taken as 1.5. At heating rates less than 150 °C/min the reaction is mainly endothermic, while at heating rates higher than 150 °C/min we have observed an exothermic reaction behavior. The activation energy of the reaction were calculated based on the peak temperatures of heat flow curves obtained from DSC measurements, using the isoconversional methods suggested in literature. We estimated the activation energy of the system PTFE/Al_2O_3 in both endothermic (Fig. 1, a) and exothermic (Fig.1,b) modes. In endothermic mode the dominating reaction is the decomposition of PTFE with activation energy of 265 kJ/mol, and at heating rates higher than 150 °C/min we observed the exothermic mode where the dominating mechanism is the reaction of PTFE with Al_2O_3 with estimated activation energy of 21 kJ/mol.

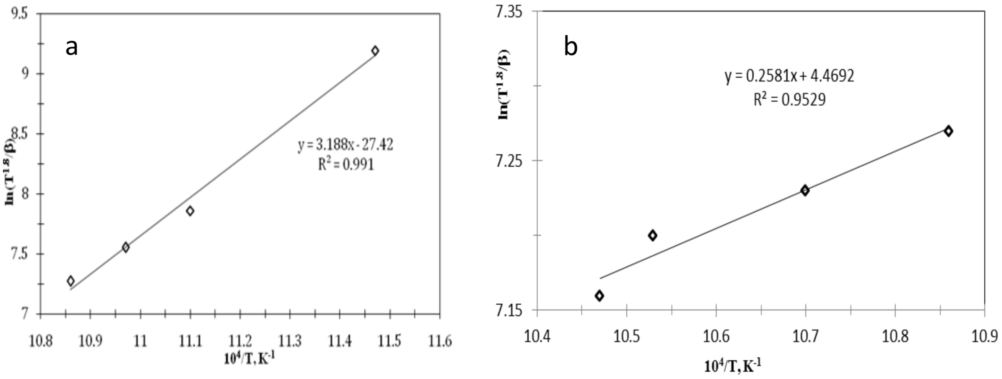

Figure 1. Arrhenius plot for the system PTFE-Al_2O_3: (a) - endothermic peaks of the DSC curves at heating rate of <150 °C/min; (b) - exothermic peaks of the DSC curves at the heating rate of >150 °C/min.

Experimental study shows that at the exothermic mode the PTFE reacts with Al_2O_3 in a single step producing AlF_3 and carbon. It was demonstrated that the system PTFE/Al_2O_3 is sensitive to heating rates and at the heating rates higher 150 °C/min will be a single stage with exothermic behaviour. The study shows that the PTFE can potentially remove the oxide layer from aluminum and increase the direct contact area between oxygen and aluminum, which increases the reaction velocity and improves the energy discharge in nano systems.

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INTEGRATION OF pGLO TRANSFORMATION OF BACTERIA AND NANO-STRUCTURED THERMITES FOR BIO AGENT DEFEAT SYSTEMS

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Introduction

The possibility of bioterrorism events that can involve the intentional release of airborn contagious agents demand for new and effective approaches for biological agent defeat systems both indoors and outdoors. Novel approaches, including nanostructured high density energetic composites, have strong request for new active materials which can be effective in short period of time in the infected areas. The nanoenergertic gas generators (NGG) [1] can rapidly generate temperature and pressure waves and are currently subject of extensive research. The novel nano-structured thermite formulation I_2O_5/Al was shown to have long term stability and superior release of biocidal substances for destruction of spore forming bacteria [2]. The system of I_2O_5/Al is highly energetic with enthalpy of -25.7 kJ cm^{-3}, which generates high temperatures and large quantity of vaporized iodine for spatial deposition onto harmful bacteria for their destruction. This study shows that the system I_2O_5/Al is extremely effective to sterilize the potentially harmful bacteria in seconds, where the miligrams of nano-thermite is able to disinfect several squares of meters.

Experimental Results and Discussion

The thermodynamic analysis was used to predict the combustion behavior of nanoenergetic system and to predict the optimal concentration of components that will generate maximum vaporization of biocidal substances and adiabatic temperature. The stoichiometric reaction to release iodine gas occurs by the reaction $3I_2O_5+10Al=5Al_2O_3+6I$. The maximum adiabatic temperature reaches 3830 K with huge amounts of gaseous iodine which is in atomic state due to high temperatures, and is the main active disinfection and biocidal product.

To obtain quantitative results with statistical data we use the technique called the pGLO transformation of bacteria with a gene that codes for Green Fluorescent Protein (GFP). We use the Escherichia coli bacteria HB101 K-12 strai which is not a pathogenic organism like the E. coli strai O157 H7 that has sometimes been implicated in food poisoning. HB101 K-12 has been genetically modified to prevent its growth unless grown on an enriched medium. Following the transformation procedure, the bacteria express their newly acquired jellyfish gene and produce the fluorescent protein which causes them to glow a brilliant green color under ultraviolet light, which allows us to use UV microscope technique. We exposed the colonies of bacteria to the nanothermite explosion. The samples were attached inside hermetic container far from explosion center from 0.25 m to 0.7 meters. A hermetically closed plexiglass chamber with dimensions 20x20x70 cm was used to make micro explosion inside, using electro detonator technique to ignite the micro charge (Figure 1.a). The effective explosion takes place if the charge mass is about 0.1 g. We prepared the thermite mixture in ratio I_2O_5:Al=7:3.

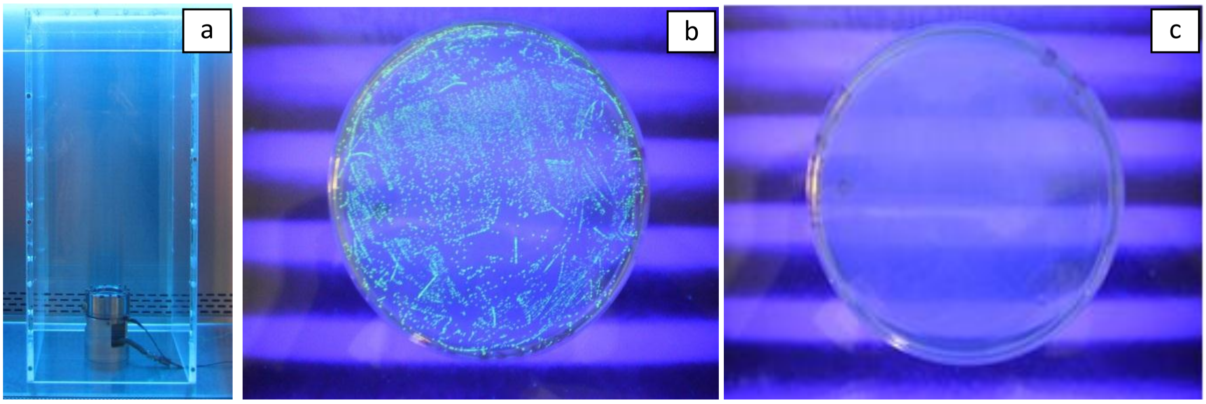

Figure 1. (a) - The hermetic explosion champer; (b) - bacteria colonies before treatment; (c) - colonies after treatment.

We investigated the effect depending on mixture weight, as well as exposure time and sample distance from explosive. All samples were completely disinfected (Figure 1, b,c). The estimation of concentration of iodine shows that minimal effective content over infected area was 22 mg/m^2. Thermite mixtures less than 0.05 g are not enough powerful to initiate explosive reaction to transfer atomic iodine to several meters. For decontamination purposes, 0.1-0.3 g capsules will be sufficient to sterilize several square meters in seconds.

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INFLUENCE OF HEATING RATE AND QUASI-STATIC COMPRESSION ON ELECTRO THERMAL EXPLOSION REGIMES IN TI–C SYSTEM

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The influence of quasi-static pressure on preheating temperature and ignition point for the Ti–C system was explored by electrothermal explosion (ETE) . The pressure used in experiments was 24 – 96 MPa and heating rates for samples reached 200 cal/s.

Stoichiometric mixtures of titanium (PTK brand) and carbon black (T804 brand) were pressed into cylinders 12 × 17 mm with a relative density of 0.6.

Dependence of ignition point (curves 1, 2) and preheating (curves 3, 4) on heating rate at pressure 24 and 96 MPa is given in Figure 1.

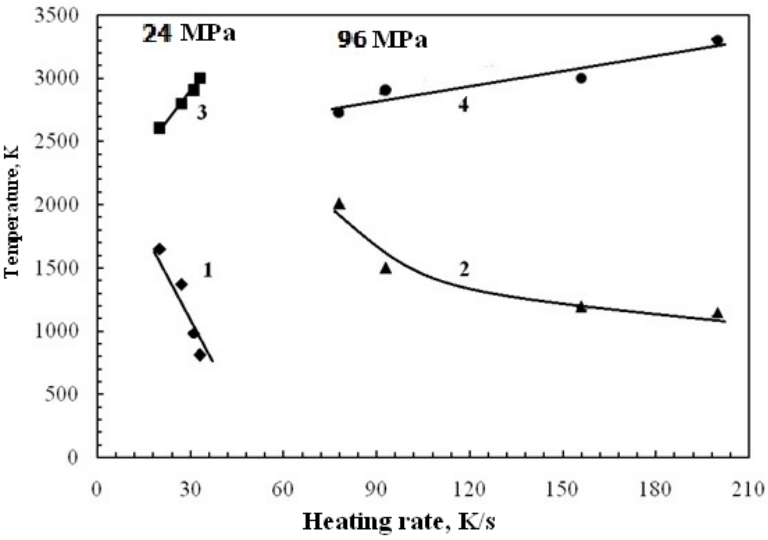

Figure 1.

The rise of heating rate causes a decrease in the ignition point (1, 2). At 24 MPa (curve 1) the ignition point dropped from 1700 to 800 K while at 96 MPa, from 2000 to 1100 K (curve 2). Besides, an increase in the heating rate leads to maximum heating (Table 1).

Table 1.

Compression, MPa	Δ in heating rate, K/s	Maximum heating, K

24	From 20 to 35	2600–3000 (curve 3)
96	From 20 to 35	2700–3300 (curve 4)

The described effects are due to interaction between the components during preheating. The interaction occurs by the mechanism of reactive diffusion. Due to formation of a layer of titanium carbide on Ti particles, the rate of the reaction decreases. The releasing heat passes into dispersed media thus decreasing the supply of reaction heat. The longer is preheating, the larger is the burning velocity and less is the heating source power. That is why the compression raise prolongs the ignition time and makes the ignition point higher.

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PRESSURE ENHANCEMENT IN Al-I_2O_5 NANOENERGETIC THERMITE

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Nano-energetic thermites are powder mixtures of metal and oxidizer components, at least one of which is in nano-metric dimensions. A promising nano-energetic thermite is the Al-I_2O_5 system [1]. In this report we studied the impact of high-energy ball milling of the oxidizer I_2O_5 on gas generation feature. Milled I_2O_5 is mixed with aluminum powders and the pressure discharge properties of nano-sized Al-I_2O_5 mixture are compared. Thermo-gravimetric analyses (Figure 1) demonstrated that short ball milling of I_2O_5 significantly decreases the decomposition energy of the oxidizer. For the milling time of 15 min, the decomposition energy of I_2O_5 was 495 J/g which is 20 % less than that of commercial I_2O_5 powder. The main assumption for milling of iodine pentoxide was that mechanical milling might increase structural defects within the oxidizer, ultimately reducing the particle dimension.

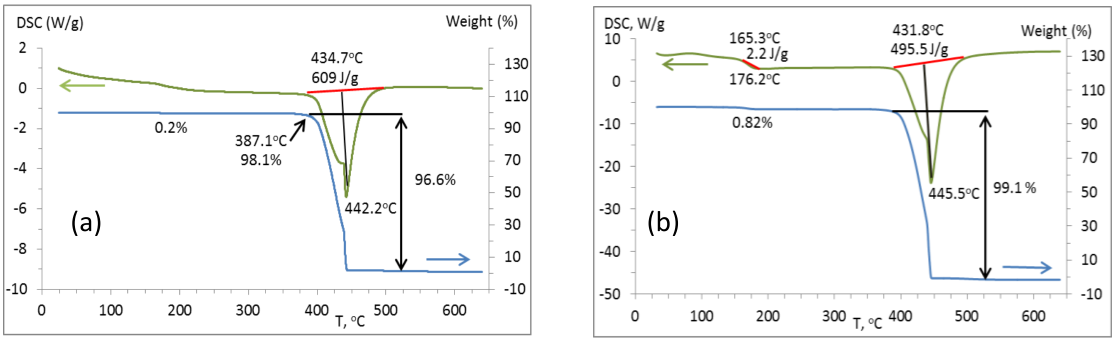

Figure 1. (a) DSC of commercial I_2O_5 (b) DSC for I_2O_5 milled 15 min with high-energy ball milling.

The increase of crystallographic defects will decrease the decomposition energy of the oxidizer, which in turn is beneficial for the thermite made with it. Some of the energy released during thermite reaction will be consumed for the decomposition of the oxidizer. Thus, if the decomposition energy is lower, the thermite will be richer with energy, which ultimately will enhance the pressure discharge value.

Pressure discharge values were obtained from various samples, including milling times of: 10 seconds, 2 min, 15 min, 20 min, and 30 min. If it is assumed that the ball kinetic energy is dissipated by the powder, the impact energy (E) during mechanical treatment is given by $E = 1/2\ m_b V^2$, where m_b is the ball mass and V is the impact velocity. The total energy transferred per unit mass of powder, i.e., the specific energy dose, D_E (= NEt/m_p), was estimated to be 1458 kJ/kg. Additionally, the oxidizer powder was milled with a roller mill for 9 hours. The estimation of the energy transferred to the powder in this stage gives values less than 1 kJ/kg, which is negligible compared with high-energy ball milling. However, the final 9 h ball milling is necessary to produce nano-sized oxidizer particles.

The mechanical treatment of iodine pentoxide oxidizer in the Al-I_2O_5 thermite system has a crucial role in increasing discharge pressure from 22 MPa/g to 44 MPa/g. Thermo-gravimetric analyses showed that the decomposition energy is minimal for the 15 min treated iodine pentoxide with the milling energy of 730 kJ/kg, resulting in the highest energy concentration for the thermite prepared with this powder. The basic reasons for the increase in potential energy within the thermite are due to the reduction in particle dimension by increasing structural defects via high-energy ball milling. The milling time of 15 minutes produces an ideal particle size 30 nm which increases the interfacial contact between the fuel and the oxidizer. Increased interfacial contact results in accelerated rates of heat transfer and mass diffusion. Pressure discharge experiments indicated that the thermite prepared with 15 min milled I_2O_5 has the pressure of 44 MPa/g, which is twice higher than the same value for the thermite prepared with commercial I_2O_5 powders, and up to 20 times higher than that of the other thermite systems such as CuO/Al, WO_3/Al, Fe_2O_3/Al and MoO_2/Al.

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THE FEATURES OF PHASE FORMATION IN PRELIMINARY ACTIVATED 3Ti +Al POWDER MIXTURE DURING THE DYNAMIC THERMAL EXPLOSION

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In the recent years, the combination of the SHS and mechanical milling has attracted a lot of interest. Intermetallic compound Ti_3Al in the bulk form and in the form of coatings is in high demand in various branches of engineering [1]. The goal of this work was to find the optimal mode of combustion of 3Ti+Al activated powder mixture in the dynamic thermal explosion mode in order to obtain the single-phase compound Ti_3Al. The mechanical milling was performed in the AGO-2 planetary ball mill with two vials. The characteristics of the mill were the following: the volume of the vial - 160 cm^3, the ball diameter - 8 mm, the powder mass in each vial - 10g, the mass of the balls - 200 g, the centrifugal acceleration of balls - 400 ms^{-2}. The milling time was 7 min. The intermetallic phases did not observe after milling process. The next stage of experiment was the synthesis of milled powder mixture. For this purpose, we used high – frequency induction heating [2,3]. High – frequency induction coil heated the graphite die in which there was a powder mixture. The next parameters of the heating were changed: 1. Heating rate (the inductor power); 2. Annealing time after realization of the thermal explosion. The characteristic thermograms are presented in Figure 1.

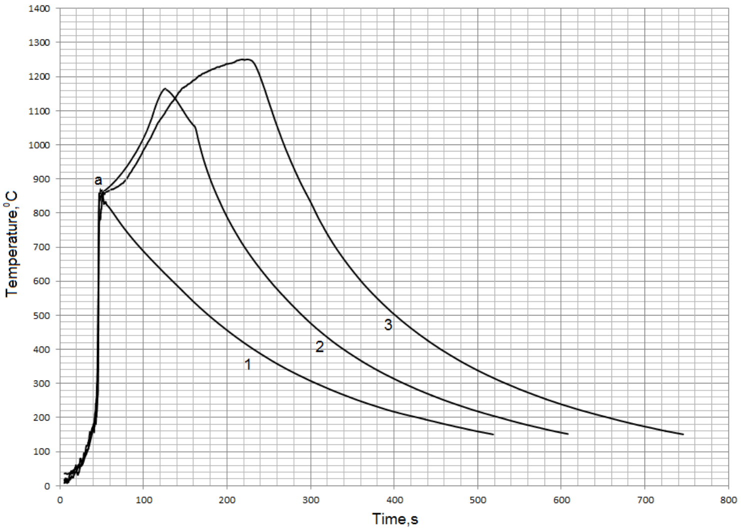

Figure 1. The characteristic thermograms for 17W of useful power of heating: 0 - 1 min. of annealing; 1 – 2 min of annealing; 3 – 4 min of annealing.

As follows from the Fig.1, the reaction occurs in the solid state. It should be noted, that there is the characteristic kink on the all thermograms (near 850^{0}C, the point a). We can assume that one of the diffusion components dissolves in another one during reactive diffusion (probably aluminum) and disappears at the point a. In the experiment 1 (Fig.1), the single phase product of reaction Ti_3Al was observed. But the diffraction peaks were abnormally broadened. Thus, the crystal lattice of the product has nonequilibrium defects. The crystal lattice moves in a perfect state only in the case 3 (Fig. 2).

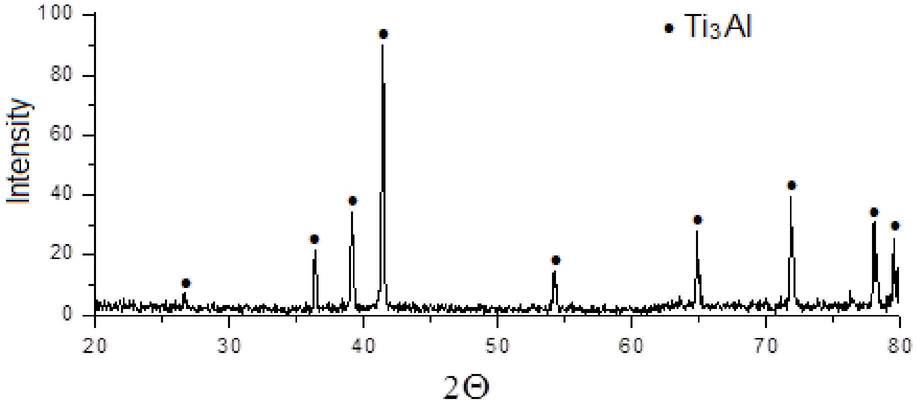

Figure 2. X-ray patterns of thermal explosion product for the case 3 (Fig.1).

In the all cases, the product is a poorly sintered powder. For the power of heating 10W, the product of reaction is not a single phase compound. The maximum temperature of the synthesis was 955^{0}C. One can observe the peaks of titanium and the peaks of product Ti_3Al which are abnormally low and broad. Consequently, the heating rate has the significant effect on the process of phase formation for activated system. For the power of heating 40W, the product is the strictly single-phase compound Ti_3Al and it has the monolithic, non-porous structure when the annealing time is 110s. It can be explained by the fact that the maximum temperature of the synthesis was 1540 ^{0}C. It is much higher than the melting point of Ti_3Al (near 1180 ^{0}C).

As follows from the above, there is a possibility to control both the phase composition and the microstructure of the reacted mixture by the change of the heating rate of the mixture and by the change of the annealing time after thermal explosion.

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HIGH DENSITY NANOENERGETICS AND MEMS PLATFORMS FOR MICROPROPULSION SYSTEMS

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Among common thermite composites, the Al/Bi_2O_3 and Al/I_2O_5 mixtures ensure high energy density and produce very high pressure impulses due to an evaporation of bismuth or iodine which boils at temperature 1560°C and 184°C, respectively [1]. The thermite reactions:

$$Bi_2O_3 + 2Al = Al_2O_3 + 2Bi + \Delta H\ (-\,15.2\ kJ/cm^3)$$
$$3I_2O_5 + 10Al = 5Al_2O_3 + 6I + \Delta H\ (-\,25.7\ kJ/cm^3)$$

lead to energy and gas release. The boiling temperatures are lower than the maximum reaction temperature, which is ~2000°C.

The integration of Al/Bi_2O_3 and Al/I_2O_5 energetic clusters with micromachining and microelectronic technologies enables advanced micropropulsion devices with microelectro-mechanical systems (MEMS) [2]. The *bulk* and *surface* micromachined, as well as the MEMS technology are used to fabricate microthrusters and functional microthruster arrays for micro- and mini flight and marine vehicles. The possible applications for our integrated platforms are: (i) High-accuracy positioning, orientation and path control for micro-satellites; (ii) Explosive, ignition and detonation structures and platforms; (iii) Energy and power systems; etc. Complex three-dimensional micro-thrusters with optimized three-dimensional chamber and nozzle geometries are designed. Silicon and silicon-compatible enabling structural materials ensure the required tensile strength, elasticity, robustness, modularity and other characteristics. The major thruster core and support structures are comprised from silicon-micromachined chamber and nozzle. There are no channels, pumps, valves, propellant tanks, fuel lines, etc.

The combustion of self-assembled nanoenergetic clusters in micromachined micro-chambers ensures high and uniform exhaust velocity v_e along the thrust axis, where the *net* thrust is $F = \dot{m}_e v_e = \dot{m} v_a + A_e(P_e - P_a)$, where $\dot{m}_e$ is the propellant exhaust gas mass flow which depends on the propellant combustion rate $\dot{m}$; v_a is the actual exhaust velocity at nozzle exit plane; A_e is the flow area at the nozzle exit plane; P_e and P_a are the static pressure at the nozzle exit plane and ambient pressure. An array configuration of the microthruster cells, as illustrated in Figure 1 (left), ensures desired fast burning and specific impulses. The self-assembled nanoenergetic clusters can be encapsulated or embedded using robust encapsulation or dispensing. The schematic of single micro-thruster structure (center) and fabricated MEMS and sensors are shown in Figure 1.

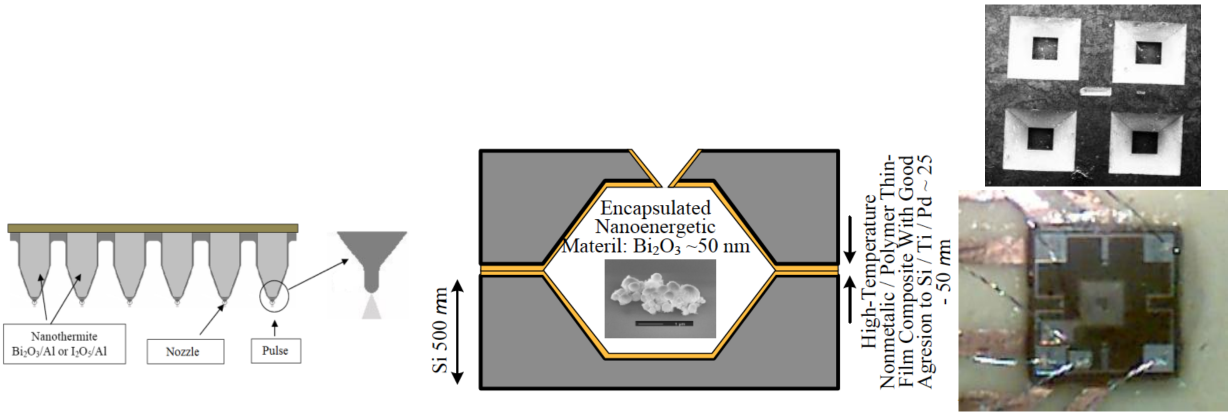

Figure 1. Left: An array configuration of the microthruster cells; Center: Schematics of single micro thruster structure; Right: Silicon MEMS structures for microthruster arrays.

We consider different concepts and designs of encapsulated nanoenergetic clusters within integrated MEMS, which include microelectronic controlling, sensing, diagnostics and processing ICs. The microthruster arrays can be made by using multi-layered silicon, glass and polymer layers, while the middle layer or cavities consist of encapsulated combustible solid nanoenergetic propellants. The polysilicon heaters can be activated by applying a dc voltage. The heater temperature reaches ~700°C due to the flow of current thereby igniting the encapsulated nanoenergetic propellant. As a propellant is ignited, a high-pressure is formed within a high-temperature gas phase. Cells can be separately ignited, producing desired thrust. Microthrusters can be controlled and ignited within the desired sequence using ICs. Various sensors can be used in our highly-integrated and modular MEMS platform. The microthruster array may be designed within different micro-chambers configurations and optimized three-dimensional geometry.

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HIGHLY ALIGNED GRAPHENE-INCORPORATED DOUBLE BASE TYPE PROPELLANTS FOR DIVERSE ENERGY APPLICATIONS

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Extensive research in the area of nanoenergetic materials for propellants and energetic fuels has led to the development of new reactive systems. These reactive systems must possess high ignition sensitivity, reaction rates, and high adiabatic temperature. Different compositions and synthetic routes have been investigated during the past several years. These materials are mainly a mixture of two components: one is defined as a fuel and the other is an oxidizer. Nitrocellulose (NC) based propellant formulations are well studied [1], and have a wide range of aerospace and civilian applications. These formulations are highly used as smokeless explosives for small arms, solid fuel rockets engines and in the construction industry. Conventional NC based double base solid granular propellants generally include NC, NG, organic or inorganic salts as a modifier or stabilizer, and other fillers such as carbon black or graphite powder. The sensitivity of the propellant depends on the type of filler material, its particle size and shape [2]. These materials have been modified for their particle size and method of use such as coating or mixing directly in a propellant where they are mixed with binders and plasticizers in a composition. Recently, graphene has been identified as the next generation filler material for propellant formulations for military applications.

Due to its remarkable properties such as high electrical, mechanical and thermal properties, it opens a new class of energetic materials. However, its use in energetic materials is not fully explored.

In this report, we describe innovative approach for incorporating graphene into energetic formulations with minimum restacking of the sheets and improving the intermixing properties based on the phenomenon of solution processing. The effort aim is to disperse and align the graphene-based fillers through innovative methods. We propose to synthesize highly reactive energetic homogeneous double base propellants with high burn rate performance adapting the slurry casting methods. Graphene, which is a one atom thick planar sheet of sp2-bonded carbon atoms, has been attracting great interest in the field of nanoenergetic materials due to its structure and properties. Graphene is potential nano filler that dramatically improves the properties of polymer-based composites at a very low loading. Properties like tensile strength, elastic modulus, thermal conductivity etc. are greatly improved. However, to take full advantage of its properties for the proposed applications, integration of individual graphene or functionalized graphene in polymer binder matrix with uniform alignment is a key to enhance composites energetic properties.

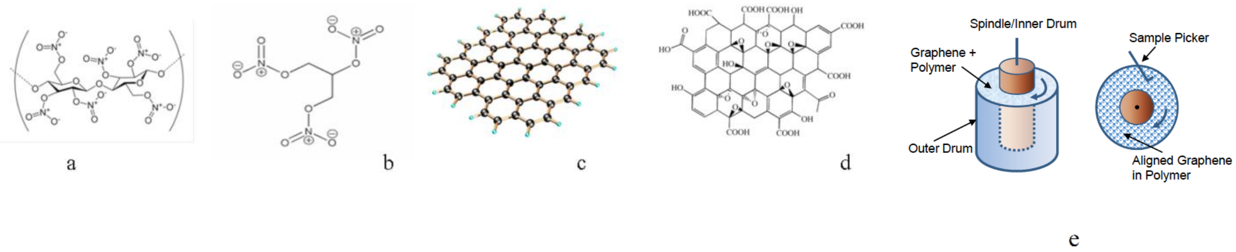

Figure 1. Chemical structures of (a) Nitrocellulose, (b) Nitroglycerine, (c) Pristine graphene, and (d) graphene oxide, (e) shear flow method apparatus to rotate the dispersed graphene-propellant polymer solution.

A chemical approach (cross or non-cross linking) to disperse these graphene-based fillers in an orderly pattern without restacking is the focus of this project. We used shear flow method to align graphene in an NC based formulation. A simple shear flow set up is shown in Figure 1, well dispersed graphene-propellant polymer solution is rotated in uni-directional motion using an inner spindle rotating inside an outer cylindrical drum. This motion of the graphene-propellant solution does not damage the well-dispersed state of graphene particles and at the same time aligns the graphene particles. The morphological structure and extent of energetic properties like impact, friction and front wave velocity against the standard graphite-based propellants are evaluated by using methodology described in Ref [3].

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THE INFLUENCE OF MECHANICAL ACTIVATION CHARACTERICTICS ON THERMAL EXPLOSION FOR TI-NI SYSNEM

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The work presents experimental study of influence of conditions of Ti – Ni mechanical activation (MA) on temperatures of following thermal explosion and composition of synthesized product. Changes in morphology and composition of the powder mixture under study caused by variation in total MA time were found to markedly affect the thermal parameters and composition of synthesized product. It shown, dependences of thermal explosion characteristics as function MA time are non-monotone. The cause of discontinuous changes is sticking a plastic component to the surface of milling bodies and deviation of activated composition of green composition of mixture.

EXPERIMENTAL

MA was performed in planetary ball mills with 45 *g* and 60 g. under argon and air atmosphere and time periods of 1–9 min. Starting equiatomic Ti–Ni blends were prepared as containing 55.06 wt % Ni. Sample temperature was monitored with a chromel–alumel thermocouple linked to a PC to determine the critical and maximal temperatures. Green mixtures and combustion products were characterized by SEM, optical metallography (Anxiovert 200M), and XRD (DRON-UM).

RESULTS AND DISCUSSION

The dependences of thermal explosion characteristics (critical and maximum temperature of thermal explosion) as function MA time have non-monotonous behavior at any variation MA conditions [1, 2, 3]. The dependences of synthesized phase quantity as function MA time also have the same non-monotonous behavior. The MA process is also accompanied by sticking a plastic component to the surface of milling bodies, which can be expected to affect the Ti and Ni content.

Study of XRD patterns follows that the Ti lines attain their minimal intensity at the same MA time when dependences of thermal characteristics and synthesized phase have jumps.

Therefore, changes in critical and maximum temperature of thermal explosion and quantity of synthesized phases can be associated with the adhesion of Ti to the surface of milling

bodies and subsequent return (desorption) after some MA time.

CONCLUSIONS

The changes of temperature characteristics of the thermal explosion take place because of sticking a plastic component to the surface of milling bodies that leads to composition changes of powder mixture.

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CONVERSION OF ALUMINUM FOIL TO POWDERS THAT REACT AND BURN WITH WATER

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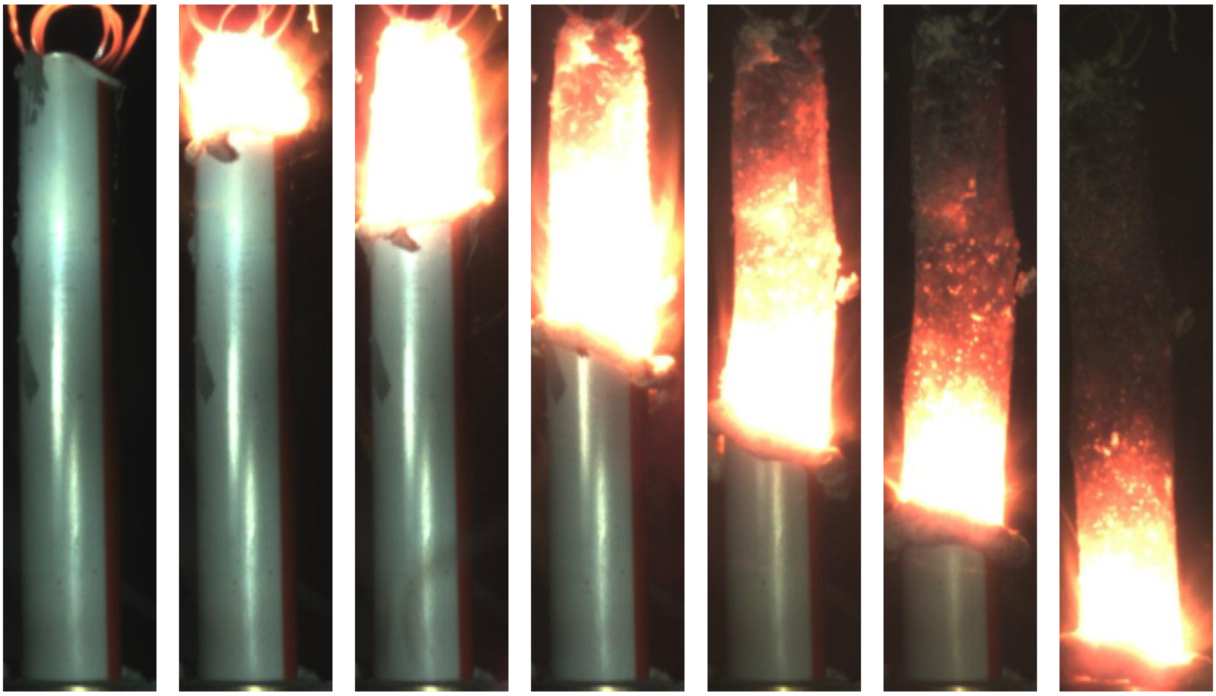
In the U.S., the total amount of aluminum scrap and waste, including foil, is outpacing efforts to recycle it into conventional aluminum materials [1]. It would be attractive to develop technologies for converting aluminum foil scrap and waste to useful products and energy carriers. The present paper focuses on the feasibility of converting foil to activated Al powders that chemically split water, releasing hydrogen.

Aluminum foil (thickness: 15–100 μm) was converted to a powder by high-energy ball milling with sodium chloride. The powders were characterized using BET specific surface area analysis, laser diffraction particle size analysis, scanning electron microscopy, and energy dispersive X-ray spectroscopy.

The reactions of the obtained powders with deionized water were studied over a temperature range of 35–80 °C. Hydrogen evolution was studied using water displacement, while solid byproducts were examined by X-ray diffraction and thermal analysis. It was shown that the obtained micron-sized powder readily reacts with hot water, releasing hydrogen. Milling in inert (argon) environment increases the final reaction extent up to 98%. After washing NaCl out of the powder, using cold water or methanol, the remaining Al powder retains the high reactivity with respect to hot water.

The obtained Al powder was mixed with gelled (3 wt% polyacrylamide) water over a wide range of Al–H_2O mass ratios and combustion of these mixtures was studied in argon environment at 1 atm. Stable propagation of the combustion front was observed at Al concentrations from 40 wt% to 80 wt% (Fig. 1). The obtained micron-sized Al powders provide the combustion front velocities that are comparable with those for nanoscale Al powders [4, 5], while offering a higher content of active aluminum.



0 2 s 4 s 6 s 8 s 10 s 12 s

Fig. 1. Propagation of the combustion front over Al/H_2O mixture at 40 wt% Al. Time zero was selected arbitrarily.

The conversion of aluminum foil to activated powders may help mitigate the problem of growing surplus of Al scrap and waste in the U.S. The obtained powders could be used for low-temperature and combustion reactions with water in various applications.

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CHARACTERIZATION OF RAPIDLY-REACTING POROUS SILICON FILMS

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The material properties of porous silicon; high surface area, nanometer scale features, and potential for high energy density make it an intriguing candidate for a variety of applications, including in energetic materials. The use of readily available silicon substrates and MEMS fabrication processes further its value and allow for relatively easy integration with existing MEMS technologies. There are limited studies on the key components of porous silicon combustion [1, 2, 3, 4], and none have performed an in depth study on the role of material properties on rapidly combusting systems. Our group has previously demonstrated the fastest propagation speeds for porous silicon combustion (>3000 m/s [4]), but only basic analysis on the effects of pore size, surface area, porosity, etc. This work investigates the role that various material properties play in the reaction of rapidly combusting porous silicon/sodium perchlorate systems.

Porous silicon films are formed on boron doped, <100> oriented wafers with an LPCVD silicon nitride (Si_3N_4) front side, and a platinum back side. Basic photolithography techniques can be used to selectively expose bare silicon in 2.5 x 0.3 cm strips, which also contain a gold igniter wire. These strips are subsequently exposed to an electrochemical etch process involving a hydrofluoric acid/ethanol/hydrogen peroxide solution to form porous silicon strips. Sodium perchlorate is used as the oxidizing agent in this system, and a 3.2M solution with methanol is allowed to soak into the pores and then dried prior to combustion. Porous material characteristics can be easily altered through variations of the etch solution, i.e. increased concentrations of hydrofluoric acid typically result in smaller pores. Alternative wafer resistivities are also employed to produce an even wider range of pore size. Flame speed characterization is done with a Photron FASTCAM SA5 high speed camera at 930,000 frames per second.

To determine the role of porous silicon material properties on combustion, the pore size, porosity, surface area, film depth, are all related to the flame speed for each respective etch condition. A clear trend is demonstrated for the pore size as shown in Figure 1, with a peak in flame speed at ~3.3nm. This is consistent with some works performed at slower flame speeds [2], but does not agree well with others. The trends for other material properties are less clear, suggesting that pore size and diffusion distance between the fuel and oxidizer are the limiting conditions for combustion. At very small pore sizes we predict that oxidizer impregnation is limited, resulting in fuel rich mixtures and lower flame speeds.

This is a necessary fundamental study for porous silicon combustion, and is providing the basis for other works. Experiments currently underway include implementation of microstructure in porous silicon films, novel oxidation methods, analysis of reaction products, and combustion under various environmental conditions.

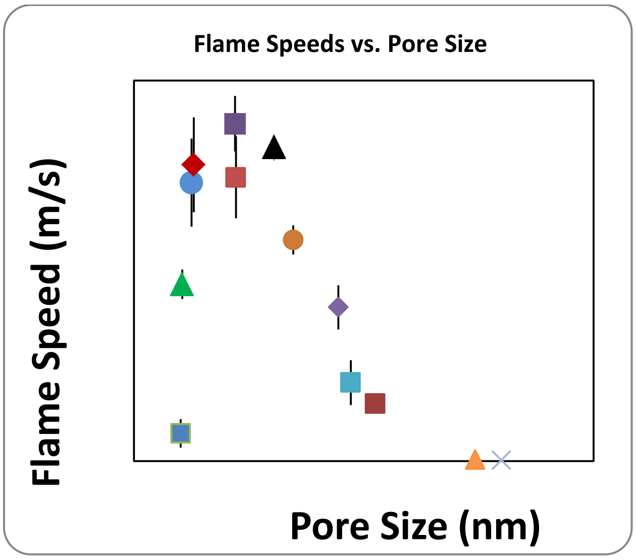

Figure 1: Flame speed dependence on pore size for porous silicon/sodium perchlorate systems.

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COMBUSTION CHARACTERIZATION OF BLADE CAST MAGNESIUM AND MANGANESE DIOXIDE

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There is a current need for low cost heat sources for a variety of applications, from local joining and welding, to providing local heat for power sources. Thermite energetic composites have been developed for use in welding and joining [1] as well as for thin film heat source applications [2]. Thermite, consisting of a metal fuel and an oxidizer, has been extensively researched for a large variety of specific formulations. Recent developments have included the study of nanopowder materials, which are, in general, more energetic. Many of the thermite compositions studied have a high degree of gas generation. However, for some applications, high gas generation may not be desirable.

In this work, powders of magnesium and manganese dioxide were mixed with a fluorpolymer or paraffin binder and blade cast onto a stainless steel foil substrate. The three binder-solvent systems investigated were Methyl Pyrrolidone (NMP) and Polyvinylidene Fluoride (PVDF), Acetone and Viton A, as well as Paraffin and Xylene. Films were prepared by mixing the energetic composites with the binder and solvent to create a 40% solids content suspension, and then casting onto stainless steel foil to a 200um wet film thickness. In this study, binder content and type was varied and calorific output and open flame propagation speed was investigated for each mixture ratio. Additionally, SEM images of sample cross sections were taken to obtain some information about the mixing condition.

It was found that calorific output increased with increasing binder content, to a maximum observed value of 954 calories per gram, indicating participation of the binder in the exothermic reaction. As Viton and PVDF are both fluorocarbons know to be used as oxidizers, this result is not unexpected. Additionally, Paraffin has been used as a fuel for some applications, and may have participated in the reaction in this capacity.

Flame speed was shown to decrease with increasing binder content, with a maximum recorded value of 0.14 m/s for unconfined tests. As the Magnesium and Manganese Dioxide thermite is a theoretically gasless reaction, flame propagation relies heavily on convection and particle advection. Decreased flame speed with increasing binder content may be due to the lower thermal conductivity of the binder, which lowers the thermal conductivity of the overall composite. This inhibits the primarily convectively driven flame front, or promotes some mechanism that blocks propagation with increasing binder content. Although conventional wisdom would suggest that high calorific output results in higher flame speeds due to more available thermal energy, the converse relationship was shown in this study, showing that the increase in available chemical energy was not enough to overcome the decrease in thermal conductivity necessary for propagation.

Confined tests were also conducted for the PVDF/NMP system, with a maximum recorded flame speed of 3.46 m/s. High speed video of the flame propagation shows the flame front, the formation of the solid products, and a small amount of gaseous products generated by the reaction, probably composed of unreacted oxygen and gases produced by the reaction of the binder. The directionalized ejecta plume at the flame front, in conjunction with the pressure wave created by the confined hot gas products, may explain the observed difference between confined and open burn speeds. As the ejecta preheats and ignites the reactants via particle advection, and the gaseous products push the flame forward, the order of magnitude difference between the confined and unconfined tests is entirely expected.

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METAL-BASED REACTIVE MATERIALS WITH BIOCIDAL REACTION PRODUCTS

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Recently, research has been active in developing reactive materials with biocidal combustion products capable of inactivating aerosolized microorganisms. Primarily, the focus is on additives to energetic formulations involving halogens, known to have strong biocidal properties. Materials developed to date can be classified into three main groups: metal-based fuels, oxidizers, and thermites (metal fuel and oxidizer compositions) with at least one component producing biocidal combustion products. In addition to generating the desired combustion products, reactive material components must be stable and compatible with common binders to endure conventional processing routine. Furthermore, insensitivity to spark and other common ignition stimuli is also desired for material handling.

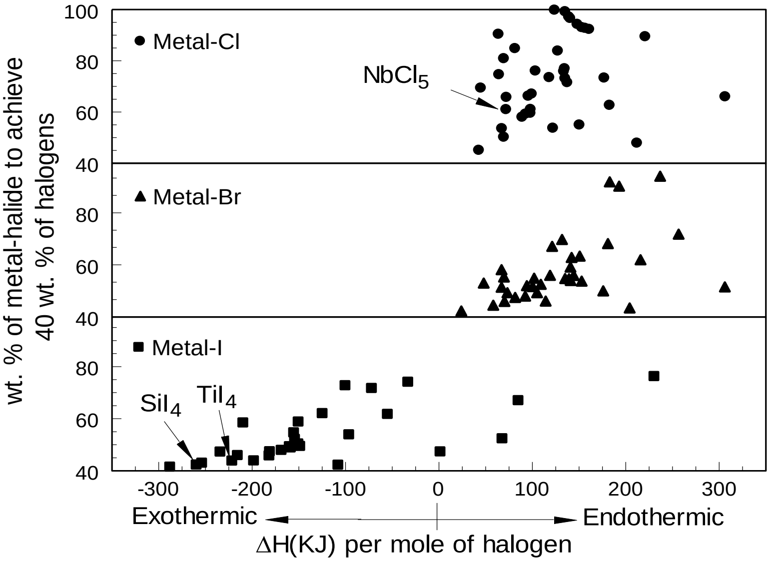
Our work has focused on incorporating halogens or halogen containing compounds in metal fuels. Specifically, aluminum-based powders containing up to 20 wt % of iodine with compositions of $Al\text{-}I_2$ [1], $Al\text{-}B\text{-}I_2$ [1], and $Al\text{-}CHI_3$ have been developed and tested. In this paper, efforts aimed at developing new metal-based components with substantially increased halogen contents will be discussed.

The main challenge is to stabilize the halogen in a reactive metal matrix, so that the material can be handled and formulated as a regular metal fuel, e.g., aluminum powder, commonly added in energetic formulations. The approach taken in this study is based on mechanical alloying (or ball milling) starting metal powder and a halogen-containing material to produce a stable composite powder. Previous work showed that cryo-milling was necessary to stabilize iodine in aluminum matrix. Milling at room temperature could be used to stabilize iodine in a binary Al-B composite. However, the amount of iodine that could be stabilized could not exceed 20 wt %. Thus, new material compositions need to be explored to produce materials with greater halogen concentrations.

To select most promising halogen-containing starting components, properties of different metal halides were surveyed ranking them based on the maximum enthalpy, ΔH, required to convert the halide into the most stable metal oxide and oxidized halogen. This enthalpy is taken per mole of halogen. The results are shown in Fig. 1 where the estimated reaction enthalpy is plotted vs. the weight % of the respective halide that should be added to aluminum in order to prepare a reactive material with 40 wt. % of halogen. The 40 wt % benchmark doubling the presently achieved content of iodine in the Al-based powders serves as a target halogen content for the new reactive materials. In Fig. 1, the most desired compositions would have the greatest negative reaction enthalpy and the lowest wt. % of metal halide (allowing their encapsulation into aluminum matrix); thus, they would be represented by symbols located at the lower left portions of the plots, shown separately for chlorine, bromine and iodine. It is clear that the iodine-containing materials are most favorable energetically. Among all materials considered, only a few could be selected taking into account their toxicity, stability, and cost. In particular, TiI_4 is selected for initial experiments. Because SiI_4 is not readily available commercially, ball-milling elemental iodine with Si and Al is also of interest. In addition, a chlorine-containing starting material, $NbCl_5$ was selected to evaluate the effect of chlorine as a biocidal fuel additive.

Preparation, characterization, and testing of several new halogen-containing Al-based fuels will be discussed. Both stability and oxidation mechanisms of the prepared materials are assessed using thermal gravimetry performed, respectively in inert and oxidizing gas environments. Materials are further characterized using x-ray diffraction and electron microscopy. Ignition of the prepared powders is studied by coating them onto an electrically heated filament. Combustion dynamics of the prepared powders is tested by feeding them into a hydrocarbon flame and measuring intensities and durations of the emission pulses produced by particles.

Figure 1: Survey of metal-halide oxidation enthalpies



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MULTISTEP REACTION MODEL FOR IGNITION OF NANOCOMPOSITE THERMITES WITH DIFFERENT COMPOSITIONS

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Nanocomposite thermites are composed of a reactive metal, in most cases aluminum, mixed on the nano-scale with a relatively easily reduced metal oxide. The nano-scale mixing results in a highly developed interface area between reactive components. The high interface area assures a high reaction rate, attractive for many applications. Over the years, nanocomposite thermites have been actively investigated for a wide range of potential applications including propellants, explosives, and pyrotechnics [1-3]. This work considers fully dense nanocomposite powders prepared using arrested reactive milling (ARM) [4] and characterized by high reaction rates associated with nano-scale mixing of reactive components and respective high specific surface area of the reactive interfaces, while offering relative simplicity of handling and mixing, typical for conventional micron-sized powders. The unique interface morphology is thought to cause the exothermic redox reactions in such materials to begin at lower temperatures compared to other types of nanocomposite thermites.

Low temperature exothermic reactions are expected to contribute significantly to the processes that lead to ignition in fully dense nanocomposite thermites [5, 6]. For aluminum-based compositions, there are multiple reaction steps associated with formation of different polymorphs in the growing alumina layer [7], which are qualitatively similar to the steps observed for aluminum oxidation in gaseous oxidizers [8]. Recent work attributed the accelerated oxidation in the ARM-prepared nano-thermites at low temperatures to Cabrera-Mott (CM) reaction [5, 6], where the growth of very thin oxide layers is accelerated by electric field induced across such layers. A reaction mechanism including multiple oxidation steps starting with the CM reaction followed by direct oxidative growth of and phase changes in different alumina polymorphs was developed for a stoichiometric $2Al \cdot 3CuO$ nanocomposite powder prepared by ARM [7]. The reaction kinetics describing these reaction steps were shown to remain valid for the ARM-prepared reactive composites with different scales of mixing, interface morphologies, and component ratios, as long as the components remained Al and CuO [9].

This work presents a further validation and development of this multistep model to describe reaction in another ARM-prepared thermite system, $8Al \cdot MoO_3$. The powder particles comprise a fully dense Al matrix with nano-sized MoO_3 inclusions, similar to those observed in $2Al \cdot 3CuO$ composites. The structure, morphology, and compositions of the $8Al \cdot MoO_3$ nanocomposite powder were characterized using x-ray diffraction, scanning electron microscopy and energy dispersive x-ray spectroscopy. Differential scanning calorimetry (DSC) and thermal gravimetry (TG) data were collected at varied heating rates, in addition to micro-calorimetry data collected both isothermally and at very low varied heating rates. Ignition of the prepared materials was studied using an electrically heated filament coated with a thin powder layer.

The shapes of the recorded DSC and TG traces at low temperatures were substantially different compared to those obtained earlier for $2Al \cdot 3CuO$. The measurements were interpreted for $8Al \cdot MoO_3$restricting the exothermic reaction steps to the same sequence as was identified earlier for $2Al \cdot 3CuO$, including the CM reaction followed by diffusion limited oxidation accompanied by polymorphic phase changes in the growing alumina layer. In addition, endothermic release of adsorbed moisture had to be taken into account in order to match the predicted and experimental thermo-analytical data. The formation of hydrated structures is tentatively assigned to interaction of the MoO_3-containing composite with hexane used as a process control agent and as storage medium for the prepared powders. It was found that the present model, describing multistep exothermic reaction based on changes in transport resistance of the alumina film growing between reactants, remains valid. Activation energies for each reaction step were quantified.

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COMPARISON OF ALLOYING MECHANISM OF Mg-Al HYDROGEN STORAGE ALLOYS PREPARED BY COMBUSTION SYNTHESIS AND MECHANICAL ALLOYING

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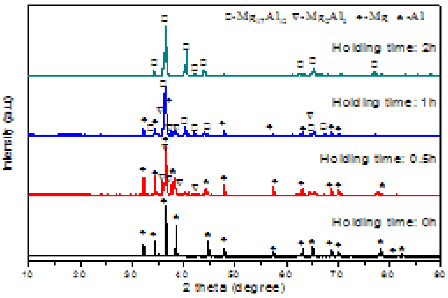
The application of Mg–Al alloys, as well as the hydrides, for hydrogen production has been attracting more and more attention because of their light weight, low cost and high hydrogen storage capacity. However, the preparation of Mg–Al alloys with desired composition is difficult due to its high pressure of vaporization during the conventional melting process of ingot metallurgy. The combustion synthesis (CS) of Mg-based hydrogen storage alloy $Mg_{17}Al_{12}$ has been tried successfully recently by our research team [1] with some advantages, such as low energy consumption, short processing time and high purity of products. Furthermore, an alloying mechanism of $Mg_{17}Al_{12}$ prepared by combustion synthesis method has been proposed, namely, Mg_2Al_3 phase is synthesized first, and then Mg_2Al_3 phase reacts with residual Mg, forming $Mg_{17}Al_{12}$ alloy, which is not consistent in reported results with other preparation process [2]. Fig.1 shows the X-ray diffraction (XRD) patterns of CSed samples prepared at 733 K with different holding times (0 h, 0.5 h, 1 h and 2 h) under argon atmosphere (0.3 MPa). Although there are still many problems for the industrialization of $Mg_{17}Al_{12}$ by CS method, we believe that this alloying mechanism will act as an important role in the research on the application of Mg-Al alloys for hydrogen production. In this work, we conduct the process of mechanical alloying (MA) for the comparison of the alloying mechanism of Mg-Al hydrogen storage alloys prepared by CS and MA. The same commercially available Mg (99.9 wt.% in purity and 45μm in size) and Al (99.85 wt.% in purity and 19-21μm in size) powders at the molar ratio of 17:12 as in our previous CS process were milled in argon atmosphere using a planetary ball milling machine. Fig.2 shows the X-ray diffraction (XRD) patterns of the samples prepared by MA with different milling times. It is revealed that when the milling time is less than 15 h, the phase compositions are Mg and Al and no distinguishable Mg-Al alloys can be observed in the XRD patterns and when the milling time is more than 20 h, the products are amorphous. However, the relative peak heights of Mg and Al are changed apparently because of the large ductibility of raw materials and the formation of specific texture during the milling process. A further study on the microstructure transformations during the mechanical alloying of Mg-based hydrogen storage alloy $Mg_{17}Al_{12}$ in detailed is under going, which should be significant to understand the alloying mechanism of hydrogen storage alloy $Mg_{17}Al_{12}$ prepared by combustion synthesis.



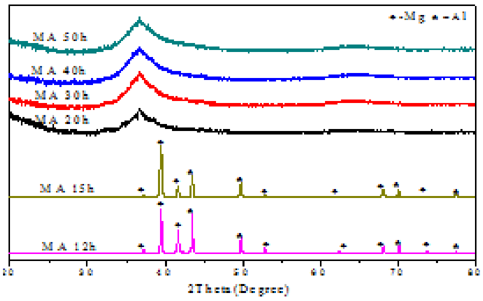


Fig.1. XRD patterns of CSed Mg-Al alloys prepared at 733K with different holding times

Fig.2. XRD patterns of Mg-Al alloys prepared by MA with different milling times

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UNDERSTANDING THE FATE OF NANOPARTICLE REACTANTS DURING THERMITE REACTIONS.

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It is axiomatic that the burning time dependence on particle size follows an integer power law dependence. However, a considerable body of experimental data shows a power dependence less than unity. This implies there are mechanistic aspects of nanomaterial reactivity that are not immediately obvious. In that context we explore through time-resolved mass spectrometry , time-resolved and high heating stage microscopy, and post-inspection of reactive products some concepts on how nanomaterials might be reacting. In particular we find, from MD simulation and time-resolved microscopy that heat generation due to reaction can result in rapid loss of surface area that can help to explain the poor particle size dependence seen in burning studies. This is corroborated by post-inspection which shows that a large faction of product mass is micron sized, and thus must have existed during the whole combustion event. These results imply that loss of surface area mitigates some of the advantages in having used nanomaterial in the first place.

THE PROMISE AND COY OF NANOENERGETICS

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Metallic fuels are attractive alternatives to organic fuels and energetic materials due to their higher energy density and favorable mechanical properties. So far, however, the addition of reactive metals into explosive systems has been limited to blast enhancement due to the relatively slow rate of energy release. It has been proposed that overcoming this limitation requires that the domain sizes of the fuel be reduced to the nanoscale, where the kinetics may reasonably be expected to approach those of conventional molecular explosives. Investigations of such nanometric metal fuel particles have been limited to a small number of systems, and are complicated by the fact that oxidation at the surface of the fuel particles is difficult to avoid. At the smallest domain sizes (< 10 nm), where the kinetics should be most favorable, the oxide layer at the surface of the metal fuel particles takes up a significant portion of the volume, thereby introducing unacceptable amounts of inert material. Recent promising experiments have revealed that certain compositions and morphologies of nanometric clusters[13](e.g. Al_{13}) are preferentially resistant to unintentional oxidation; however, a general methodology for producing such clusters and investigating their macroscale stability is still lacking.

In order to investigate the limits of solid state reaction rates for such systems, AFRL has constructed an instrument capable of assembling energetic core-shell nanoclusters at low temperature and deposit them onto a substrate to build up a thin film. The new instrument, known locally as the Superfluid Helium Droplet Assembler (SHeDA), utilizes the low temperature dissipative environment of liquid helium to cool and condense material picked-up into the droplets and then transports them to the deposition substrate.

Over the last few months, this program has focused on developing tools that can fully characterize the cluster formation and deposition process. These efforts include:

1. Characterization of deposition rates and sticking coefficients for as-assembled and deposited energetic nanoclusters composed of Al, Mg, and Ni.
2. Evaluation of the structure, morphology, and reactivity of as-deposited nanoclusters via X-ray diffraction, electron microscopy, and burn rate analysis.
3. Incorporation of an infrared optical parametric oscillator, which will be an in-situ probe of reactivity and structure of clusters in flight.

Additionally, films of HI_3O_8 (a hydrated form of I_2O_5) were investigated for their potential as an oxide matrix for future inclusion/blending with fuels (Al, Mg, etc). Recrystallization of HI_3O_8 in various alcohol/ketone/ester blends using ultrasound will be presented and discussed. Furthermore, utilizing the aforementioned suspensions, the effects of relative humidity (RH) and spin coating rate on the film properties are investigated and reported. Sonication of HI_3O_8 in alcohol blends is an effective method for decreasing the particle size and improving the uniformity of the particle morphology, which is desirable for blending purposes. However, UV-visible spectroscopy and gravimetric evidence suggests that minor side reactions are occurring between the alcohol and iodine oxide species thus forming iodine (I_2) which has been showed to lower the pH (~7 → 4) of alcohol/water mixtures. Powder X-ray Diffraction (PXRD), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), IR and Raman spectroscopy show that the deposited films are of equal or higher purity than that of the starting material. PXRD results suggest that films generated from increasing the spin rate are more inclined to align their crystal lattice planes normal to the substrate surface. Scanning

Electron Microscopy (SEM) images showed that layering of individual oxide coatings can be influenced by the spin rate. Adsorption of H_2O vapor by the particles are most prominent with smaller particles (few microns), which are highly susceptible to deliquescence. Particle structure due to RH and/or spin coating rate was observed and showed that smaller particles are more susceptible to undergo morphological changes into specific crystallites given certain conditions (particle → rods, plates, etc). Ultimately, these oxide films generated with the above mentioned processes provide an alternate route to engineer unique structural motifs for future sub-gram scale energetic materials.

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RECENT ADVANCES IN THE FORMATION OF THIN SELF-PROPAGATING COMPOSITE SUBSTRATES AND REACTIVE INKS

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Scaling of reactant particles or reactive layers from micron size to the nano-level is a concept that has received much attention over the past two decades in the study of thermite, intermetallic and other strongly exothermic reactions. The reduction in size and subsequent increase in specific surface area allows for much faster reaction rates, easier ignition, and a wider range of tunable energy outputs. Commonly comprised of micron scale aluminum and iron oxide powders, thermites are characterized by their very exothermic heats of reaction (up to 6 kJ/g) and high reactions temperatures (in excess of 3000 K) [1]. The reaction that occurs is simply an oxidation/reduction reaction between the aluminum or another elemental fuel and the metal oxide oxidizer. This oxidation/reduction concept has been extended to include multiple different oxides to investigate the effect of oxidizer on reactivity with aluminum. The metal oxides that have received significant attention include Fe_2O_3, CuO, WO_3, MoO_3, and Bi_2O_3 [2,3].

While much research has been accomplished in the area of nanothermite materials, there are still many aspects to be investigated thoroughly. The research to date has focused on the effect of both particle size and ratio of fuel to oxidizer on combustion front propagation velocities, both under confined and unconfined conditions. Some research efforts have begun to focus on ignition behavior and others have focused on possible mechanisms by which nanothermite materials react and propagate. Nanothermite reactions are driven by conductive, convective, and radiation heat transfer mechanisms. The majority of the research has been focused on investigation of bulk or pressed nanothermite systems.

This presentation will focus on next generation of reactive films derived using bottom-up approach. A special attention will be paid to the formation of self-supporting pyrophoric composite substrates, reactive composite films and inks based on nanothermites [4,5]. Different formation techniques, including tape casting, will be compared and discussed. A photograph of reactive composite films generated by the tape casting technique is shown in Figure 1. The thickness of these films can be varied from 20 to 500 microns, depending on type of reinforcing material. A significant portion of the discussion will be on key rheological aspects and how these properties relate to the final performance of derived products. The summary of up to date state-of-the-art of scientific and technological development in this area of nanotechnology will be presented as well.

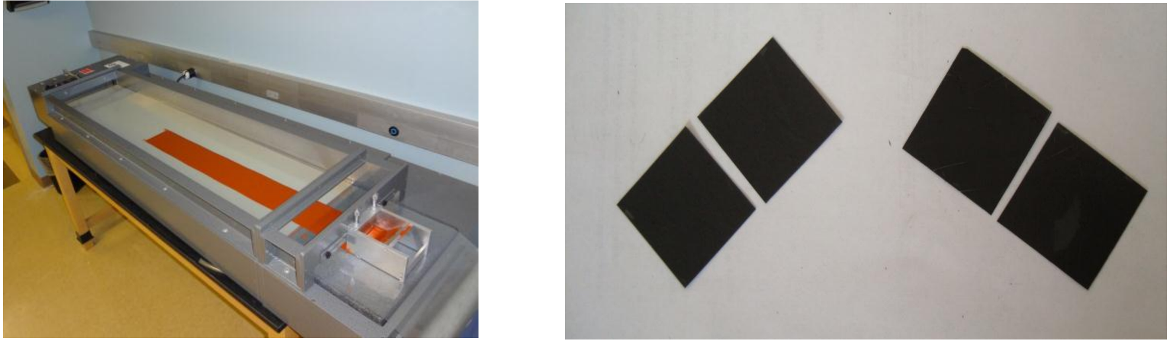

Figure 1. Photographs of a tape casting machine (left) and cut pyrophoric substrates (right).

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DECOMPOSITION FEATURES OF AMMONIUM NITRATE WITH DEXTRAN

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Although the system NH_4NO_3-Dextran is frequently used in the pyrotechnic mixtures, the fundamental kinetic study is still required for this system. In this work, we deploy thermo-gravimetric analysis to reveal activation energy change in this system depending on the Dextran concentration Fundamental study of the kinetics of combustion process allows us to precisely control parameters such as thermal front velocity, temperature, and the activation energy of the reaction. In this study we present the DSC/TGA analyses performed using Q600 analyzer (TA Instruments). The experimental setup is shown in Figure 1. The experiments were conducted at heating rates 5, 10 and 20 ºC/min under ambient (air) atmosphere. The following reaction was used for experiments:

$$12NH_4NO_3+C_6H_{10}O_5=6\,CO_2+12\,N_2+29H_2O$$

The systems with the Dextran concentration up to 20 wt. % were studied. We estimated the activation energy from the DSC data by using the isoconversional method suggested by Starink [1,2], which was shown in (Ref. [3]) to provide a more accurate value than the Kissinger and Ozawa methods. The

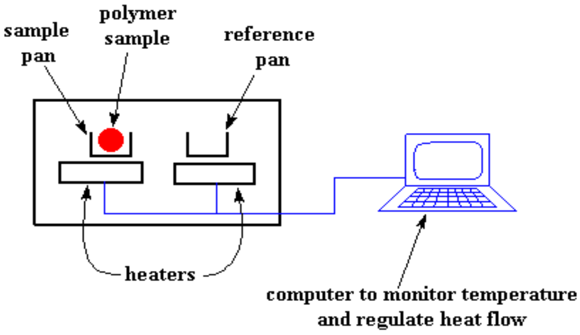

Figure 1. Schematic diagram of the experimental setup.

Starink method determines the activation energy from the equation:

$$\ln\left\{\frac{T^{1.8}}{\beta}\right\} = (1.0070 - 1.2\times10^{-5}E_a)\frac{E_a}{RT} + const$$

where E_a is the apparent activation energy (in kJ/mol), β the heating rate in thermal analysis (in K/min), T is the peak temperature of the exothermic curve (in K), and R the universal gas constant. E_a is estimated from the slope of the graph of $\ln(T^{1.8}/\beta)$ vs. 1/T. Figure 2 is presenting the decomposition pathway for the mixture NH4NO3-20 wt. % Dextran. The decomposition takes place at ~250 ºC. The small endotherms before decomposition are due to small amounts of moisture in

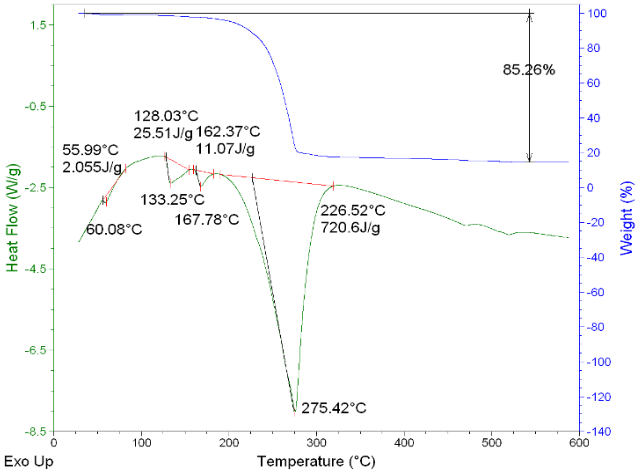

Figure.2. DSC/TGA analysis for the system NH_4NO_3-20 wt. % Dextran at heating rate of 20 ºC/min.

the mixture, as well as polymeric chain scission of Dextran molecules. For all mixtures the peak temperatures were taken and the Activation Energy calculations were made by plotting the $\ln(T^{1.8}/\beta)$ vs. 1/T. Figure 3 is showing the plots for 5, 10 and 20 wt. % Dextran containing compositions.

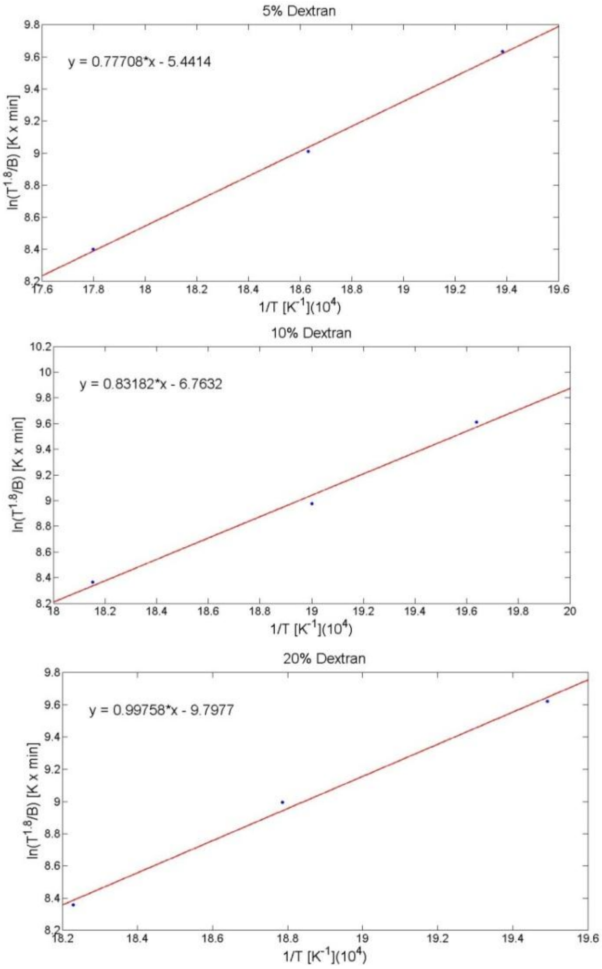

Fig. 3. Arrhenius plots for the exothermic peaks in the system NH_4NO_3 /Dextran

The calculated Activation Energies were in the range of 65-82 kJ/mol, and the energy values increase for the systems with higher Dextran concentration (Table 1).

Table 1. Calculated activation energy for different ratio of NH_4NO_3/Dextran

Conc. Wt. % Dextran	Heating rate	E(a)	T_{peak}
5	5 10 20	64.606 KJ/mole	242,78 263,6 288,72
10	5 10 20	69,15 KJ/mole	236,07 253,14 277,73
20	5 10 20	82.93 KJ/mole	239,89 259,17 275,42

The lowest Activation Energy has the system with 5 wt. % Dextran concentration. Lower activation energy ensures complete combustion at lower temperatures. It should be noted that the decomposition Activation Energy for the NH_4NO_3 was around 90 kJ/mol, which is in good agreement with literature data [4]. Thus, small amount of Dextran is acting as a catalyzer for decomposition reaction of NH_4NO_3 with lesser amount of Activation Energy.

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CARBON NANOFOREST TO REINFORCE ENERGETIC MATERIALS

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Thermite reactions are highly exothermic and may rapidly release high amount of stored chemical energy in the form of heat, light and wave. Nanothermite formulations that use aluminum or magnesium as the reducing agent and Fe_2O_3, MoO_3, WO_3 etc as the oxidizer have wide range of potential applications due to high energy density and the large energy release in a shorter time than by conventional thermites [1]. We present here a novel nanoenergetic yarn composite that was fashioned by composing multi-walled carbon nanotube (MWCNT) sheets embedded with I_2O_5/Al clusters. The NM composites were twisted to create a nanoenergetic yarns. MWCNTs were selected as the substrate matrix due to their unique intrinsic properties of high heat dissipation, high tensile stress and elasticity, all of which can be used in the manipulation and distribution of thermal energy. Figure 1 shows ignition of nanoenergetic yarn and their SEM images before combustion.

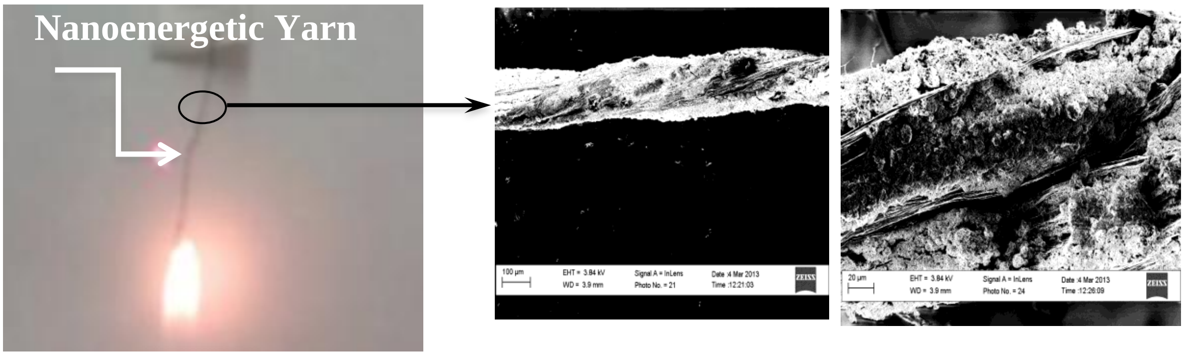

Figure 1. Combustion of nanoenergetic MWCNT yarn and SEM images.

The experimental system, shown schematically in Figure 1, was used to measure, the peak pressure, ignition temperature and the pressurization rate ($\Delta P/\Delta t$). The reactions were conducted inside a commercial stainless steel, high pressure, cylindrical reactor, 30.7 mm ID and 115 mm long (Parr, V=0.342L). High-frequency pressure transducers (PCB Piezotronics Inc.) on top of the reactor measured the pressure up to 14 MPa. A loose reactants mixture (0.1-0.5 g) was loaded into a ceramic boat, placed in the reactor. Due to the high energetic nature of the reactions they were conducted with a small sample, i.e, not exceeding 0.5 g reactant mixture.

The experiments show that addition of single wall CNT can increase gas peak pressure for some thermite nanocomposites by more than twice, while addition of MWCNT not increasing pressure. Figure 2 shows that addition of 3 wt. % of single wall carbon nanotubes (SWCNT) increased the pressure discharge by the Bi_2O_3/Al reaction by about 30 % [2]. The same bahaviour was observed during detonation of I_2O_5 system. The pressure discharge was increased by about 35 %.

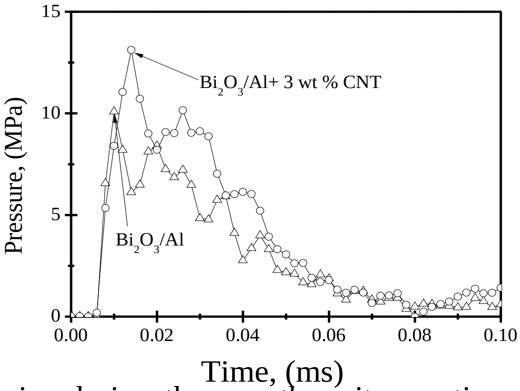

Figure 2. Peak pressure rise during the nanothermite reactions Bi_2O_3+Al with 3 wt % of carbon nanotube addition.

One of the reasons that the addition of MWCNT is not increasing the pressure discharge during the combustion is that the MWCNT yarn does not burn and their shape and structure remaining with initial state. Figure 3 shows the SEM images of the yarns after combustion that demonstrates that MWCNT yarns are not damaged.

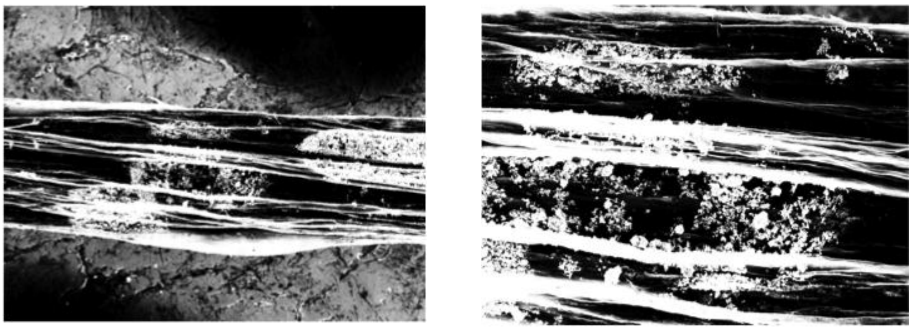

Figure 3. SEM images of MWCNT yarns after combustion.

The thread-like structure of the composites allows the utilization of textile technologies to create complex weaves which can be used in new industrial and scientific applications.

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5. BIOMATERIALS AND COATINGS

ENTROPY MAXIMIZATION PRINCIPLES FOR ANTIMICROBIAL AND BIOFILM PREVENTIVE MICROSTRUCTURES FORMED BY MICROPYRETIC SYNTHESIS

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We study extremely rapid micropyretic reactions for maximized entropy generation pathways and discover that steady state regimes for the rapid high temperature reactions exist when a combustion wave may appear at a fixed velocity [1-7]. These steady state diversions are a way to maximize the entropy generation rate for chemical reactions that can thus produce unique microstructures that are useful for antimicrobial surface properties [1, 3]. Quantitative and qualitative morphological results are provided to describe the action of micropyretic and other surfaces for bactericidal and bacteriostatic action. Biofilm formation is correlated to colony formation. Silver and Molybdenum disilicide (MoSi2) nanostructures are found to be the most effective bactericidal agents with MoSi2 being particularly effective in both low and high humidity conditions [1]. The surfaces are tested by controlled exposures to several microbial species including (Gram +ve) bacteria such as Bacillus Cereus, and (Gram-ve) bacteria such as Enterobacter Aerogenes. The resistance to simultaneous exposure to diverse bacterial species including to Arthrobacter Globiformis, Bacillus Megaterium and Cupriavidus Necator is also studied. Some micropyretic surfaces are found to eliminate or delay bacterial colony formation even with short exposure times. The efficacy of surfaces against colony formation of E-Coli (two strains) and virus Phi 6 Bacteriophage with a host Pseudomonas Syringae is studied. Results are presented that show possible anti-fungal properties by the $MoSi_2$.

We show that bacterial action results from both curvature and chemical influences. Surface drying rate and the dynamics of the droplet spread rate are studied as quick methods that correlate for a quick assessment of residual anti-microbial activity after abrasion. Early stage conclusions are offered for the chemical and topological influence of the surfaces on the bioactivity, including on the long-term biofilm formation behavior. The growth, rotation and clustering of such biofilms when they form on the control surfaces is also discussed.

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APPLICATION OF PROTECTIVE COATINGS AND DEVELOPMENT OF DEPOSITION MATERIALS BY SHS METALLURGY

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High exothermic mixtures including metal and non-metal oxides, metal reductants, non-metals and various functional additives are used at SHS – metallurgy to synthesize refractory inorganic and composite materials. Such mixtures can burn and the combustion temperature can exceed 30 000 C. Using the liquid-phase state of the combustion products we either apply protective coatings (SHS surfacing) directly or obtain cast ceramics and composite materials to be used for applying protective coatings by industrial methods. The lecture reviews the investigation results since 1980 to the present time [1-6].

SHS surfacing. Experimental and theoretical studies show that SHS surfacing is a multi-stage process including auto-wave synthesis of high-temperature molten ceramics, its heat and mass transfer with a "cold" support, and formation of cast coating. The method is based on the investigation of dynamics of interaction between combustion product melts and metal supports. The thorough experimental studies have shown the ability to control the SHS surfacing process as well as the coating composition, structure and properties. The most efficient ways of the control are gas pressure and overloading action, variation of the green mixture composition and calorific effect, introduction of functional additives, variation of scale factor, etc. The optimal conditions for SHS surfacing of composite materials (Cr-C-Ni, Ti-Cr-C-Ni-Mo, Cr-B-Ni, Ti-Cr-B-Ni-Mo, Ni-Ti-Al, and etc.) on steel supports have been determined. SHS surfacing of hard alloys has been efficiently used to increase the operation life of machine parts working under the terms of intensive friction and wear (mixers, agricultural machines, etc.). The industrial tests have proved that the operation life of different parts with SHS surfacing is 3-20 times higher. Some new results in the study of SHS surfacing of ceramics on titanium and aluminum supports have been obtained recently.

SHS of cast materials for protective coatings. Ceramic and composite materials are widely used in industry for applying protective coatings on machinery parts working under the terms of impact and friction, high temperature and aggressive media. The methods frequently used for surfacing are plasma and detonation spraying, electric, induction and plasma welding, etc.

SHS metallurgy is a promising method for obtaining new surfacing materials based on titanium and chromium carbides and borides, aluminum and chromium oxides, intermetallic materials and their application as protective coatings. Experimental studies and pilot production of ceramics are carried out in the SHS-reactor under the inert gas pressure of 4-5 MPa. They show that it is possible to distinguish 3 main stages in SHS-metallurgy: (1)- burning and chemical conversion of an initial mixture into final products; (2) - gravity separation of metal and oxide phases of combustion products; (3) – cooling and crystal structure formation. Also we can define characteristic times for description of the combustion synthesis: 1- time of burning, 2 - time of gravity separation of metal and oxide phases, 3 - cooling time of the melt. The process duration is the total sum of these three times. The time of synthesis varies from 1 minute to 1 hour depending on the initial mixture mass.

SHS surfacing materials are produced as granules or powders of 60-300 μm in grain size and electrodes of different types. SHS surfacing materials were tested in industry. Protective coatings based on SHS powders increased the operation life of road-building machines and metallurgical equipment parts 3-5 times. SHS-rods of heat-resistant cobalt-based alloys were successfully used for aircraft engines.

ACKNOWLEDGMENTS

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SURFACING of PROTECTIVE COATINGS on TITANIUM SUBSTRATES by SHS METALLURGY

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Centrifugal overloading is an efficient way to influence thermite mixture combustion with liquid-phase chemical conversion products and combustion regularities: gravity separation of metallic and oxide phases of combustion products, formation of chemical and phase compositions, and structure. Foundations of centrifugal SHS metallurgy of cast ceramics, alloys and composite materials, centrifugal SHS welding on steel substrates, etc. were developed on the base of the basic research results [1-4].

This paper demonstrates new results of SHS centrifugal surfacing of composite materials based on intermetallic and carbide compounds on titanium substrates. Highly exothermic mixtures of nickel, molybdenum, aluminum and carbon oxides with functional additives were used in the work. Green mixtures were placed on the surface of the substrates in graphite molds. The syntheses were carried out under centrifugal overloading ranging from 1 to 300 *g* at the mode of steady-state rotation. For experimental investigation we used image acquisition, methods of thermocouple and optical measurements, quenching and local analysis of the area of chemical conversion, SEM, metallography, X-ray diffractometry, etc. Thermodynamic calculations were used for selecting chemical schemes of the synthesis and mixture compositions, estimation of combustion temperature and product.

The following stages are shown to exist during the process of SHS surfacing: 1– combustion of the mixture layer and formation of the chemical composition of melt, 2 – gravitational separation of the combustion products (metal and oxide phases), 3 – formation of cast coatings, their macro- and microstructure. The detailed experimental investigations expose the combustion, gravity separation and coating formation limits depending on the reagent ratio in the initial mixtures, the overloading value and the weight ratio of the substrate and initial mixture. Optimum terms of surfacing of the mixtures under study have been defined. Cast coatings uniformly distributed by the titanium substrate and strongly adhered to it are formed within these terms. SEM of the obtained coatings prove that the surface layer of the support melts during the process of surfacing mixes the metal product and takes part in the coating formation. The elements of the coating (Ni, Mo, Ti, Al and C) are uniformly distributed over the deposited layer, except for the boundary layer between the substrate and the coating.

It should be noted that titanium and carbon form very hard titanium carbide which provides high hardness and wear resistance of the deposited SHS coatings. During SHS surfacing chemical interaction of titanium and carbon results in additional heat release and therefore high temperature on the surface of the titanium substrate; it is necessary for achieving excellent adhesion of the coating with the support.

ACKNOWLEDGMENTS

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SHS JOINING OF NiAl TO Ni: STRUCTURE OF TRANSITION LAYER

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Due to their excellent properties, nickel aluminides are being regarded as promising candidates for development of a next generation of high-performance high-temperature structural materials. As is known, SHS in powder compacts is a useful tool for production of advanced materials [1, 2]. The process seems to offer just a kind of innovative method for joining different (not only parent) metals and intermetallics [3, 4]. In this work, we report on load-assisted SHS joining of NiAl to Ni substrates.

The strength of the joint is known to strongly depend on F [5]. It is necessary to provide a good contact between the parts to be joined, which can be expected to give good wettability of Ni substrate with liquid products of the Ni–Al reaction. In control experiments we have found that, with increasing F, the sample porosity decreased, which was accompanied by improvement in the strength of the seam zone.

Figure 1 shows the microstructure and concentration profiles of Ni and Al for the NiAl/Ni transition layer. Different areas of the NiAl/Ni joint exhibited different phase morphology and composition. The diffusion depth of Al was less than 50 μm.

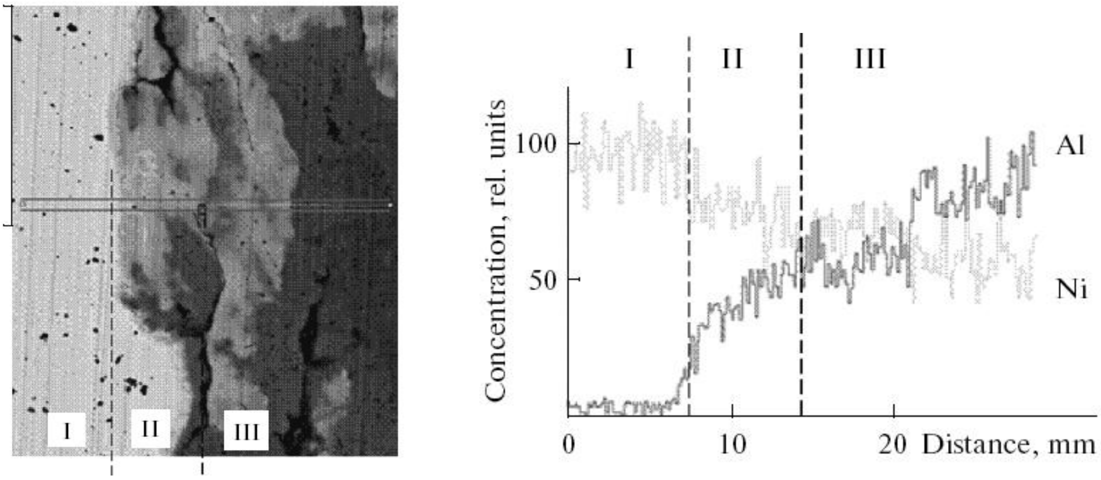

Fig. 1. Microstructure and concentration profiles of Ni and Al within the NiAl/Ni transition layer: *F* = 2 tons, exposure time 10 s: Ni substrate, I; transition zone, II; and NiAl layer, III.

The heat effect of the SHS reaction giving rise to formation of a high-temperature melt in the Ni–Al layer is regarded as a major factor regulating the process of SHS joining. The transition zone is composed of the AlNi and AlNi$_3$ phases in a layer less than 15–20 μm thick. The intermetallic phases in the transition layer can be identified as AlNi$_3$, AlNi, Al$_3$Ni$_5$, and Al$_3$Ni$_2$.

A residual porosity was found in the reaction products. These pores and voids were formed due to differences in specific volumes of the products and Ni substrate, gas release during reaction, thermal expansion, and the Kirkendall effect. The porosity of resultant seam was found to depend on preheating temperature and applied force (pressure).

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SHS JOINING OF DISSIMILAR MATERIALS IN Ti-RICH SYSTEMS

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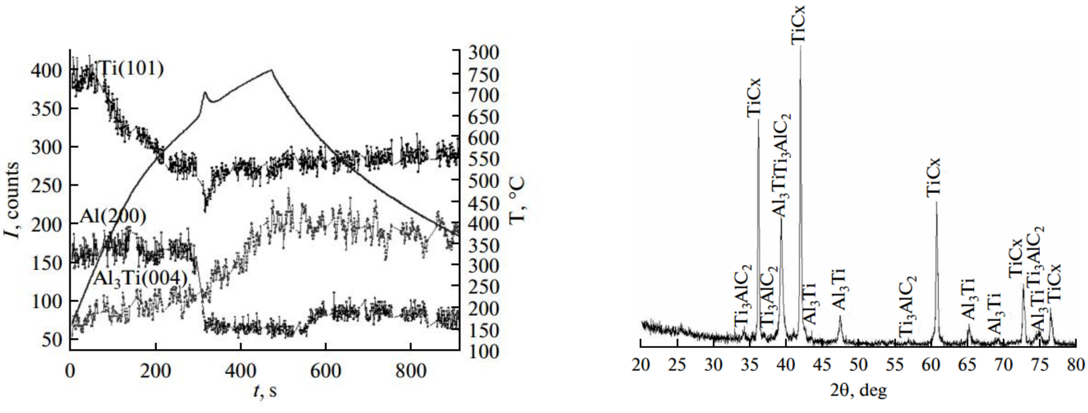
The heat released in SHS reactions can be utilized not only for heat treatment of synthesized materials but also in the processes of joining (welding) dissimilar materials [1]. This kind of reaction seems to be of great interest for welding applications, especially if some of concerned materials may suffer from long-term heat exposure [2-3] because of very fast processing times of these reactions. When joining dissimilar materials, a marked difference between the expansion coefficients may also result in apparition of cracks, and thus result in a weak bonding between the parts to be joined. Fortunately, SHS reactions may be adjusted to produce most suitable (including graded) transition layers.

In this work, we explored SHS reactions with the aim of joining dissimilar, titanium-rich materials, especially in the (Ti + Al)–(Ti + C) system. The composition and state of transition layers was studied as a function of such factors as the external force exerted to the sample, pre-compaction conditions, and initial state of substrate surface.

For Ti-Al-C system Ti begins to dissolve in Al to give solid solutions in Al above 500°C. Titanium as an element with a higher melting point has not enough time for dissolution. As a result, only Al-rich intermetallics may form, and the diffraction pattern in Fig. 1a exhibits the presence of Ti and Al_3Ti.

After cooling down, the sample was grinded to powders to perform XRD powder analysis. The diffraction pattern in Fig.1b exhibits the presence of TiC, $TiAl_3$, and a small amount of Ti_2AlC. The reaction with carbon is therefore possible in these experimental conditions but does not take place at the surface of the sample, where the time-resolved X-ray diffraction study took place. The Ti_2AlC phase is formed from the reaction between Ti, C, and Al-rich intermetallics. In addition, TiC diffraction peaks reveal a lattice parameter smaller than its standard value meaning that, due to an incomplete reaction, off-stoichiometric TiC was formed during the SHS reaction; partial substitution of Ti atoms by Al atoms may also have taken place.



(a) (b)

Fig.1. Variation in diffraction peak intensities (indicated) upon heating to 760°C and subsequent cooling down (a) and diffraction pattern of the synthesized sample (b).

TiAl–TiC composites were obtained. On the boundary between layers, the SHS reaction of starting Ti, Al, and C begins with the melting of Al and dissolution of Ti in the liquid Al followed by the formation of Al-rich intermetallics. After that, the Al–Ti melt begins to react with carbon to yield TiC by reactive diffusion through the layer of the formed product. Thus, mutual interpenetration of the two reactive mixtures yielded the Ti_xAlC ternary compounds formed at the interface, which were found to improve the strength of weld seams.

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SHS OF POROUS CERMETS FROM Ti-B-C PREFORMS

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Owing to good physical, mechanical, and biological properties, porous materials on the base of titanium are widely used in mechanical engineering, metallurgical, chemical, gas and oil industries as filters, catalyst carriers etc., and also in medicine as artificial bone graft substitutes and cell tissue carriers. SHS approach provides a possibility to fabricate the porous Ti-containing materials by a simple and resource-saving way.

This work is devoted to fabrication of porous cermets via SHS from Ti-B-C performs. The green mixture of powders consisted of three parts. The 1-st part was the stoichiometric blend of powders of titanium and boron to form ceramic titanium monoboride:

$Ti + B = TiB.$ (1)

The 2-nd part was the nonstoichiometric blend of powders of titanium and carbon black to form ceramic titanium semicarbide:

$Ti + 0.5C = TiC_{0.5}.$ (2)

Due to the high exothermity of the reactions (1) and (2), the 3-rd part – a considerable excess of titanium metallic powder (x) could be added to the blends (1) and (2) to form a ceramic –

metallic composite (cermet) and obtain a nonbrittle porous material. So, the total formula of the green mixture was

$(Ti + B) + (Ti + 0.5C) + x\ Ti$. (3)

The blends (1) and (2) were prepared separately and then mixed together in accordance with formula (3). The green mixture was compacted under various pressure (p) into cylindrical preforms 23 mm in diameter and 10-15 mm in height. Combustion wave was ignited by an electrically heated wire at room temperature on an end of the preform and propagated towards the other end synthesizing a final porous sample.

The effect of various experimental parameters (surroundings, Ti excess x, wt. %, compaction pressure p, MPa, warming up by a chemical oven) on the phase composition, morphology, porosity, %, and compression strength σ, MPa of the synthesized samples was investigated.

a) b) c) d)

Figure 1. Porous samples after burning in various surroundings

The influence of surroundings was investigated through burning of the preforms in the open air (a), under sand covering in the ambient air (b), in a reactor with the argon atmosphere (c) or a vacuum (d). Fig. 1 shows the samples after burning the preforms (Ti + B) + (Ti + 0.5C) + 30 wt. % Ti compacted at p = 55 MPa. The compression strength σ of these samples synthesized was very small in the cases of (a) and (d): 3 and 4 MPa respectively, but rather significant in the cases of (b) and (c): 43 and 58 MPa respectively. Because of this the subsequent experiments were conducted with the sand covering that was more simple than that with the argon atmosphere.

At p = 55 MPa, the increase of Ti excess from 0 up to 30 wt. % caused an increase in the compression strength σ from 10 up to 43 MPa. The combustion product consisted of four main phases: TiB, TiC, TiN, Ti and the impurity of TiO_2. At $x \leq 20\%$, the combustion wave propagated in the pulsating mode to yield low-strength products with a lamellar porous structure. The increase of Ti excess more than 20% resulted in the stable wave propagation yielding around 50% homogenous porosity. The interconnected pores of an elongated shape were from 20 up to 100 μm in height and from 100 up to 500 μm in length. At $x > 30\%$, the combustion wave propagation became impossible.

The increase of the compaction pressure p of the preforms with x = 30% from 55 up to 130 MPa added the compression strength σ up to 69 MPa. At p > 130 MPa the combustion became impossible.

Application of a chemical oven consisted in the layer of blend (Ti + C) around the perform extended the combustion limit up to x = 50% and p = 215 MPa, and allowed us to obtain the compression strength σ = 105 MPa at x = 45% and p = 215 MPa.

ELECTROSPARK DEPOSITION OF MAX-PHASES BASED COATING USING SHS-ELECTRODES

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As is known, the so-called MAX phases represent a family of ternary carbide or nitride compounds of the general formula $M_{n+1}AX_n$, where $n = 1, 2, 3$; M is a early transition metal; A some Group IIIA or IVA element; and X = C and/or N [1–3]. A distinctive feature of these compounds is their layered structure with alternating $M_{n+1}X_n$ and A layers, the carbon atoms occupying the octahedral voids formed by M atoms, without contact with atoms A. Similar to respective carbides and nitrides, the MAX phases exhibit high stiffness, good thermal and electrical conductivity, resistance to aggressive media, and low thermal expansion. Due to their layered structures, the MAX phases are surprisingly soft (hardness 2–8 GPa), machinable but yet heat tolerant and thermal-shock resistant. The M–A–X systems are known to admit the formation of high-temperature and heat-resistant carbides or nitrides MX compounds. This predetermines incongruent melting of the $M_{n+1}AX_n$ phases and formation of impurity phases in resultant bulk materials [1–3] and coatings [4]. To date, rich experience has been assimilated in deposition of MAX-based coatings by different physical (PVD) and chemical (CVD) methods. Among physical methods, the techniques of ion-plasma sputtering and laser-assisted pulsed deposition have become most popular. CVD methods are rather complicated and require elevated temperatures. Deposition of thick coatings encounters some serious difficulties. Gas-thermal methods had failed in deposition of coatings with a desired phase purity, although these techniques are regarded as most promising for deposition of corrosion/oxidation-resistant MAX coatings onto large-size machine parts. Deposition of thick coatings by the pulsed electrospark (PED) is a challenge. The incongruent melting of MAX phases can also be expected to result in formation of impurity phases (products of thermal decomposition) in coatings obtained by PED. This is more likely in case of the MAX phases whose thermal decomposition yields refractory compounds, such as titanium carbide and titanium nitride. Special features of the PED process—short heat-up pulses (10^{-6}–10^{-3} s) and high rates of warm-up and cool-down—require that deposition conditions (pulse duration, current, frequency) should be optimized in order to avoid overheating and thermal decomposition of deposited material. To our knowledge, the application of PED to deposition of MAX coatings has never been reported so far. In this context, it seemed interesting to explore the kinetics and mechanism of mass transfer from a MAX electrode in typical conditions of PED. In case of Ti substrate, it seemed reasonable to select Cr_2AlC for use as an electrode material. This MAX phase is known for its high heat resistance. This work aimed at PED onto Ti substrates of Cr_2AlC coatings with a maximal amount of MAX phase. Coatings with a high amount of MAX phase were obtained onto Ti substrate using the pulsed electrospark deposition (PED) technique and Cr_2AlC electrode material produced by the force SHS-pressing technology. The structural-phase states of the coatings generated at different modes were studied. It was defined, that TiC layer develops during the initial stage of the coatings development at the interface as a result of chemical reaction between electrode of Cr_2AlC and Ti substrate which further acts positively as a diffusion barrier. When deposited under Ar, the TiC layers continue to grow over the entire process and there is no loss of electrode material. In case of the high-energy mode of PED process under Ar TiC layer quickly develops which will further positively act as a diffusion barrier and erosion-resistant cathode. Cr_2AlC becomes a basic phase of the coating.

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OPTIMIZATION OF PARAMETERS FOR NiAl COMPOSITE COATINGS PRODUCED CAFSY METHOD

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In recent years, nickel aluminides have attracted considerable attention because of their great potential for high temperature protective applications, attributed to their high melting points, excellent resistance to environmental degradation and good mechanical and chemical stability at high temperatures.

This paper presents further results of our study to produce high quality NiAl intermetallic coatings on stainless steel by an Combustion Synthesis-assisted thermal spraying process wherein metallic Ni and Al powders react and produce intermetallic coatings *in-flight* during the spraying process and on the substrates. This became possible by optimisation of the flame-spraying process and materials parameters. We call the new spray-coating process "Combustion-Aided Flame SpraYing" or "CAFSY" (Greek for combustion).

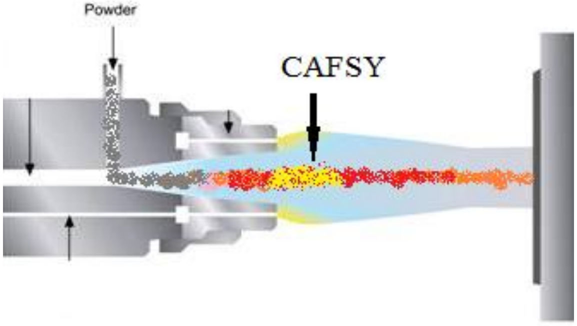


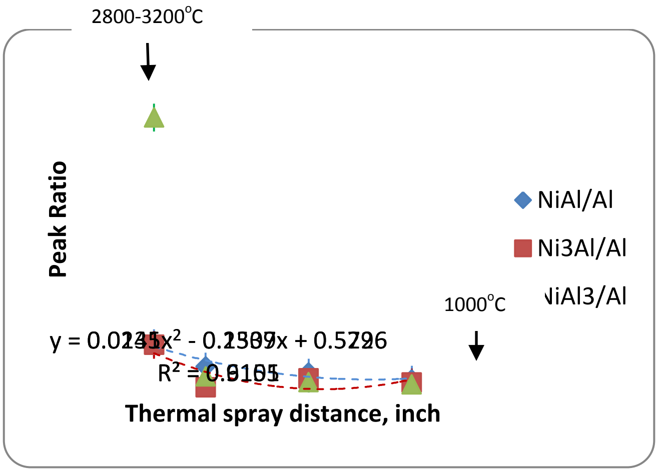
Figure 1: CAFSY method

The present work is part of a wider study aimed at developing the CAFSY method with particular emphasis on developing it as a low cost, rapid NiAl coating method for several applications.

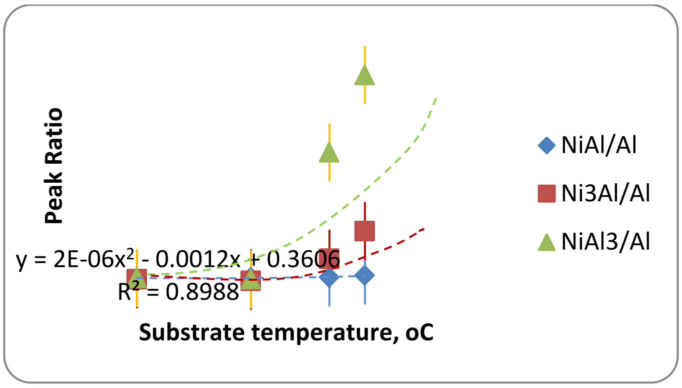
The grain size range of the Ni and Al powders used were 45-75µm and 5-100µm respectively and, prior to spraying, the SS304 substrates were sand-blasted to obtain a rough surface as per normal procedure. During spraying, the Ni + Al powder mixtures are ignited by the combustion flame and react. Various NiAl intermetallic compounds are formed on the substrates due to exothermic reactions taking place in the flame in-flight over times of milliseconds.

The morphology and microstructure of the coatings produced were examined by scanning electron spectroscopy (SEM) and X-Ray Diffraction (XRD). Porosity, surface roughness, microhardness and adhesion of the coatings were also determined. In addition, the coatings were tested for erosion and corrosion resistance.

The results of the investigations show that coating quality and performance is at least as good as that obtained using previously alloyed expensive powders and is influenced by thermalspray distance, substrate temperature and flame temperature of the powder. Increasing thermal spray distance decreases NiAl, Ni_3Al and $NiAl_3$ intermetallic phases (Fig.2a) whereas increasing substrate temperature increases $NiAl_3$ and Ni_3Al phases (Fig.2b), adhesion strength and reduces porosity and surface roughness. Finally, electrochemical testing of the CAFSY coatings in 3.5%NaCl indicates that they are very resistant to pitting corrosion. The work is continuing. The ratio O_2/C_2H_2 influence yield of nickel aluminides and maximum is at the stoichiometric ratio when flame has maximum temperature (Fig.2c).



a



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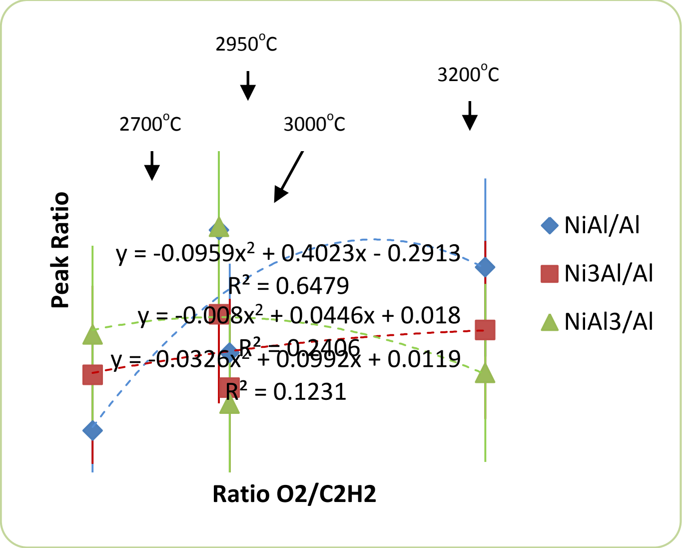

c

Figure 2: Synthesis of Intermetallic phases during CAFSY method

HYDROXYAPATITE COATED NiTi SHAPE MEMORY ALLOY OBTAINED BY COMBINING ELECTROPHORETIC DEPOSITION AND MICROWAVES-IGNITED COMBUSTION SYNTHESIS

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Porous NiTi intermetallic phase (Nitinol) is one of the most promising materials for advanced biomedical applications, mainly due to its superelasticity, shape memory effect and porous structure. Among the wide number of different manufacturing procedures [1-3], combustion synthesis (CS) received great research interest [4-6] since it demonstrated the ability of fulfilling the main prerequisites of implants in terms of interconnected and open porosity, pore size, strength, recovery strain and Young's modulus.

However, since the biocompatibity of Nitinol still represents a subject of controversy, surface modification techniques are practically considered mandatory in order to improve biocompatibility and reduce the dissolution of Ni from NiTi intermetallic in physiological environments [7]. Moreover, a bioactive surface would be welcomed to faster cell growths and integration. Particularly, hydroxyapatite (HAP) coatings strongly increase biocompatibility and promote the attachment of bone tissue providing a mechanically stable interface with the Nitinol implant [8, 9]. One of the most promising coatings manufacturing technique for complex shape parts is electrophoretic deposition (EPD), mainly due to the low cost of the equipment, simplicity of the process, control of coating thickness, short processing time and no substrate-shape restriction [10]. However, a further sintering step is usually required to develop satisfactory mechanical properties in the coating, and it represents the major inconvenience to an otherwise versatile and cost-effective technique. To solve this problem, in a recent work [11] the present authors exploited the excess heat released by combustion synthesis reactions in order to reach sintering of a ceramic phase previously deposited via EPD over the metallic powders compact.

Aim of the present work is the study of the applicability of a similar approach (i.e. the combination of EPD and CS) in order to obtain porous NiTi substrates coated by well-adhered and sintered HAP layers. In this framework, microwave energy as ignition technique, besides its CS intensification characteristics [12], was used also for the widely recognized advantages of microwave sintering over conventional techniques arising from the direct interaction of electromagnetic energy with the green sample [13, 14]. Hence, the ceramic coating is subjected to both heat coming from the substrate and to heat volumetrically generated in the coating, by microwave heating. This provides a unique temperature distribution in the coated sample, allowing to rapidly densify the coating, with good adhesion to the substrate. Moreover, the rapid sintering inhibits grain growth, with further improvement of mechanical properties (measured by nanoindentation) compared to conventional two-step processes.

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SHS HYDROGENATION OF TITANIUM SPONGE

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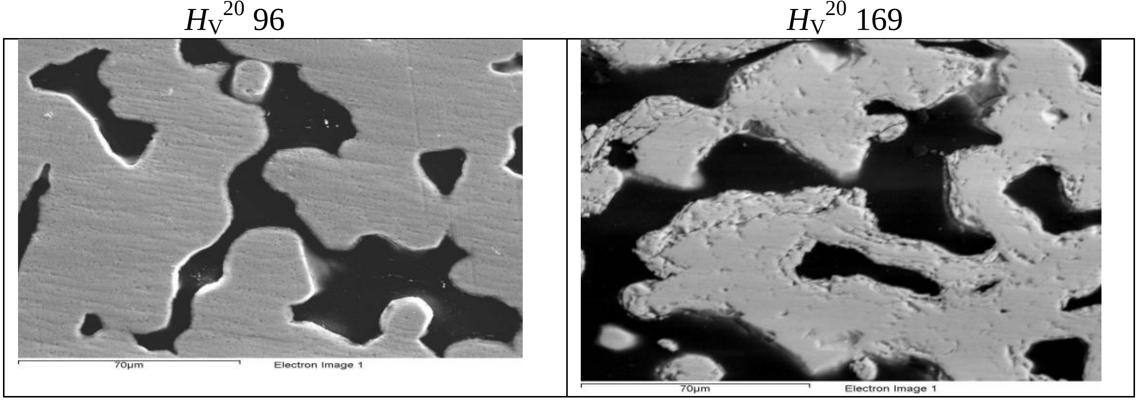
Hydrogenation was carried out in a 2-L SHS reactor as described elsewhere [1] using commercial titanium sponge (TG-110 brand, globule size 12 ± 2 mm) and hydrogen gas.

Sub-stoichiometric titanium hydride, TiH_x, was synthesized under 50 atm of hygrogen gas pressure (conditions of hydrogen deficiency) Upon combustion, a pressure in the reactor reduced down to below 1 atm. After cooling down, combustion product was cut into several pieces for analysis. The synthesized TiH_x samples were found to have x = 0.7–0.9 at the sample top and center, $x = 0.02$ at the low reactor zone. The XRD data suggest that the product contains the Ti and TiH_x phases whose relative amounts change with a reactor height. The upper parts of the product are comprised of $TiH_{1,5}$ + Ti mixture, the relative amount of hydride diminishing from 46 wt % at the top down to zero at the very bottom.

As is seen in Fig. 1a, starting Ti sponge has the uniform and defectless surface at particles' edge, while after hydrogenation it acquires lateral pores and cracks (Fig. 1b).



H_V^{20} 96 H_V^{20} 169

(a) (b)

Fig. 1. SEM images of Ti sponge (a) before and (b) after SHS hydrogenation.

The microhardness of hydrogenated sponge (169 kg/mm^2) was higher than that of starting one (96 kg/mm^2). Titanium hydride is known to possess higher hardness (up to 250 kg/mm^2) and brittleness compared to starting Ti sponge (110 kg/mm^2). Comparison of the above values with the measured magnitudes gives still another evidence for incompleteness of the reaction within the entire sample volume. In order to make the extent of conversion more uniform, it can be recommended to use a finer sponge (5–8 mm), higher hydrogen pressure, and/or larger pilot-scale reactors, as evidenced by [2, 3].

Stoichiometric TiH_2, was prepared using the following schedule of hydrogen admission into the reactor. When the pressure in the reactor dropped down to 1–2 atm, we allowed hydrogen to let in until a pressure of around 10 atm and then sustained this magnitude until the completion of reaction. Thus prepared product represented single-phase TiH_2.

According to the time-of-flight mass spectrometry (TOF SIMS 5 apparatus) data, the samples synthesized in conditions of hydrogen excess were found to contain TiH_2 within the entire globule volume. There were also some indirect indications for the formation of overly stoichiometric titanium hydrides TiH_x, which was confirmed by weight gain measurements ($x = 2.35$) and chemical analysis ($x = 2.25$). The possibility of SHS fabrication of overly stoichiometric hydrides was demonstrated in [4] on the example of hafnium hydride.

Some experiments were performed in a TRXRD (time resolved X-Ray diffraction) facility modified to work under hydrogen for the first time. Results show the combustion product can be assumed to form through a sequence of the following stages: α-Ti → α-Ti[H] → β-Ti[H] → TiH_2. The kinetic data in Fig. 2 suggest that the dwell time of the system within the two-phase range β-Ti[H]/TiH_2 (T = 350–300°C) is 15–20 s. Our results are in agreement with the Ti–H phase diagram.

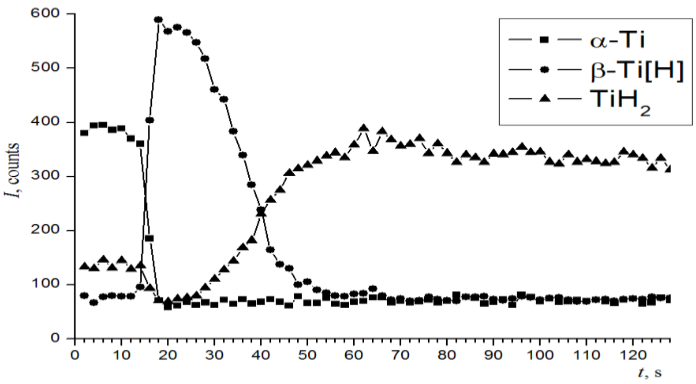


Fig. 2. Time evolution in intensity of the diffraction peaks

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SHS OF Ti–Al–Ta BASED ALLOYS

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Titanium and its alloys are being widely used as biocompatible materials in reconstructive surgery. For fabrication of endoprostheses and implants most popular are Ti–A–V alloys in which V is known for its slight toxicity. Among other candidate materials there are some porous materials, such as Ti–30Ta–Al and Ti–30Ta–Sn, capable of supporting regeneration of tissues and exhibiting shape memory effect [1, 2]. In this communication, we will report on the preparation of materials based on Ti–Al–Ta alloys by SHS in a frontal and thermal explosion mode, with special emphasis on the effect of particle size/morphology of starting blends and their mechanoactivation.

We explored thermal explosion (TE) in Ti–3Al–0.5Ta, 3Ti–2Al–Ta, and 3Ti–Al–Ta systems. Mechanical activation of powder blends was found to intensify the reaction due to diminution of reagents, accumulation of structural defects, and growth in the surface energy of ground particles. An increase in the Al content of green mixtures was found to improve the solubility of Ta during combustion reaction. With increasing fraction of added activated powder to mixed green composition, the solubility of Ta in product increased but remained incomplete. The best results were obtained for Ti–3Al–0.5Ta mixtures when starting reactive blends contained 50% non-activated and 50% activated mixtures.

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CATALYST ACTIVITY OF NiAl COMPOSITE COATINGS PRODUCED BY IN-FLIGHT SHS DURING THERMAL SPRAYING

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In the present research, Ni-Al composite coatings were elaborated by in-flight SHS during flame spraying process. As an advanced coating process, Reactive Flame Spray combines conventional Flame spray process and self-propagating high-temperature synthesis (SHS) reaction into a single step. Resently, Zhu et al [1] studied; Fe-Al_2O_3-$FeAl_2O_4$ composite coatings were successfully deposited by reactive plasma sprayed Al/Fe_2O_3 agglomerated powder. There are many differences between Plasma Spray and Oxy-Acetylene Flame Spray Processes. Table 3 shows the main differences. Even if Plasma has better performance than Flame there are many advantages for using the Flame Spraying Process [2, 3, 4]:

- Simple operation – requires minimal operator training
- Designed for hand-held operation
- High spray rates and deposit efficiencies – applies coatings quickly and economically.
- Integrated powder feed canister – eliminates the need to purchase a separate powder feeder.
- Works also with low cost and wide range powders of size 5μm – 300μm

Table 1: *Comparison of Flame and Plasma spraying*

	Oxy-Acetylene Flame Spraying	Plasma Spraying
Gas temperature, °C	3000	12000-16000
Spray rate, kg/h	2-6	2-10
Particle velocity, m/s	Up to 50	Up to 450

The present work use CAFSY method for developing low cost, rapid NiAl coating method for preparation of catalysts on carriers and study catalytic activity of these coatings. Figure 1 shows the surface of the coatings and the formation of the intermetallic phases NiAl and Ni_3Al. The initial powder composition was 86.8%Ni-13.2%Al. XRD results show the formation of some traces NiO and spinel $NiAl_2O_4$. Also there are non reacted phases Ni and Al in the final coating, for improving reaction between Ni and Al optimization of the spraying conditions were done (spraying distance, thickness of coating, flame temperature, composition of carrier and initial Ni-Al mixture for spraying (Fig.2)).

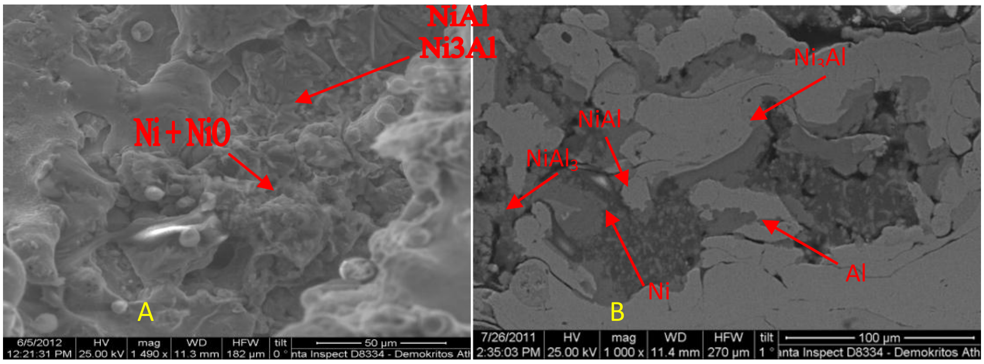

Figure 1: *SEM analysis of a) catalytic sample and b) cross section of the coating*

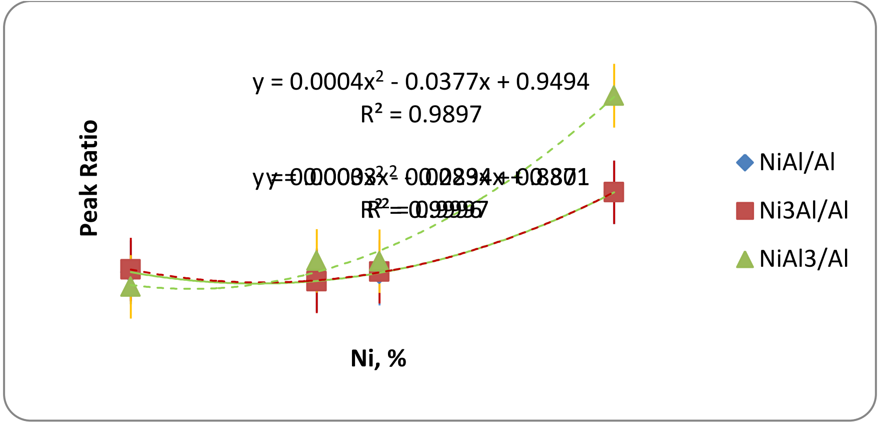

Figure 2: Synthesis of Intermetallic phases during CAFSY method

The mitigation and utilization of greenhouse gases, such as CO_2 and CH_4, are among the most important challenges in the area of energy research. CO_2 reforming of CH_4 has received much attention from both an environmental and an industrial perspective because the reaction can convert these greenhouse gases into synthesis gas with a low H_2/CO ratio. The catalytic reaction was carried out at 750, 800, 850, 900 and 950°C. For the catalytic reaction, we used a gas mixture of CO_2-CH_4-N_2 at a flow rate of $860h^{-1}$. The reaction products were analyzed by chromatography and FTIR. The basic reaction of CO_2 reforming of CH_4 is:

$CO_2+CH_4 \rightarrow 2CO+2H_2$. For the first time it was found that thermal spraying coatings has high catalytic activity: conversion of CH4 and CO_2 reach 86 % and 89% respectively (Fig.3a). Figure 3b shows very good (close to equilibrium ratio 1.00) product selectivity in terms of the H_2/CO molar ratio at different temperatures, over Ni-Al catalyst.

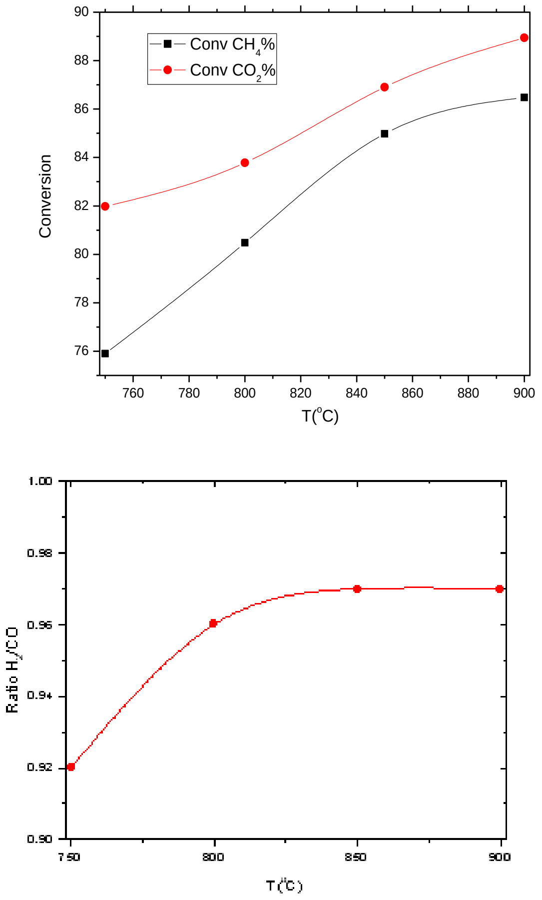

Figure 3: a)Conversion of CH_4 and CO_2 and b)product selectivity at different temperatures

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6. SINTERING AND CONSOLIDATION

COMBUSTION SYNTHESIS OF POROUS OXYNITRIDES

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Introduction. Oxynitrides of silicon and aluminum (β-SiAlON) have great potential for the development of the new class of porous penetrable materials because of their resistance to aggressive media at high temperature, low CTE etc. Sialon powders can be successfully prepared by combustion synthesis (CS), but producing of high porous sialon-based materials with specified porous structure (pore size in the range of 10÷1000μm) in CS mode is still a problem. In this work a two-stage technique of energy-efficient synthesis of porous oxynitrides was investigated. The first stage was a preparation of porous reactive preforms by means of foaming with following induration of aqueous slurry from powder reagents. The second stage was the CS of preforms in nitrogen aimed at formation of nitrided materials with fixation of shape and porous structure of the preforms.

Investigation techniques. β-SiAlON with Z = 2 can be described by the relation $12Si+2Al+2Al_2O_3+N_2 = 3Si_4Al_2O_2N_6$. The starting materials used were: silicon metal CR-1, aluminium ASD-4, alumina 99.9 purity; average particle size was < 10 μm. Powder green mixture was thoroughly mixed according to previous relation. Topaz powder (Al2SiO4(F;OH)2) in the amount of 1 mass percent was added into the green mixture in order to strengthen the "vapor-liquid-crystal" mechanism of nitrides formation during CS. It is well known that CS of the green mixture without any dilution results in formation of oxynitride products with cracks and low nitrogen saturation degree (NSD). NSD is defined as a ratio between nitrogen saturated during CS and nitrogen required for the total conversion of nitride-generating reagents. Thereby the combusted products themselves (once combustion synthesized green mixture with NSD ≈ 0.5, well-milled < 10 μm) were used as diluent.

The experimental procedures were as follows. Slurry was prepared via mixing the diluted green mixture with water; liquid/solid ratio was 0.63. Then the slurry was cast in a cylindrical mold with $V=105.62\ cm^3$ (D=41 mm, H=80 mm). Controllable heating of the mold in a muffle furnace (up to 373 K) was used for production of reactive porous preforms – foaming of the slurry take place owing to hydrogen generation in the process of aluminium oxidation; perform porosity could be regulated by changing the volume of filling slurry. The preforms were further roasted in the muffle at 870 K in order to eliminate moisture. CS of foamed preforms was realized in the nitrogen atmosphere at 8 MPa pressure. The maximal temperature of combustion wave was measured using a W-Re thermocouple. The combustion rate was calculated as height-to-time ratio. The porosity structure of the synthesized product was studied by means of metallographic analysis of the product cross section using a microscope CarlZeiss «Axiovert 200 M-Mat» and special stereometric techniques [1].

Results. CS of preforms from green mixture with 60 ÷ 70 mass % dilution leads to formation of porous materials with defect-free structure. Combustion rate was 1 ÷ 3 mm/s; maximal temperature was 1550 ÷ 1750 K. Fig.1 gives the images of cross sections of the synthesized preforms. It was determined that parameters of porous structure could be varied in wide range: average diameter of the skeleton elements 250 ÷ 750 μm, diameter of porous channel 10 ÷ 200 μm, specific surface of open porosity $4 \div 15\ mm^{-1}$. A XRD analysis shows *β*-

SiAlON phases, but the residual components of the charge are also present; NDS = 0,7 ÷ 0,8. The main reason of the last fact could be a low NSD of the diluent [2].

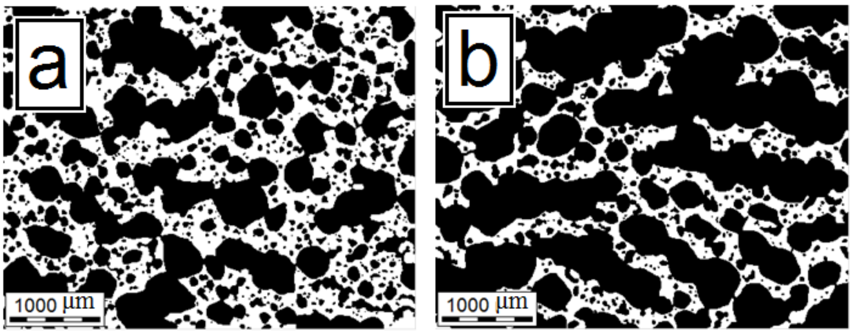

Fig.1. Longitudinal cross sections of the combustion synthesized porous preforms. (a) and (b) – porous structure of the samples with 58% and 75% porosity respectively.

Conclusion. Two-stage technique consisting in preparatory structuring stage with subsequent CS stage was successfully used for synthesis of a highly porous oxynitride material. It was determined that the technique makes it possible to vary porous structure of synthesized material. To obtain single-phase β-sialon porous materials should be studied prospects of using single-phase sialon as diluent agent.

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RESEARCH OF FORMATION OF TITANIUM ALUMINIDES IN HYDRIDE CYCLE METHOD

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For the modern material science, the problem of elaboration of new light high-temperature-resistant alloys with exploitation temperatures higher than 550-600°C is a big challenge. From this point of view, titanium aluminides are promising constructional materials, which advantages are: the high absolute level of exploitation properties; low density; relative cheapness. Titanium aluminides are very resistant to oxidation and heat, which defined their use in air, space and ground machine-engineering as construction materials [1,2]. The wide application of titanium aluminides is hindered by absence of industrially reliable technologies for obtaining homogenous alloys of the given composition. The traditional methods of producing titanium aluminides are the induction or arc melting, powder metallurgy, mechanical alloying and SHS method. The elaboration of a relatively simple and cheap method for synthesis of intermetallics in Ti-Al system is an actual and so far unsolved task.

The “hydride cycle” method of synthesizing refractory alloys and intermetallics, applied in the present work, has been developed in our Laboratory of High-Temperature Synthesis of IChPh (NASRA) [3], The essence of the method is in using the hydrides of transition metals as source materials. This highly effective method has essential advantages over the traditional ones. The our researches of Ti-Al system showed that the HC method successfully used for synthesis of aluminides. In this work was the detailed study of the process of formation of intermetallics in Ti-Al system in the HC, as well as of their possible interaction with hydrogen in SHS with formation of hydrides. The objectives involved experimental investigation of the influence of TiH_2 and Al powder ratio in the reaction mixture; of dimensions of the hydride powder grains (micro-nano-size); of pressure at compacting the reaction mixture; as well as of the regimes of dehydrogenation and sintering (temperature and velocity of heating), on the characteristics of the produced intermetallics (crystal structure, density, porosity, etc). Formation of aluminides in the HC proceeds in accordance to the reaction: $xTiH_2 + (1-x)Al \rightarrow Ti_xAl_{1-x} + H_2\uparrow$ where $0.25 \le x \le 0.9$.

Table 1. X-ray analysis and density data of titanium aluminides

№	Formula of intermetallics	Basic phase: crystal lattice type	Lattice constants (Å),		The density of alloys, g/sm^3
			Experimental date	Literary date	
1	$Ti_{0.8}Al_{0.2}$	hexagonal α-Ti + hexagonal α_2	a=2.928; c=4.654 a=5.822; c=4.677	a=2.947; c=4.836 a=5.77; c=4.62	3.43
2	$Ti_{0.7}Al_{0.3}$	hexagonal α_2-Ti_3Al	a=5.83, c=4.647	a=5.77; c=4.62	3.35
3	$Ti_{0.6}Al_{0.4}$	tetragonal γ-TiAl +	a=4.02, c=4.151	a=3.98; c=4.08	2.65

		hexagonal α_2-Ti_3Al	a=5.854, c=4.64	a=5.77; c=4.62	
4	$Ti_{0.5}Al_{0.5}$	tetragonal γ-TiAl	a=3.986; c=4.065	a=3.98; c=4.08	2.75
5	$Ti_{0.25}Al_{0.75}$	tetragonal	a=3.848; c=8.614	a=3.849; c=8.61	-

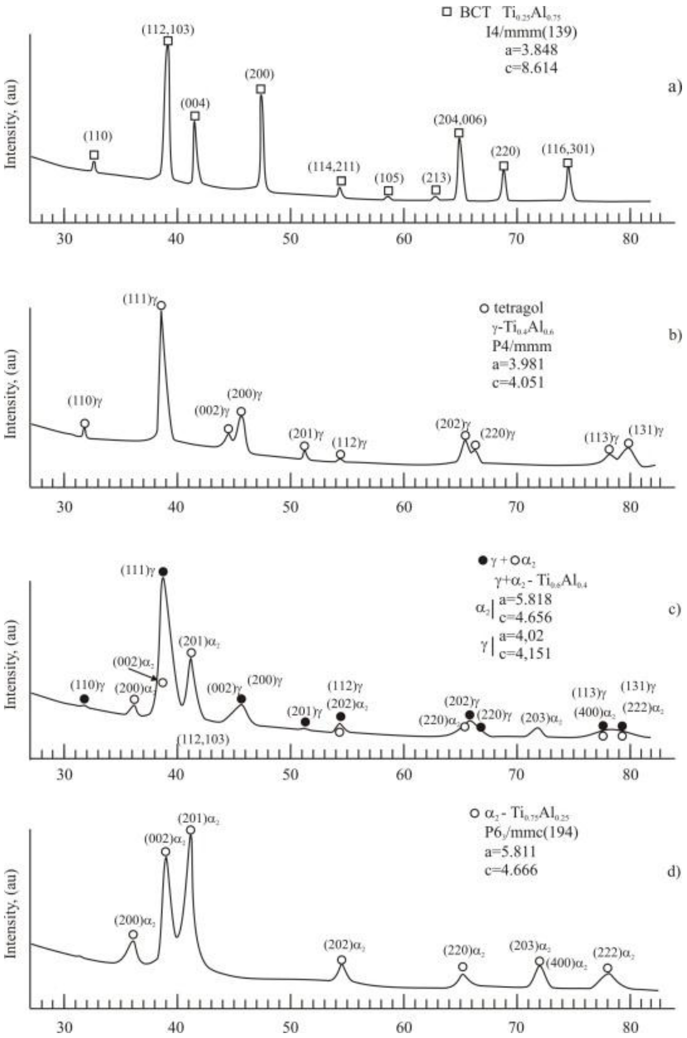

Fig. 3. The diffraction patterns of titanium aluminides: a) single-phase tetragonal $TiAl_3$; b) tetragonal γ-TiAl; c) tetragonal γ-TiAl + hexagonal α_2-Ti_3Al; d) single phase α_2-Ti_3Al

To obtain titanium aluminides the powder of SHS TiH_2, grinded down to 50 µm, was carefully mixed with the Al powder. Dehydrogenation process was carried out at temperatures 800-1000°C, exposition 30-60 min, and pressing pressure 10000-45000 kgF. In Table 1, presented are the data of X-ray analysis and density of titanium aluminides, obtained in the HC mode.

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DENSE SiC PRODUCED BY REACTIVE SINTERING FROM MECHANICALLY ACTIVATED REACTANT MIXTURE

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Refractory ceramics exhibit thermal properties that make them suitable for high temperature applications. Among these applications, aerospace and future nuclear industries have specific requirements for the structure materials that will be submitted to extreme environments. SiC-based materials appear as good candidates because of their specific characteristics: high hardness, good oxidization and thermal shock resistance, good thermal and chemical stabilities… but their brittleness appears as a very limiting drawback. However, mechanical behavior can be improved by reducing the grain size according to the Hall-Petch relation. In addition, the high grain boundary density can also enhance the trapping of irradiation induced defects in irradiative environments. To elaborate SiC nanostructured ceramics, Spark Plasma Sintering (SPS) appears as the suitable sintering technique because SPS is known to allow reducing the high temperature dwell time. In this study, the starting powder is a reactive mixture (Si+C). This latter is obtained by planetary ball milling, in the vario-mill Pulverisette P4, which allows selecting independently the speeds of the vials (ω) and disk (Ω). Different mechanically activated mixtures were obtained by varying ω/Ω ratio, milling time as well as ball size and silicon and carbon powder characteristics. The mixtures contain silicon crystallites of 30nm approximately with microstrain rate depending on the milling conditions. For carbon, grains are too small or too large to get information on crystallite size and microstrain by XRD. The mixtures are composed of particles with a large size distribution, ranging from several nanometers to several microns.

The (Si+C) mechanically activated powders were sintered in the Spark Plasma Sintering apparatus (HPD125, FCT System GmbH). Dense samples of 30 mm diameter and 5 mm thickness were sintered into a graphite die. The powders were first cold compacted in the die lined with graphite foil (graphite foil is also inserted between the powder and the punches) at the sintering pressure (40 MPa) during 5 minutes. They were sintered by SPS, at 1500°C, just above the melting temperature of silicon. An exothermic phenomenon is observed around 1380°C for some of the mixtures, which results in the formation of silicon carbide. However, the exothermic reaction magnitude and the nature of end-products depended on ball milling conditions and carbon particle size as well (figure 1). Indeed sometimes, (i) bulks are characterized by concentric circles which correspond to the alternation between pure silicon carbide and silicon carbide in presence of both reactants. The sample shrinkages are in this case small even a sintering temperature of 2000°C (ii) another specimens lead to samples more dense and homogeneous (no circles).

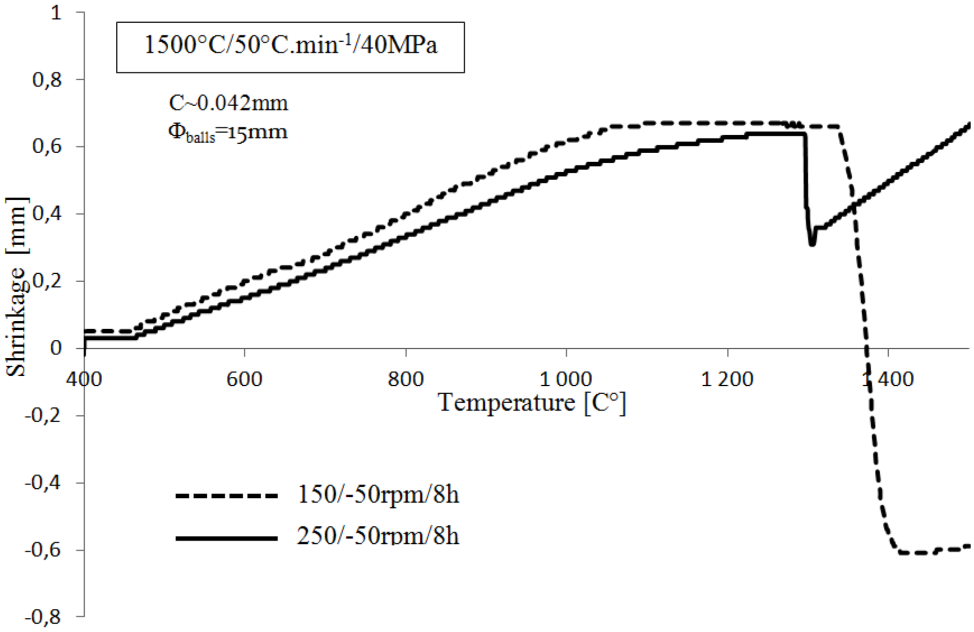

Figure 1 : Shrinkage curves obtained in SPS device of two milled powder mixture prepared according two ball milling conditions

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ALUMINIUM OXYNITRIDE – BORON NITRIDE COMPOSITES PREPARED FROM SHS-DERIVED POWDERS

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Materials based on polycrystalline aluminium oxynitride (γ-alon, AlON), being in fact the solid solution of Al_2O_3 and AlN, have great potential application as high-performance structural ceramics. Since the 1960s, many investigations have been focused on electrical, chemical, mechanical and especially on optical properties of γ–alon materials [2–9]. AlON powders were usually synthesized by direct solid-state reaction between Al_2O_3 and AlN in pure nitrogen or vacuum [10,11]. Main purposes of the paper were preparation of composite powders in the AlON – BN system using SHS technique and examination of possibility of obtaining dense polycrystalline samples using HP and HIP method. Realizations of these purposes were based on obtaining of active in further sintering powders in the AlON – BN system. AlON – BN powder was prepared using SHS method. Metallic aluminium (pure grade – 99.5%) and γ–aluminium oxide (Taimei Chemicals Co. Ltd, Japan) and the amorphous boron powders (Fluka, 15580) were used as the substrates. Weight proportions between the substrates were established as follows: 20 % aluminium – 80 % aluminium oxide and 2.5, 5, 10, 15, 20 and 25 wt % of boron powders. The powders were homogenized for 2 h in propanol using rotary vibration mill and alumina grinding media. The mixtures with weight of 50 g were poured into graphite crucible in a form of a loose bed and placed into steel water-cooled reactor. The reactor was vacuumed and filled twice with pure (99.8%) nitrogen of 2.5 MPa pressure. The combustion synthesis was initialized by electrical pre-heating of the graphite crucible by electric current flow for several seconds. The combustion got start rapidly, the reaction mixture reached temperature exceeded 2000ºC in few second and after next about 60 second the reaction was completed. The synthesized powders were crushed and then ground in dry iso-propyl alcohol for 6h using rotary-vibratory mill and alumina grinding media. As a result of SHS synthesis active and sinterable powders were obtained. Dried and granulated powders were sintered (HP, HIP technique) at 1850ºC and 1900°C for 1h in nitrogen. After sintering operations the authors obtained dense composite materials in the AlON – BN system. The phase compositions of such obtained samples are controlled and depend on the amount of the boron powders in the SHS starting mixtures. SHS, Hot Pressing and HIP methods allows authors to obtain practically pure AlON – BN material. The optimal mixture composition for SHS synthesis and temperature of further sintering treatment are shown. In this work investigations of structural properties of powders and sintered samples as well as their mechanical properties were also shown.

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BORON CARBIDE SYNTHESIS IN THE INDUCTION FURNACE WITH CONTROLLED MEDIUM (CO)

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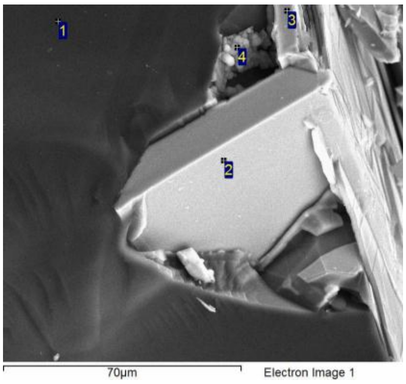
Boron carbide items are known to have some characteristics which allow them to be used under the terms of shock actions, intensive abrasive wear and nuclear radiation. Boron carbide items can be used as protective units from neutron radiation in nuclear industry, and for manufacturing sandblast devices. Therefore, investigation of methods allowing one to decrease the number of technological operations in the production process of boron carbide items. Self-propagating high-temperature synthesis (SHS) makes it possible to combine two stages: a stage of the material synthesis and that of its sintering. However, in the case of boron carbide the heat effect of the reaction $4B+C=B_4C$ is low. That’s why it is impossible to realize the process of self-propagating high-temperature synthesis of boron carbide without additional heating or introduction of energy-releasing additive [1].

The paper demonstrates the results of SHS of boron carbide. During the experiments the initial mixture was heated in the induction furnace with the controlled medium – CO up to the temperature of self-ignition.

Besides, we used reactive Ti+0.5C granules for some additional heat release in the combustion front. The amount of the additive was up to 40 %. The following initial powders were used for the experiments: amorphous black boron B 99A, lamp black, titanium of ПТМ type. The mixtures were granulated by the conventional method using polyvinyl alcohol. The diameter of the compacted cylinders was 45 mm. The material microstructure and phase composition were studied were studied using Jeol-JCXA-733 microanalyzer, “Neofot-30” microscope, and X-ray diffractometer “Dron-2”.

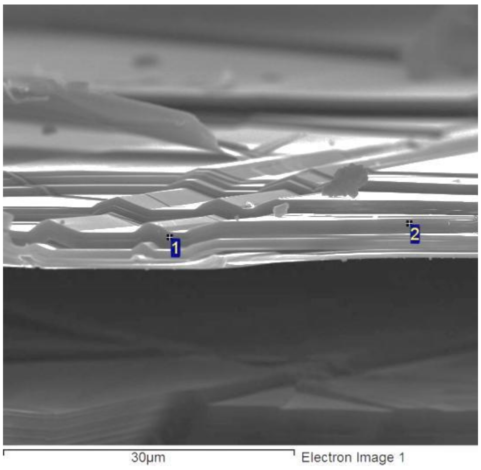
According to X-ray analysis titanium diboride (TiB_2) and crystal graphite were found in boron carbide samples. During the experiments the samples melted and lost their cylindrical shape. The structure and analysis of specific plots of the sample fracture are shown in Fig.1 and 2.



Spectrum	In stats.	B	C	O	Al	Si	Ti	Fe	Total
1	Yes	64.05	35.87			0.09			100.00
2	Yes	32.50	29.26		0.19		38.06		100.00
3	Yes	43.49	21.94		0.23		34.35		100.00
4	Yes		3.31	57.28	15.11	1.82	2.17	20.31	100.00
Max.		64.05	35.87	57.28	15.11	1.82	38.06	20.31	
Min.		32.50	3.31	57.28	0.19	0.09	2.17	20.31	

Processing option: All elements analysed (Normalised), weight%

Figure 1



Spectrum	In stats.	C	Ca	Total
1	Yes	99.51	0.49	100.00
2	Yes	99.59	0.41	100.00
Mean		99.55	0.45	100.00
Std. deviation		0.05	0.05	
Max.		99.59	0.49	
Min.		99.51	0.41	

Processing option : All elements analysed (Normalised), weight%

Figure 2

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ELABORATION OF TECHNOLOGY FOR FABRICATION MULTIFUNCTIONAL CERAMIC MATERIALS ON THE BASIS OF CARBIDES, NITRIDES AND BORIDES

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In the presented work the investigations were carried out that which prescribes to create the materials by SHS which will be ultrafine and partly nanostructured, that will have high viscosity on blow, together with the properties of hard alloys. This will give possibility to use these SHS materials for preparation of product which will work under high intensity dynamic loadings.

The knowledge of transformation of initial components to the final product gives us possibility, on the one hand, to the optimal parameters and technological parameters to obtain materials, also to make prognosis about exploitation properties of those materials.

In the heating zone start the processes of melting of Cupper and Titanium and capillary flow in one case on the particles of boron nitride, and in another case on the particles of boron nitride and carbide. In the next, active heat educing zone there is active interaction between Titanium and Boron Nitride in one case and between Titanium, Carbon and Boron Nitride in another case.

According to the interaction of particles we may say, that the formation of final product in the first case there is boron (which was in boron nitride) interaction to the melted titanium, as a result we obtain titanium boride and there is dismissal of boron nitride by active separation of Nitrogen and by interaction of Nitrogen melted Titanium, we obtain Titanium nitride.

In the second case during the synthesis takes place by interaction of boron nitride containing boron, carbon particles with melted Titanium, afterwards by interaction of separated nitrogen with Titanium Carbide, is obtained titanium carbide nitrides. By the end of reaction, practically all titanium is converted in ultrafine state and is presented as titanium borides, nitrides and carbon-nitride form. The pores are filled with melted consolidating alloy. In the zone of crystallization the final process of formation of product structure takes place.

The study of regulations of synthesis in Ti-B-N-Me and Ti-B-N-C-Me systems gave possibility to make conclusions about peculiarities of process. In particular, in spite of that all components in chasm are solid, the character of synthesis is not typical to systems solid-solid, as far as during the synthesis the BN is dismissed by intensive separation of Nitrogen, therefore during the experiments in atmosphere condition there is process of dismissal of nitrogen from reaction zone which causes the decrease of synthesis parameters 2 times for Ti-B-N-Me and almost 4 times for Ti-B-N-C-Me systems. As a result when obtaining material in atmospheric conditions, the speed and temperature is decreased of synthesis, also the content of nitrogen in material is also decreased. On the basis of discussion of presented material we may conclude that by pressing the synthesized hot SHS material, in order to obtain synthetic composite ceramic material, it is very important to select optimal characteristics of time and pressure. After right selection of technological parameters by authors will be obtained ceramic materials with the following parameters in Ti-B-N-Me and Ti-B-N-C-Me systems: practically non porous 0,4% and 1,2% consequently to the systems, hardness- 91,5-92,5 HRA and 92,3-93,3 HRA consequently, density-4,3-4,4 g/cm^3 and 4,5-4,7 g/ cm^3 consequently. These materials can resist single 18000-20000 J energy loads on 68-65kg/m^2 (6,8-6,5g/cm^2).

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HARD ALLOYS OBTAINRD BY THE METHOD: SHS-CENTRIFUGAL CAST

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Cutting tools for road and mine machines have huge application in the industry, their classification by assortment, appointment and the requirement is quite wide and diverse [1]. All these cutting tools generally mechanical, interacts in cold processing mode[2] with the working surfaces of roads, soil. Production of hard-alloy tips for cutting tools of road and mike machines by powder metallurgy, is connected with the high cost of chasm materials and complexity of technology.

Proceeding, from this interest for the solution of tasks to obtain hard-alloy tips by cheaper way is an actual issue. The task can be successfully decided by SHS method, namely the SHS technology - centrifugal casting [5,6,7].

Under the influence of centrifugal force cast products was obtained by the use of cheap oxide materials. For receiving materials and products from them the following systems were investigated: Ti-Cr-Ni-C, Ti-Ni-C and x (W-Co-C)+yNi.

By experiments established that:

- in order to obtain optimal technological parameters, for mixtures with the minimal losses of reaction mixture and accordingly having the maximum exit of casted hard alloy, it is necessary to use carbon as a graphite with dispersion of particles of d = 90 - 160 microns, at a/g ~ 1200 overloads.
- Heat treatment increases hardness a little and considerably reduces strength of casted hard alloy in Ti-Cr-Ni-C system. Before heat treatment the hard alloy consists of grains of over saturated solid solution of Chromium carbide in TiC, and after heat treatments there is a disintegration of over saturated solid solution with separation of carbide of chrome and its dissolution in a matrix.
- Received casted hard alloys in Ti-Ni-C system with the physical and mechanical characteristics don't meet the set requirements
- During the ratio of components x70% + y30% of system x(W-Co-C)+yNi, material has dendrite structure,

On the basis of the conducted researches the industrial equipment is developed for receiving a material and a product in one technological stage. Products in the form of tips for cutters, road and milling cars are prepared which have passed successful natural tests.

Estimated market research showed that cost only of chasm materials, depending on a ratio of components of initial mixture, by offered innovative technology is 10 - 15% lower than existing industrial ways of production hard-alloy tips.

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HOT PRESSING COMPOSITE POWDERS CONTAINING NITRIDE

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At present, there is a need to create ceramic materials with high performance. One of the promising materials is silicon nitride (Si_3N_4) that has a high hardness, mechanical strength and low thermal conductivity compared to metals and metal nitrides. To obtain ceramic materials based on silicon nitride with a high density and strength, it is used an activating additive (MgO, Al_2O_3, Y_2O_3, BeO), including zirconium oxide ZrO_2. Introduction of ZrO_2 into silicon nitride increases a heat resistance and crack resistance of materials compared to silicon nitride without activators. For example, materials on the basis of Si_3N_4 – ZrO_2 are used to create electroinsulating refractory materials, as well as biomaterials for medical applications.

The technological process for production of ceramic materials by hot pressing or casting from thermoplastic slips is highly energy intensive and multistage. In addition, there is a need to use previously synthesized powders of silicon nitride and additives for activation of the sintering process.

At the Department for Structural Macrokinetics of TSC SB RAS we have developed a technology for production of a composite powder based on Si_3N_4 – ZrO_2 in the single-stage combustion mode [1, 2]. In this case, silicon nitride and zirconium oxide, formed during high-temperature synthesis, are mixed at the level of crystallites.

The powdered fraction of ferrosilicon that is formed during grinding of ferrosilicon was used as a raw material containing silicon. The basis of the synthesis is the reaction between silicon and nitrogen with a high heat effect (750 kJ/mol). The heat of the reaction during the formation of nitride allows us to initiate a coupled endothermic process of zircon dissociation and obtain a composite powder containing nitride (Si_3N_4 – ZrO_2 – Si_2N_2O – Fe) without additional energy costs. The content of zirconium dioxide in the final product is determined by the amount of zircon in the raw material. The presence of silicon oxynitride (Si_2N_2O) in the synthesis products is caused by nitriding SiO_2 formed due to dissociation of zircon. Acid enrichment of combustion products allows us to obtain the Si_3N_4 – ZrO_2 − Si_2N_2O powder with a residual content of iron less than 0.5 wt.%.

This paper presents the results obtained in a study of obtaining a compact material from the Si_3N_4 – ZrO_2 − Si_2N_2O composite powder by hot pressing.

In the work we used the Si_3N_4 – ZrO_2 – Si_2N_2O powder with a specific surface of 3.0 m^2/g. Hot pressing a powder was conducted on the UGP-02 hot pressing installation, and the parameters of temperature, molding pressure and shrinkage were recorded. Hot pressing was performed in a graphite press mold at an average heating rate of 10°/min in a nitrogen atmosphere. The molding pressure was 40 MPa, the temperature was 1500ºC and 1650ºC. The process of pressing lasted 2 hours at the maximum temperature. The study have shown that ceramic compositions based on silicon nitride are not sintered during hot pressing at a temperature of 1500ºC and 1650ºC. For example, the open porosity of the material at a temperature of 1500º C was 41.3% and 39.4% at 1650ºC.

To increase the density of hot-pressed materials, we introduced the additives of plasma-chemical powders $ZrO_2 \cdot Y_2O_3 \cdot Al_2O_3$ and $Al_2O_3 \cdot Y_2O_3$ (5wt.%) into the initial composite powder. The studies have shown that the introduction of the $ZrO_2 \cdot Y_2O_3 \cdot Al_2O_3$ additive allows us to obtain a composite ceramic material based on silicon nitride with an open porosity less than 4.3% and Rockwell hardness (HRA) more than 87.

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MECHANICAL ACTIVATION OF Ti - Al POWDER MIXTURE: XRD STUDY

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Mechanical alloying (MA), that is, prolonged processing of Ti–Al powder blends in ball or vibration mills is widely used as an industrial method for production of TiAl intermetallic. Typically, the processing time attains a value of several dozen hours. In case of equiatomic Ti–Al blends, complete amorphization is reached after 25 h of processing in a vibration mill [1]. It seemed interesting to perform MA in high-energy activators such as planetary mills with a centrifugal acceleration of 90 g and higher. In case of Ni–Al blends, such a treatment resulted in the synthesis of NiAl intermetallic after 8 min of mechanical treatment [2]. We investigate on the changes of the equiatomic Ti–Al blends during their mechanical processing in a high-energy planetary mill by XRD analysis. Mechanical activation (MA) was carried out in an AGO2 planetary mill at a ball/mill ratio of 20:1 under Ar. 10 wt. % Si were added as in inner standard and XRD analysis was performed using Cu-*K*α radiation. The size (**L**) of the coherent scattering regions (CSR) and the values of microstresses (**σ**) were calculated on the basis of the profile analysis of the x-ray peaks with the use of a specialized software system that involves a pseudo-Voigt doublet function for profile approximation.

It was found that, MA did not result in formation of intermetallic. Even at **τ** = 25 min, the diffraction patterns only showed the presence of starting Al and Ti (Fig.1). MA for 25 min results in partial amorphization of Ti and complete amorphization of Al. A strong decrease in the intensity of Ti and Al lines can be associated with formation of amorphous structure. This is also supported by a gradually increasing intensity of the halo.

The character of deformation for Al and Ti is different (Fig.2). For Al, the **L** values rapidly decrease and then level off. The growth in broadening for Al lines can be associated with an increase in **σ**. An increase in time activation leads to a complete loss of long-range order in Al. Micro stresses in Ti attain a value of about 200 MPa at **τ** ≈ 10 min, while the **L** values remain practically intact. These observations well agree with those reported previously for the Ni–Al system [2]. But in contrast to the above system, we did not observe the formation of Ti–Al intermetallic. This can be associated with different formation enthalpies for TiAl and NiAl. A high extent of material amorphization during mechanical activation is insufficient for initiation of mechanochemical synthesis; a necessary condition is a high level of heat release in a given reaction.

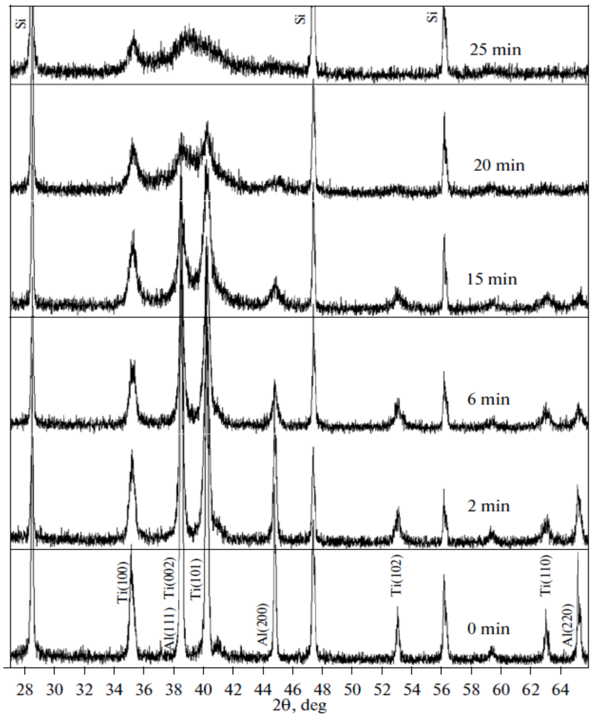

Fig.1 Diffraction patterns of starting and mechanically activated Ti–Al blends

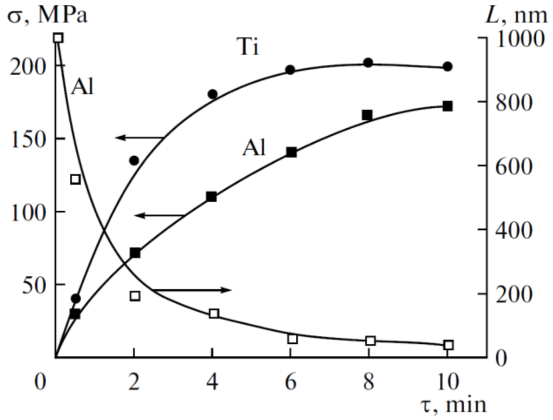

Fig.2 Micro stress (**σ**) and size of CSR (**L**), as a function of activation time.

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DIRECT SHS PRODUCTION OF ITEMS FROM COMPOSITE MATERIALS BASED ON FLUOPHLOGOPITE

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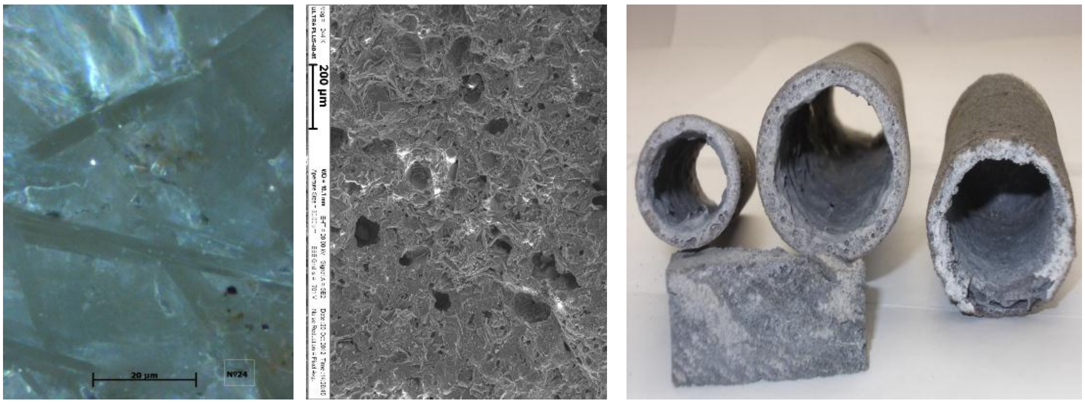
Items of melted mica-crystalline materials are successfully used as corrosion-resistant refractories working in the medium of aggressive non-ferrous metals (aluminum, zinc, bismuth, chlorine salts) [1], easily machined and characterized by rather high chemical and thermal stability [2, 3]. It is well known that homo- and hetero-valence replacement of K+ ions with ions of alkali and alkali-earth metals (Na^+,Li^+,Rb^+,Ca^{2+}, Cs^+, Sr^{2+}, Ba^{2+}) is possible [3], and if it is combined with the possibility of obtaining a melted final product in the combustion zone, it can be used for solving the problem of nuclear waste immobilization. Besides, when the artificial mica $KMg_3[Si_3AlO_{10}]F_2$ is obtained by pyrogenic method with its crystallization from the melt [4], even significant deviation from the stoichiometric composition in the melt does not inhibit crystallization of fluophlogopite from it. Isomorphous replacement of silicon with aluminum and backwards can range from complete replacement of aluminum with silicon with the formation of aluminum-free mica $KMg_3[Si_{3.5}O_{10}]F_2$ to Al_2O_3 content equal to 2 moles that corresponds to $KMg_3[Al_{1.95}Si_{2.75}O_{10}]F_2$. It allows carrying out SHS of fluophlogopites with initial reactive mixtures in which the reactive component can be changed in a wide range. It will make it possible to regulate the combustion temperature and organize synthesis with changing the state of aggregation of the substance in the combustion zone (in the melt) as well as without it [5]. It explains the actuality.

During our work fluophlogopites were synthesized with the structure identical to pyrogenic fluophlogopites. It was established that technological characteristics of the process (synthesis temperature, combustion rate) can be controlled by changing the content of energy-producing additive in the initial mixture. It allows controlling the state of aggregation of the product during the combustion process and obtaining porous or dense cast material based on monoclinic fluophlogopites.



a) b) c)

The picture demonstrates the structure of cast (a) and porous (b) fluophlogopite and an SHS item obtained from fluophlogopite.

The work was carried out with the financial support of the branch of chemistry and materials science of the Russian Academy of Sciences within the Program OXHM-5.

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PECULIARITIES OF STRUCTURE AND PHASE FORMATION OF BORON NITRIDE POWDERS AND COMPACT MATERIALS AT SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) WITH HIGH NITROGEN PRESSURE

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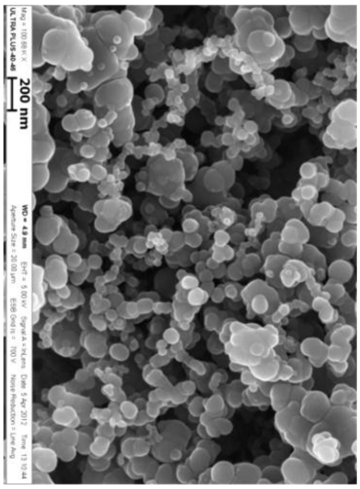
Boron nitride is remarkable due to its physicochemical properties which allow obtaining ceramic materials with high operation characteristics. Therefore, investigation of regularities of combustion of boron and boron-containing mixtures in nitrogen under the mode of self-propagating high-temperature synthesis (SHS) resulting in boron nitride powder and compact materials thereof is an actual task nowadays.

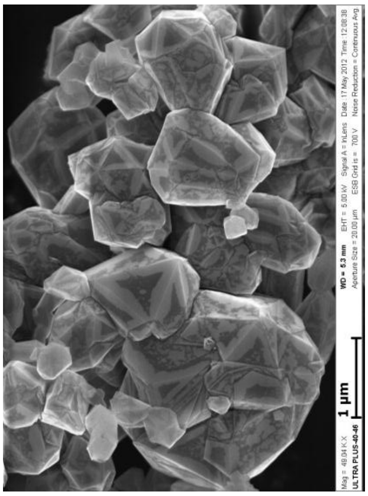
It is also important to study physicochemical processes occurring during the synthesis, particularly, phase formation and densification mechanisms in the combustion wave because namely these stages are responsible for individual peculiarities (size, phase, morphological, structural) which define the material properties.

During the work we determined such conditions of SHS realization (temperature, nitrogen pressure, combustion rate) when the product conglomeration is excluded and its particles grow due to the volume effect of boron-nitrogen reaction, i.e. to synthesize nano-sized boron nitride powder from nano-sized boron powder no technological powder changes are required either before or after the process. So SHS is shown to be a nanotechnological approach. Its application for synthesizing nano-sized powders is not restricted by the essence of SHS as a phenomenon but also by possible development of a specific raw material source: when new materials adopted for the synthesis of nano-sized powders appear, some stages of SHS of nano-powders will change. Boron nitride powders with nano-sized constituent have been synthesized from boron powders with nano-sized constituent (Fig. 1a). Besides the particles with the laminar structure, particles with the imperfect icosahedral structure are shown to be formed (Fig.1b). The investigations are partially published in [1].

Within this work, some investigations of SHS BN compact items and compact materials based on boron nitride (Fig.1c) were carried out at high pressures of the reactive nitrogen gas (up to 300 MPa) in the SHS gasostat [2, 3]. Previously [4], the efficiency of application of high nitrogen pressures in removing diffusion problems and suppressing dissociation at SHS of aluminum nitride-based compact materials was shown.



1a



1b

1c

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NET-SHAPE MANUFACTURING OF METAL-METAL SULFIDE CERMETS BY SHS

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Ceramic-metal composites (cermets) offer interesting combinations of hardness and toughness, making them attractive materials for a variety of applications such as protective coatings or armor. Existing fabrication techniques for cermets include reactive sintering, sol-gel synthesis, coat-mix process, tape casting, etc. Conventional techniques for manufacturing of metal sulfides are complex, environmentally harmful, energy and time consuming, and not suitable for producing complex net-shape articles. The products fabricated by these methods can also be highly porous, which can be a significant drawback for applications where high structural performance is needed [1, 2]. To overcome these disadvantages, we propose a new method for the preparation of the metal-sulfur precursor charge based on the ability to melt-cast the precursor mixture (by increasing the temperature above the melting point of sulfur). We have used self-propagating high-temperature synthesis (SHS) to produce a chromium/chromium sulfide cermet, using the ability of the mixture of metal and sulfur to support the propagation of reactive waves. This ability and the properties of the reaction products (low gas evolution and liquid sulfide products) enable the possibility to perform net-shape synthesis of dense, near theoretical density product with a relatively simple and low-cost set-up.

The thermochemical properties of the chromium-sulfur system are investigated using FactSage, a comprehensive multi-phase, multi-component equilibrium database [3]. The FactSage package was used to compute the adiabatic flame temperature and amount of volumetric gas production (volume of gas at pressure normalized by volume of initial composition, giving an indication of the porosity of the final product) as a function of Cr:S ratio at various pressures, as shown in Fig. 1.

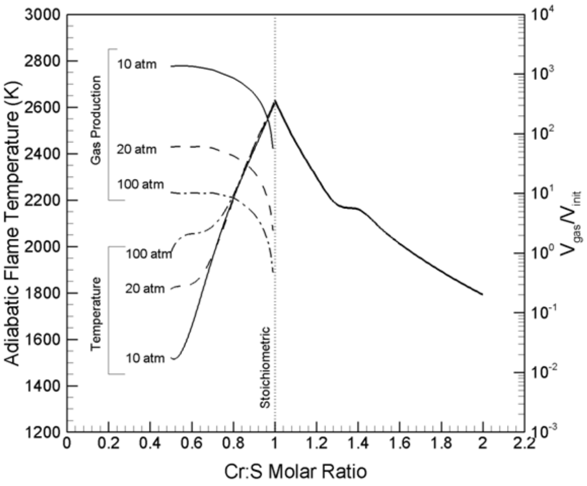

Fig.1. Adiabatic flame temperature and gas production as a function of Cr:S molar ratio

Although thermodynamics predicts that no gas is produced during the reaction for a Cr-rich formulation, synthesis performed at ambient pressure resulted in a product with considerable porosity (about 70%), limiting structural applications for this material.

The possible sources for the generation of porosity and cracks were identified and analyzed, including thermal shock, impurity-generated porosity, porosity existing within the starting powders and reactive mixture, porosity generated by sulfur vaporization within the flame front, expansion of pre-existing closed pores within the reactive mixture after reaction and porosity from molar volume changes.

We investigated the physical properties of the produced cermet with optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and X-ray diffraction (XRD) techniques. With the various improvements to the manufacturing process, the porosity was reduced from 70% to 7%. The obtained level of porosity (approximately 7% for the best samples) is considerably less in comparison to samples produced by other SHS techniques and is comparable to the bulk form of industrially manufactured ceramics.

The ability of the Cr-S system to sustain propagation in small dimension charges (quenching distance<1 mm with fine Cr powder) means that the technique developed here can be used for the net-shape synthesis of complex shapes with high tolerances. The produced cermet by this method can be used as ballistic armors, heating elements, protective coatings to resist corrosion from liquid metals and magnetic structures. A photograph of a synthesized sample is shown in Fig. 2.

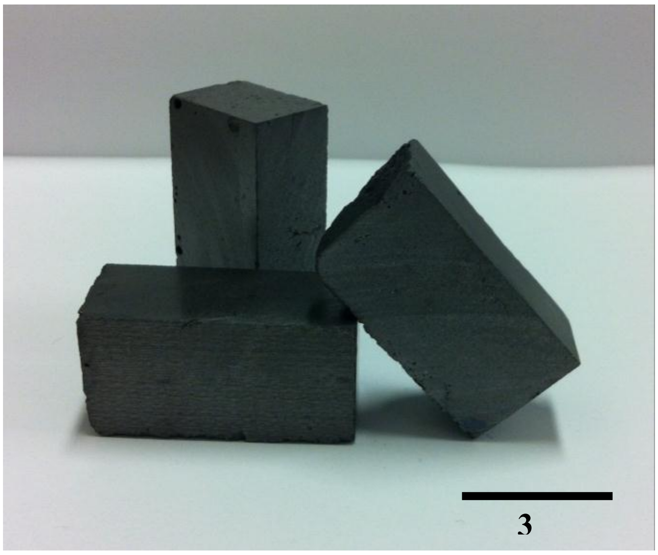

Fig.2. Photograph of Cr-CrS samples synthesized, show original and cut faces

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MICROVAWES ASSISTED SHS FOR PRODUCING POROUS NiAl

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The aim of this work is the production of porous NiAl by means of two different space holders techniques.

Porous materials, which contain large number of pores or cells, have been enthusiastically investigated because of their high energy absorbing capacity, reduced thermal conductivity, and enhanced acoustic damping ability.[1] It is well known that NiAl intermetallics have excellent characteristics of both ceramics and metals due to the mixture of metallic and covalent bonds. Thus, porous NiAl intermetallics can be used for applications in extremely severe environments, such as in thermal barrier coatings at high temperature and filter materials in corrosive environments. [2]

Among different techniques, combustion synthesis (CS) represents one of the most attractive approaches due to its several advantages with respect to the conventional ones. All Combustion Synthesis reactions ignited by conventional heating techniques usually show an inversion of the heat flow before and after the synthesis: initially heat is transferred from the ambient to the reactants; after ignition, the usually extremely high temperatures of the newly formed products cause the reversal of heat flow. For this reason, as soon as the reaction occurs, it is no longer possible to continue to transfer heat. The use of microwaves heating selectivity, instead, is expected to lead not only to a more rapid temperature increase of the whole reaction zone, but also to a continuous energy transfer during and after the ignition. Microwaves possess selective and volumetric characteristics (according to the dielectric and magnetic properties of the material to be treated) which can be proficiently exploited in the ignition and eventually in the sustaining of CS reactions.

Two different space holders have been used and different process parameters, as ignition time and input power have been investigated.

The results show how microwaves interact with materials, producing different final microstructures, allowing to control the porosity of the resulting intermetallic material.

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7. PACKING GEOMETRY IN NANO- AND MICRO-SCALE

LOCAL RULES AND GLOBAL ORDER IN CRYSTALS

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One of the most fundamental problems of crystallography is that of crystal formation. Russian crystallographer N. Belov named this problem the “501st element problem”. Since crystallization is a process resulting from a mutual interaction of just nearby atoms, it was believed (L. Pauling, R. Feynmann et al), that the long-range order of atomic structures of crystals (as well as quasi-crystals), is determined by local rules restricting the arrangement of nearby atoms. However, before 1970’s,there were neither formal statements that used mathematical language and concepts, nor rigorously proven results in this regard until B. Delone and R. Galiulin formulated a problem, and Delone’s students N. Dolbilin and M. Stogrin developed a mathematically sound *local theory of crystals*

The motivation and a sketch of the local theory of crystals are as follows. An appropriate concept for describing an arbitrary discrete atomic structure is the *Delone set* (or an *(r,R)-system*). Structures with the long-range order such as crystals also fall under the concept of the *space group*. A mathematical model of an *ideal monocrystalline matter* is defined now as the *Delone set which is invariant with respect to a space group.* It should be emphasized that under this definition the periodicity of crystals in all 3 dimensions is not an additional requirement. By the well known Schoenflies-Bieberbach theorem, *any space group contains a translational subgroup with a finite index.* Thus, a mathematical model of an ideal crystal uses two concepts: the Delone set (which is *of local nature),* and a space group (which is *of global nature*).

The main aim of local theory is to develop a methodology how to determine a space group symmetry of a crystalline structure from the pair-wise identity of local arrangements around each atom. The core of the local theory is a proved statement (Dolbilin, Shtogrin, [1][2]), that a local identity within certain radius **Q** implies a global regularity of the structure (*the local theorem*).

A Delone point set *X* is called *regular* if it is an orbit of a point with respect to some group of isometries. In other words, a Delone set *X* is regular if its symmetry group operates transitively on the set *X.*

Given Delone point set *X,* denote:
1) $N_X(\mathbf{Q})$ the *enemurative function,* i.e. the number of congruent classes of the surroundings X_x about points *x* from *X* of radius **Q** in the *X,* and

2) $S_x(\mathbf{Q})$ the subgroup of all symmetries of subset X_x leaving the central point *x* fixed.

Local Theorem. *A Delone point set with parameters r > 0 and R > 0 is a regular point set if and only if there is such a positive number* **Q** (>*2R*) *that the following two conditions hold:*

1) $N_X(\mathbf{Q})=1$; 2) $S_x(\mathbf{Q}-2R)=S_x(\mathbf{Q})$.

The local theorem has been proved for all dimensions and later has been serving as a base for obtaining many other results in the local theory ([3]-[9]) . For dimension $d=3$ (the case of real natural crystal), the following progress has been made. Let X be a Delone set with parameters r and R. It was proved that if the enemurative function $N(2R)=1$ (all $2R$ neighborhoods are identical) , then the symmetry group of the $2R$-neighborhood contains no n-fold axis with $n>6$ (Shtogrin). From this lemma and the local theorem it follows that $N(10R)=1$ implies the regularity of the X (Shtogrin and Dolbilin). However, even in this case, regardless of a significant progress, this upper bound for **Q** remains overestimated. (In fact, it was proved but unpublished that the $N(8R)=1$ implies the regularity of the X.)

At this point in time the goal of the local theory is twofold. On one hand, one should improve the existing upper bounds for **Q,** and thus try to draw a line between the local conditions of the crystals and quasi-crystals. On the other hand, the long term goal is to fill the gap between the mathematical local theory and empirical concepts of self-assembly that occurs during the formation of the crystals/quasi-crystals on the nano scale. This goal will require a close cooperation of mathematicians and specialists in crystallography and structural chemistry. In the presentation we will discuss some points of the local theory and challenges ahead.

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IMPOSSIBLE NUMBERS OF SHORTEST PATHS IN A SPACE OF COMPACTS WITH HAUSDORFF DISTANCE

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Hausdorff distance between compacts is widely used in pattern matching, liquid modeling and statistical physics [1]. Geometry of shortest paths in the space of compacts is very important and, hence, is investigated actively. In general position there are infinitely many shortest paths between two compacts in a Euclidean space. However, there exist compacts with a finite number of shortest paths between them, and, in fact, one can construct two compact sets with any number of such paths from 1 to 36, with a notable exception of 19, as proven in [2]. The aim of this talk is to improve that result. It turns out that in the range from 1 to 1500 there are only four such numbers that no two compacts have such a number of shortest paths between them.

THEOREM

Two compact sets in Euclidean space considered in the space of compacts with Hausdorff distance can have any number of shortest paths from 1 to 2500, except, maybe, 19, 37, 41, 67, 1591, 1867, 2293, 2381 and 2413. Moreover, they can not have 19, 37, 41 or 67 shortest paths between them.

The prof is based on the following idea. The number of shortest paths between two compact sets in closely related to the number of edge coverings of a bipartite graph [2]. This result allows us to reformulate the problem in terms of Graph Theory and to attempt to solve it using machine computation. We construct every connected bipartite graph having at most 17 edges, which can be constructed from simple *atomic* subgraphs whose number of edge coverings being no more than 67, and calculate its number of edge coverings.

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NANOPARTICLES, FULLERENES AND RELATED PROBLEMS IN DISCRETE AND COMPUTATIONAL GEOMETRY

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The study of nanoparticles in general, and fullerenes and carbon tubes particularly, in the last few decades has been accompanied by geometric observations, computations and utilization of recent and classical results (like Euler theorem, or group theory studies) . With the current research of the subject by chemists and physical chemists, and interesting geometry, like fivefold local symmetry of icosahedra, a noticeable trend is developing to connect and relate results and problems in physical chemistry with cutting edge research in discrete and computational geometry. Though sphere packing, lattices, and polyhedral in general , and Platonic solids particularly, have been studied by geometers for hundreds of years, these studies have recently received a strong impetus because they arise naturally in a number of diverse problems in physics, chemistry, biology, nanotechnology, and a variety of other disciplines. A lot of interesting mathematical results and its applications can be found in [1], [2],[4],[5].

In this presentation we'll focus on some specific areas of research in geometry with the goal to establish an association between well known (mostly still open or partially solved) problems in geometry, and nano sciences studies. We'll also establish some related to nano science terminological equivalency between various problems in mathematics, like the Tammes' problem, and well-distributed points on the sphere problem [1], [2], [4],[5].

Though some define fullerene as any molecule composed entirely of carbon in the form of a hollow sphere, ellipsoid, or tube, we'll adopt a "more geometric" definition, referring to a fullerene as a closed cage molecule containing only hexagonal and pentagonal faces [3]. It follows from the Euler's theorem that a fullerene must contain exactly 12 pentagonal faces but could differ in the number of hexagonal faces. Theoretically, fullerene C_{20} is feasible with only 12 pentagonal faces and no hexagonal faces. In 1970 Osawa [9] suggested that an icosahedral C60 molecule might be stable chemically. Experimental work of Kroto, Smalley and co-workers in mid- 80-s established the stability of C60 molecule in the gas phase [8]. Experimental data indicates that there exists a plethora of problems in discrete and computational geometry that could be attributed to two or three types and broadly described as:

(1) What (how many/much) might be inside a cage type molecule or spheres associated with it, for instance, inscribed or subscribed spheres;

(2) How to place circular areas (cups) on these spheres to maximize/minimize certain values;

(3) What is the configuration of projections of carbon atoms on these spheres.This question is particularly interesting because of the observation that the distance between various pairs of atoms in fullerene (C60 is an example) is not exactly the same. What is the

relation between an optimal configuration, as defined in [2] and the projections on associated spheres.

The first problem (1) is naturally related to the packing problem in geometry. Problem (2) is directly related to the Tammes' problem. (The Tammes' problem is presently solved only for several values of N: for N<14 and for N=24. We recently solved the Tammes' problem for case N=13 [7].) Problem (3) is related to the "best" configuration of points on a sphere, where best means optimal configuration as defined in [2].

In this talk we consider jammed equal circle packings on the sphere with N circles. Namely, all irreducible contact graphs with N<12 vertices are enumerated. We also consider periodic planar circle packings with the maximal circle radius. In other words, we consider packings of congruent circles on a square flat torus [8]. This problem is also interesting due to another practical reason - the problem of "super resolution of images." We have found optimal arrangements for N=6, 7 and 8 circles. Surprisingly, for the case N=7 there are three different optimal arrangements. Our method is based on computer enumeration of spherical and toroidal irreducible contact graphs.

Acknowledgment
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8. SPACE APPLICATIONS

COMBUSTION AND SHS COMPACTION OF LUNAR REGOLITH MIXED WITH MAGNESIUM

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It would be attractive to use lunar regolith for the production of construction materials that will be needed for radiation shielding, landing/launching pads, and other structures on the Moon. Combustion-based methods involve the addition of materials that react either between each other or with regolith. Addition of a highly exothermic titanium/boron mixture to JSC-1A lunar regolith simulant led to self-sustained combustion and formation of TiB_2 mixed with the regolith, but the required amount of the additive was as high as 40 wt% [1]. Mixing JSC-1A with Al/$FeTiO_3$ thermite created a combustible mixture, but the required amount of the additive was as high as 70 wt% [2]. The large amounts of additives [1, 2] are explained by the fact that the regolith remained an inert material, decreasing the combustion temperature.

To minimize the additive content, it is attractive to consider methods where the added metal reacts with the regolith, leading to self-sustained combustion. Combustion of JSC-1A/Al mixtures was possible only after significant preheat of the mixture [3]. Use of nanoscale Al does not make the mixtures combustible. In contrast with Al, mixtures of milled JSC-1A with a relatively coarse (325 mesh) magnesium powder ignited easily at 26 wt% Mg [4-6]. With decreasing Mg loading, however, pulsations and spin combustion were observed [6]. Another problem in prior experiments with Mg was a low strength of the combustion products. The present paper focuses on two goals: (1) to decrease the content of magnesium in the JSC-1A/Mg reaction and (2) to obtain denser and stronger products. To minimize the magnesium content, we investigate the addition of a preheating step before ignition of the JSC-1A/Mg mixture. To produce denser and stronger materials, we use SHS compaction involving quasi-isostatic pressing, where the products are compressed immediately after combustion.

The effect of preheating on the combustion of JSC-1A/Mg mixture pellets was studied in argon atmosphere. With preheating to 100°C, the minimum concentration of Mg for steady combustion wave propagation decreased from 13 wt% to 10 wt% and the lower limit of combustibility (which includes unsteady propagation such as spin combustion) decreased from 10 wt% to

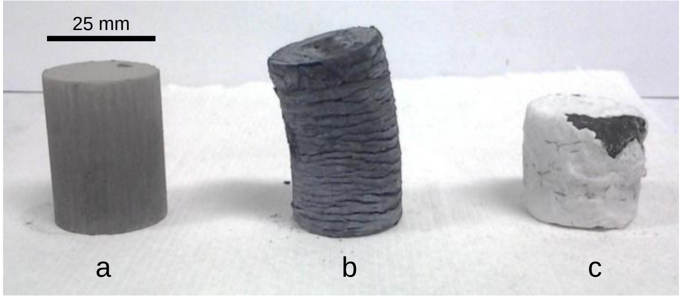

Fig. 1. Photographs of (a) original JSC-1A/Mg pellet, (b) product obtained after combustion in argon, and (c) product obtained after SHS compaction.

8 wt% Mg. At the same concentration of Mg, preheating increases the maximum temperature and the front propagation velocity.

SHS compaction of JSC-1A/Mg mixtures resulted in a 60-66% increase in the products density as compared to the materials obtained after combustion of these mixtures in argon atmosphere (Fig. 1). The compressive strength of the compacted products exceeded 10 MPa, i.e., it was higher than the compressive strength of common bricks (5 MPa) [7].

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CONSOLIDATION OF LUNAR REGOLITH SIMULANT BY ACTIVATED THERMITE REACTIONS

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Introduction

It is widely recognized that future exploration missions to the Moon will include construction of permanent lunar bases to support long term missions. The construction will involve radiation shielding, landing and launching pads, thermal wadis and other structures on the lunar surface. For the construction of protective buildings on the Moon, fabrication of solid bricks from lunar dust is critical. Lunar dust is covering the surface of Moon with thickness of up to several meters and actually is the eroded lunar regolith with particle sizes of mainly 100 μm and less. There are several methods for fabrication of sintered regolith on the moon by different techniques. However, all proposed methods consume huge amounts of energy and/or materials from Earth. The transportation of any material from Earth should be extremely minimized due to high cost of carriage. In this view there is an attractive method for sintering of regolith by using combustion synthesis [1], which does not require external energy for self-sustaining combustion even in vacuum or inert atmosphere, and can be applied on the Moon. There are several works on this direction [2, 3]. However the effectiveness is not high and, as mentioned, there must be used only local resources.

In the present work the consolidation of lunar regolith by using thermite reactions activated by fluorocarbons is reported. The thermodynamic calculations of regolith-thermite reactions as well as the experimental procedure are discussed. Thermo-chemical activation of aluminum with negligible content of Polytetrafluoroethylene (PTFE) allows us to utilize very high rate of regolith (up to 85 wt % in initial mixture).

Experimental Results and Discussion

The simulant of regolith has the following molar composition (according to the weight percentages): $1.26SiO_2+0.19Al_2O_3+0.03Fe_2O_3+0.13FeO+0.23CaO+0.28MgO$. According to thermodynamic calculations, adiabatic temperature (T_{ad}) was predicted about 1500 K. The HSC-7 Software suggests for Regolith-20 wt % Al system reaction enthalpy of ΔH=-5.44 kJ/cc [4]. We investigated the following system:

$$(1.26SiO_2+0.19Al_2O_3+0.03Fe_2O_3+0.13FeO+0.23CaO+0.28MgO)+nAl \qquad (1)$$

where n is the stoichiometric coefficient matching the moles of Al added to initial regolith powder. According to thermodynamic calculations (Fig. 1.a) the maximum adiabatic temperature 1700 K generated at n=1.05 mol (22 wt % Al). However, the experiments show that this system cannot ignite in self-sustaining mode. To remove oxide layer form the Al particles and add more exothermicity to the mixture, we added PTFE into the exothermic mixture.

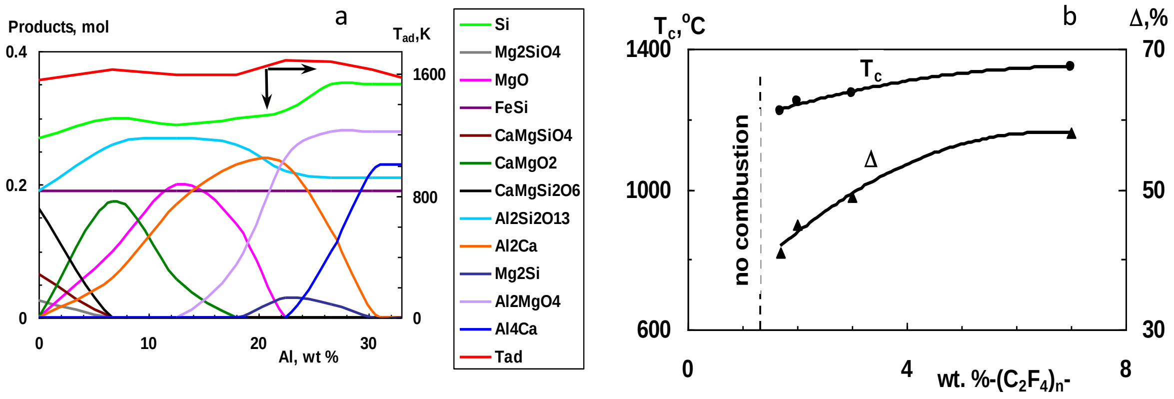

Figure 1. Thermodynamic calculations of the system (1) (a) and combustion temperature and prouct porosity as a function of PTFE concentration in the mixture Regolith-20wt%Al-n%PTFE (b).

It is beneficial to use a small amount of PTFE~2 wt %, to achieve thermo-chemical activation mode. We found the smallest amount of Teflon for activation of aluminum in this system to be in the range of 1.5-3 wt %. The experiments show that the system (1) at n= 0.86 mol (or 20 wt % of Al) reacts in self-propagating mode with minimum amount of 1.5 wt % Teflon in initial mixture (Fig.1.b). We receive hard porous regolith bricks with improved thermal insulation properties, which can be used as structural material on the Moon.

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HIGH-TEMPERATURE SYNTHESIS OF TARGET PRODUCTS WITH SET COMPOSITION AND SHAPE UNDER THE CENTRIFUGAL ACCELERATION EFFECT

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Centrifugal acceleration applied in the self-propagating high-temperature synthesis (SHS) method creates conditions for more complete phase separation according to the density of the formed products. Purposeful use of this phenomenon allows for production of pure materials with set composition. Combustion of a certain metal oxide results in formation of the uniform metal and ceramic components of the combustion product. The purpose of this research is to study combustion of the multicomponental oxide systems and receive finished products as a result of the high-temperature synthesis.

The study of the combustion process occurring under the centrifugal forces effect [1] has been carried out at the specially designed and fabricated unit. This unit includes a shaft installed engine, crosspiece with three cylindrical reactors fixed on it in a balanced manner at 120^0 angle. Combustion process in the reactor is initiated by an electrical pulse at the moment when set frequency rotation is reached. The number of the centrifuge revolutions is regulated by change of the voltage supplied to the electric motor. Operating rotation frequency ranges from 500 to 2000 rpm, corresponding to the centrifugal acceleration in the ignition point from 25 to 5000 g. The effect of the centrifugal force on the substance within the hot zone gradually increases 2.5 times following propagation of the combustion wave front along the reactor axis of the unit being applied. The die-casting tool is used to collect the metal fraction of the synthesis products. The size and shape of the die-casting tool varies in accordance with the composition of the initial components mixture and set shape of a metal ingot. The die-casting tool walls have apertures for gas removal.

Behavior of the combustion of NiO, MoO_3, WO_2, Cr_2O_3, Fe_2O_3, SiO_2 based oxide systems has been studied considering change of the centrifugal acceleration within the range from 1 up to 2,000 *g* [2]. Liquid-phase reduced metals and melted alloys are poured into the die-casting tool so that they get appropriate shape when hardened.

Metal melts with essentially different densities can be separated in the course of the combustion process provided rotation intensity is sufficient [3]. Before chemical interaction or intersolution with the light metals particles is completed, more dense particles gain higher acceleration and reach the die-casting tool. Thus, metal fraction of the combustion product of 50 %NiO - 5 %

Fe2O3 - 16 % Al - 23 % Al_2O_3 - 6 % W oxide system received at 1200 rpm visually seems non-uniform. According to the X-ray phase analysis data, the amount of tungsten increases up to 26.1 mass percent at the site utmost removed from the rotation axis. Rotation of the reactor around the axis that is perpendicular to its own axis provides leading motion of the reduced metal particles towards the die-casting tool due to their higher density and, accordingly, kinetic energy. This fact proves the possibility to concentrate a heavy metal upon its extraction from low-grade feedstock.

Ceramic component of the synthesis product remains in the cylindrical part of the reactor. Continuous heat removal through the reactor walls considerably decreases the melt motion speed in the wall layer. As a result of heat removal the melt quickly hardens and forms a ceramic tube. The centrifugal acceleration ranging from 800 $n \cdot m/s^2$ up to 3500 $n \cdot m/s^2$ provides complete separation of metal and ceramics and also formation of the ceramic component of the SHS product in the form of a tube with set external and internal diameters. E.g. corundum with set contents of chromium admixture, alumino-magnesium and alumino-cobalt spinel, mullite, and mullite-corundum mixture has been synthesized during metals extraction from the conventional i.e. weak feedstock.

Thus, a single process based on the SHS method with application of the centrifugal acceleration provides two finished target products, namely a die-casted metal ingot and a ceramic tube of set size and composition.

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SOME RESULTS OF SHS EXPERIMENTS IN SPACE

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In this communication, we report on the results of the SHS experiments performed aboard International Space Station (ISS, missions 21/22). This work aimed at elucidating the effect of microgravity on combustion synthesis of porous functionally graded materials (FGMs) with special emphasis on interaction between melted reactants and products with various metals, including capillary spreading. It was also planned to characterize combustion processes, pore structure of products, and transition layers (in case of SHS joining), and the kinetics for formation of intermetallics and other refractory compounds at the interface with metals. Because of high cost of space experiments, the relevant literature data are relatively scarce.

Experiments were performed in the cells (50 cm^3 in volume, 0.4 bar Ar) shown in Fig. 1. To start up the reaction in multilayered sample *5*, coil *3* (Fig. 1) was electrically heated for a period of 5–7 s. A lower thin (1 mm) layer of bulk-density NiO–Al powder mixture acted as an igniter and did not affect the overall reaction. Layered samples *5* were also stuffed with spherical particles and foil/wire pieces of various metals and nonmetals. The addition of low-melting additives might expectedly promote combustion via capillary spreading of the melt. Individual layers in sample *5* were arranged in the order of decreasing heat effect of respective SHS reactions. The video tapes and burned samples were delivered to the ground for analysis.

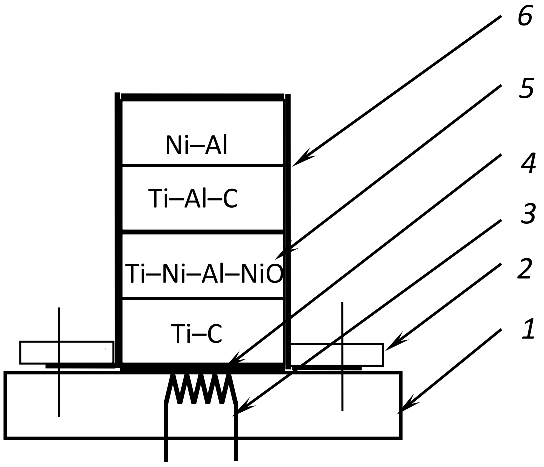

Fig. 1. SHS of functionally graded materials in space: *1* footstall, *2* fit ring, *3* igniting coil, *4* intermediate igniting NiO–Al mixture, *5* multilayer sample, and *6* protective Al foil.

The obtained results imply that SHS production of high-porosity foam materials and coatings thereof seems promissory for use in in-situ repair works such as SHS joining, SHS surfacing, SHS soldering, and healing holes/defects during space lights. It seems interesting to perform SHS reactions in microgravity with other reactive mixtures, including moonrock as a reagent. The assimilated experience should be taken into account in designing new facilities for use aboard Foton-M.

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SHS FOR AN IN-SITU RESOURCE UTILIZATION ON THE MOON AND MARS

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Various approaches to establish permanent outposts on the Moon and Mars exploration are being considered by major space agencies and construction companies from USA, Europe, Russia, China, Japan and India. The SHS approach to ISRU focused on development of materials production, repair and habitat technologies (materials development and processes for fabricating shaped construction elements (plates, beams, bricks, roads)) on the base of Lunar and Mars regolith. Major Lunar minerals are Feldspars: Anorthite $CaAl_2Si_2O_8$, Albite $NaAlSi_3O_8$,K-Feldspar $KalSi_3O_8$; Spinels: Ilmenite ($FeTiO_3$), Chromite $FeCr_2O_4$; Pyrosenes: Diopside $MgCaSi_2O_6$, Hedenbergerite $FeCaSi_2O_6$, Enstatite $Mg_2Si_2O_6$, Ferrosilite $Fe_2Si_2O_6$; wollastonite $CaSiO_3$; Olevines: Forsterite Mg_2SiO_4, Fayalite Fe_2SiO_4. SHS reactions based on the exothermic effect of reactions between components of initial mixture and the reactants conversion to products is accompanied by a large heat release10^{12}-10^{14} W/m^3 and it is very significant advantage of method for potential in-situ fabrication of construction materials in Lunar and Martian environments. Effect of gravity on the SHS studied by A.Shteinberg et al. (SHS of Ti+C) in parabolic flights and by O.Odawara (SHS Ti–Al–B, Zr–Al–Fe_2O_3, Ga–P, In–P, Ga–In–P) in 1990 in parabolic flights, dropping tower, sounding rocket. In 1992 J.Moore et al. studied SHS in system B_2O_3–C–Al in parabolic flight, in 1993 J.Lee studied SHS of system Zn-S in parabolic flight, in 1995 C.Lantz et al. from USA studied SHS of the system Ti-C in parabolic flight, in 1997 A.Varma et al. studied SHS of the systems Ni–Al, Ni–Al–Ti–B, Ti–C–Ni–Mo, Ti–C–Ni in parabolic flight, dropping tower. From 1997 A.Merzhanov, et al. from Russia up to now systematically studied SHS of the systems Ti–C, Ti–C–Ni, Ni–Al, Ti–Si–C, NiO–Ni–Al, Ti–C–Ni–Al and etc. on the space station. It was found that gravity affected processes during SHS are: formation of eutectic melts and contact melting, gas release (gasification), melting of reactants, spreading of molten phases, coalescence of fused particles, melting of intermediate products, phase separation in products, melt crystallization upon cooling**.** The versatility of the SHS technology for ISRU and in situ fabrication and repair applications was emphasized in a paper review (Moore, H.C. et al 2005). A base for exploration of the moon must assure the safety of the astronauts, especially from the severe radiation environment existing on the lunar surface, especially the high-energy cosmic rays. Among various proposals for ensuring such protection, to reduce extremely expensive ferrying materials from earth, is the use of the lunar regolith (top-soil) either as a simple covering layer for a pre-constructed cubicle or as structural blocks. In the later case a simple technology to produce strong building blocks in-situ, under the lunar vacuum and environment is needed. SHS could be adapted to produce exactly such structural blocks relatively easily and safely in-situ, only needing aluminium in addition to regolith, which could be recycled from the number of waste pieces from lunar missions. In addition, SHS can also utilise Lunar regolith to produce flat, hard surfaces on lunar surface for various uses such as landing bases, flat surfaces for photovoltaics etc. K.White with collaborators did thermodynamic calculations of the adiabatic temperature (T_{ad}) and combustion products for the mixtures of Al and Mg with JSC-1A lunar regolith stimulant comparative analysis of different additives to regolith (Al, Mg, Ti/2B) K. Martirosyan and D. Luss (2006) and White et al, (2011). demonstrating the novel process for rapid production of dense ceramic composites from lunar soil simulant by using SHS. In this work studied combustion in mixtures of Lunar regolith simulant with Ti + 2B (heat of this reaction used for sintering of regolith). In works of G.Cao et al (2012) aluminum is used as reducing agent, whereas ilmenite and iron oxides are added to the initial mixtures to be reacted in order to increase their exothermicity (ilmenite and iron oxides are present in significant quantities on Moon and Mars respectively). The effect of starting mixture compositions on the SHS is examined under different gas pressures of the environment (atmospheric or vacuum) and gravity level (terrestrial or microgravity). The obtained product, consisting of a complex mixture of various Al-, Ti-, Mg-, and Ca-oxides along with metallic and intermetallic phases, displays good compressive strength properties (25.8–27.2 MPa) that make it promising as construction material. Faierson et al. (*2010)* demonstrated combustibility of regolith/Al mixtures. The analyses presented in this study show that a regolith-derived voussoir dome type of structure is feasible from a structural standpoint. The voussoir dome elements show tremendous promise and allow for significant variation in regolith composition. E. Shafirovich et al. (2010) published work where studied potential construction elements: bricks, tiles, ceramic layer on the Moon surface for landing/launching pads and thermal Wadis. Our works (Xanthopoulou et al (2009-2013) based on main idea that the composition of the lunar regolith around the moon is not constant, different samples giving different composition, but most contain chromites, ilmenites and similar minerals. To adapt the SHS method, it was necessary to work with each mineral separately and produce SHS materials on basis of each mineral, but not regolith stimulant. It will be very useful for future exploration to have database for each mineral separately and calculate composition and condition of synthesis for any composition of regolith of lunar surface. Aluminium was used as the reducer in every case since it can also be obtained by recycling wastes from previous lunar missions. For blocks for construction made by SHS using ilmenite-based initial powder batches, the final composition was various ratios of $FeAl_2Ti_3O_{10}$, a-Fe, a-SiO_2, TiO_2, Fe2O_3/Al_2O_3 and displayed porosity of 40–50%, density 2.4-3.0 g/cm^3 and compressive strength of 8–11MPa. For blocks for construction made by SHS using ilmenite-based initial powder batches, the final composition of various samples were found by XRD to be Mg,Fe)(Cr,Al)$_2$O$_4$ and ~ 10% of amorphous phase. Porosity of the ceramic product was about 30–36%, gas permeability 0.010 – 0.013m^2, density 3.0-3.5 g/cm^3. Blocks for construction were prepared by SHS method in vacuum also on the base of other minerals and there mixtures, which contain Lunar regolith. The properties of the produced solid blocks are appropriate for a structure such as those that may be built on the moon to protect astronauts as well as for making flat surfaces, all in-situ on the moon.ISRU research for Mars is focused primarily on providing rocket propellant for a return trip to Earth — either for a manned or a sample return mission — or for use as fuel on Mars. A typical proposal for ISRU on Mars is the use of a Sabatier reaction, $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, in order to produce methane on the Martian surface, to be used as a propellant. Oxygen is liberated from the water by electrolysis, and the hydrogen recycled back into the Sabatier reaction. Other reaction proposed for Mars is the reverse water gas shift reaction, $CO_2 + H_2 \rightarrow CO + H_2O$. This reaction takes place rapidly in the presence of an iron-chrome catalyst at 400 Celsius. The net result of this reaction is the production of oxygen, to be used as the oxidizer component of rocket fuel. Another reaction proposed for production of oxygen is electrolysis of the atmosphere, $2CO_2$ (+ energy) $\rightarrow 2CO + O_2$. We (Xanthopoulou et al.) study catalytic CO2 reforming of CH4 to synthesis gas over catalysts produced by SHS method. This process is important for Mars, because synthesis gas is source for production of large number of organic products.

9. INDUSTRIALIZATION

NON CONVENTIONNAL SOLID COMBUSTION OF NEW REDOX BINARY MIXTURE FOR HYDROGEN GENERATION

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Many innovative self-propagating high-temperature synthesis (SHS) techniques such as thermite process, field activated combustion, solid-state metathesis or flame synthesis crystallise currently scientific interest for the synthesis of "advanced materials" [1]. On the same way, in the field of "fuel cells systems", an innovating gas producing self-propagating process using redox mixtures initiated at low temperature has been used for the generation of hydrogen [2]. Indeed, for a wide range of civil and military on-board applications such as for emergency power supplies or future vehicle, the problematic of solid hydrogen storage is not an easy way : pressurized vessels (~200bar) present safety sizeable risks which reduce their utilization whereas cryogenic tanks (20K) present as for them risks of boil off. So, optimizing both gravimetric and volumetric hydrogen densities require therefore using solid storage at room temperature [3].In such context, Herakles has developed a novel solid hydrogen generating composition in the field of gas generators [2]. Based on a high exothermic self-propagating solid-solid reaction (Tad~1300K) without binders and catalysts between a hydrogen-rich compound, the ammonia borane complex BH_3NH_3 (19.6%wtH) [4], and an oxidizer salt, the strontium nitrate $Sr(NO_3)_2$, this technology generates gaseous hydrogen on demand and a small quantity of nitrogen depending on the stoichiometric ratio. In a technological point of view, this technique presents several intrinsic advantages: being safe compared to others solid hydrogen storage solutions, having a fair energetic density (>10%wt), and a long life time with no maintenance costs.In such a way, this paper will be first focused on physico-chemical characterizations (Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray Spectrometer (EDXS), X-ray Photoelectrons Spectroscopy (XPS), Dynamic Vapour Soprtion (DVS)…) realized on each material in the field of morphological, microstructural, thermoanalytical and hygroscopical aspects [5]. In a second time, a combustion chamber specifically realized, in the one hand, to the "in-situ" study of this combustion reaction and the visualization of the propagation front and, on the other hand, to evaluate the influence of two mechanical mixing processes, a turbula shaker mixer and a rotary grind machine, will be presented. The "ex-situ" characterization of combustion products (solid residues, condensates and gas phase composition) in both qualitative and quantitative aspects will be also presented. The whole obtained results allow us to determine a macroscopic mechanism.

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SHS OF ALUMOMAGNESIAN SPINEL AS AN INITIAL SUBSTANCE FOR OBTAINING OPTIC CERAMICS

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Ceramics based on alumomagnesian spinel is the most widely used ceramics among transparent ceramic materials. Spinel-based optic ceramics is remarkable due to its excellent mechanical strength, wear and erosion resistance, stability to unidirectional aerodynamic impact, chemical inertness, mechanical and optic stability at the temperatures up to 1250ºC and wide application fields [1, 2].

The technological process of transparent spinel ceramics production includes two stages: the preliminary synthesis of spinel and making corresponding items. The latter are made by the conventional methods and subjected to annealing in vacuum, hydrogen or neutral medium at 2170-2270 K [3].

But spinel is not widely used nowadays due to its high price and complicated technological process of its synthesis because of special expensive equipment and high power consumption.

We suggested carrying out synthesis of alumomagnesian spinel by the SHS method which is characterized by low price and simplicity of the technological process without any special equipment and high power consumption.

The following reactions were studied to investigate the influence of initial component character on SHS of alumomagnesian spinel:

$Mg + 2Al + 2O_2 = MgA1_2O_4$ (1)
$MgO + 2Al + 1.5O_2 = MgA1_2O_4$ (2)
$MgO_2 + 2Al + O_2 = MgA1_2O_4$ (3)
$A1_2O_3 + Mg + 0.5O_2 = MgA1_2O_4$ (4)
$2MgO + 4Al + 3O_2 \xrightarrow{0,05KClO_4} 2MgAl_2O_4$ (5)
$Mg(ClO_4)_2 + 2Mg + 4Al = 2MgA1_2O_4 + MgCl_2$ (6)

X-ray analysis of the reaction products proved that the best results could be obtained in the case of reactions 1 and 5.

X-ray analysis of sample (1) showed that the synthesized $MgA1_2O_4$ contained only a slight amount of $Mg_{0,388}A1_{2,408}O_4$ additive and it does not affect the light-transmitting ability of transparent spinel [3].

Introduction of potassium perchlorate into initial mixture 5 resulted in $MgA1_2O_4$ containing magnesia. It’s a positive feature for producing transparent ceramics since a slight amount of MgO results in an increase of the light-transmitting ability of spinel [4].

SHS of $MgA1_2O_4$ by reaction 6 without oxygen supply can be rather promising. However, it will be necessary to develop a special method for removing water-soluble $MgCl_2$ which is contained in great amounts (about 40 mass%).

The achieved results prove the prospective viability of the chosen direction for SHS of alumomagnesian spinel as an initial substance for two-stage obtaining of transparent spinel-based ceramics.

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SHS OF NEW COMPOUND IN B-C-Mg SYSTEM, CRYSTAL STRUCTURE $B_{25}C_4Mg_{1.5}$ = $[(B_{12})_2][C_2][CBC][Mg_{1,5}]$

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Magnesium-thermal SHS of boron carbide B_4C [1] result in obtaining boron carbide product (fine-grained B4C, 5-30 μm), but there were visually detected impurities – large crystals (0.5 mm) that have an isometric habit, different color (from amber to black) and insolubility in hydrochloric acid.

Obtained crystals were investigated by powder XRD (using powder obtained from single-crystals) and single-crystal XRD (using single-crystal). Single-crystal XRD method has determined the crystal structure of new compound $B_{25}C_4Mg_{1.5}$. The main crystallographic data: a = 9.626(1) Å, b = 11.329(1) Å, c = 8.966(1) Å, β = 105.80(3)°, V = 940.8 (2) Å^3, space group $P2_1/b$, Z = 4, R factor = 0.03.

Independent area of the unit cell consists of two icosahedra B_{12} (A and B), group C(sp^2)=C(sp^2), group C(sp^3)–B–C(sp^3) and two positions for the Mg atoms with incomplete occupancy (0.88 and 0.46) (fig. 1). Icosahedra linked with each other by three-dimensional net of covalent bonds B–B, B–C(sp^2) and B–C(sp^3).

Crystal-chemical analysis has shown that compounds with described composition and structure have been unknown. This is the first compound in which icosahedra linked by four types of bonds: 1) B–C(sp^3) (1.616-1.622 Å), 2) B–C(sp^2) (1.595-1.606 Å), 3) B–B (1.735-1.778 Å) and 4) B–B (1.848-1.885 Å). Similar structures such as boron carbide B_4C [2] has icosahedra linked by two types of bonds. Thus structure $B_{25}C_4Mg_{1.5}$ has a variety of covalent bonds which differs in lengths. Magnesium atoms have no clear coordination (fig. 2).

Three-dimensional net of B_{12} icosahedra with strong covalent bonds, chemical resistance to acid, unusual structure, revealing the possibility of its variations, suggest that the compound $B_{25}C_4Mg_{1.5}$ has useful properties. Incomplete occupancy of Mg atoms positions suggest this compound is an advanced model for obtaining another compounds based on boron carbide doping by any elements.

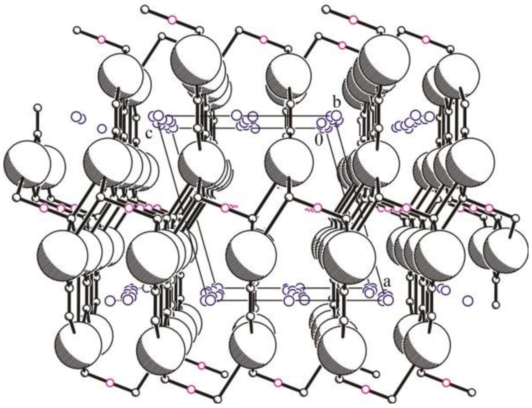

Fig. 1. Crystal structure of compound $B_{25}C_4Mg_{1.5}$.

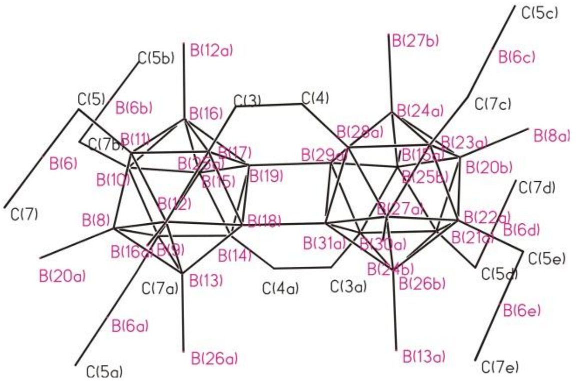

Fig. 2. Fragment of crystal structure $B_{25}C_4Mg_{1.5}$: two icosahedra and it bonds.

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SHS METALLURGY of CAST COMPOUNDS BASED on MOLYBDENUM and TUNGSTEN SILICIDES for ADVANCED STRUCTURAL CERAMICS

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Ceramic materials based on silicides of molybdenum and tungsten are characterized by high resistance to aggressive media at high temperature and being used for deposition and manufacturing machine parts operating in extreme conditions.

Such materials can be produced by SHS in their liquid state [1–2]. In this work, we synthesized cast $MoSi_2$, WSi_2, and $MoSi_2$–WSi_2 solid solutions for subsequent milling into powders with different size distribution of particles. So prepared powders were used for deposition of coatings and sintering.

The effect of blend composition on the synthesis regularities, microstructure and composition of final products was under consideration in this work.

Some highly caloric mixtures of molybdenum, tungsten, silicon and aluminum were suggested where combustion temperature exceeds the melting point of products. So the products are produced in liquid phase.

Experiments were carried out in an SHS reactor with a capacity of 20 *l* under a gas (nitrogen, argon) pressure of 4–5 *MPa*. Synthesized materials (up to 5 *kg* in their weight) were characterized by chemical analysis, XRD, and EDS.

The parameters of product milling in a jaw crusher and in a ball mill were optimized.

Powders $MoSi_2$, WSi_2, and $MoSi_2/WSi_2$ (90/10, 70/30, 50/50, and 30/70 *wt. %*) were doped with ZrO_2 (Y_2O_3) × SiC those were dry-pelleted under a pressure of 100 *MPa.* The compacts (40 × 6 × 4 *mm* in their size) were sintered at 1600–1750 *°C* in the furnace with a graphite heater under argon.
A maximum density and strength was exhibited by the sintered $MoSi_2/WSi_2$ (70/30 wt. %) ceramic composite. This ceramic can be recommended for use as a structural material.

ACKNOWLEDGMENT

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USE OF SHS REFRACTORIES IN LIMESTONE FURNACE REFURBISHMENT

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Combustion Problems Institute of Kazakhstan [1] has developed refractory materials that can be produced by means of the self-propagating high-temperature synthesis (SHS). They are manufactured in the form of the dry exothermal masonry mixtures with better operational characteristics compared to the traditional mortars and powders.

Considering the present continuous growth of prices of raw materials, energy and transportation, one of the most urgent tasks is to develop efficient limestone roasting technologies and upgrade available kilns.

From 1998 up to now, three mine limestone furnaces have been upgraded and refurbished at Nikolayev Alumina Plant (NAP). The refurbishment project has been executed by OJSC LipetskStalProject (Russian Federation) in collaboration with the research institution called Combustion Problems Institute (Kazakhstan).

Currently available reverse-flow limestone furnaces have traditional configuration, i.e they comprise heating, limestone roasting, cooling and lime offloading zones [2]. The basic constructive difference of the upgraded furnace is the presence of gas distribution core dividing the roasting zone into four sectors. The gas distribution core is made of the periclase-chromite arch refractory (PCAR) bricks.

Figure 1 illustrates layout of the roasting zone. The whole structure is supported by two air-cooled and one water cooled beams insulated by the heat resistant concrete. The two-level arrangement of 8 cyclone gas burners and presence of core in the roasting zone dramatically change the heat and mass transfer conditions. The core role is to provide distribution of a large-tonnage limestone weight among four roasting zone sectors, each maintaining a relatively independent limestone roasting process. This leads to a more uniform distribution of the gas flow velocity, alignment of the temperature field along the furnace cross-section, and increase of the limestone propagation velocity. Consequently, exceptionally strict requirements in terms of both mechanical and heat engineering characteristics have been imposed on the most important and most loaded part of the furnace, i.e. gas distribution core.

Mechanical and thermal stability of the core has been provided by means of the SHS-refractory mortars, namely by their ability to "weld" bricks into a monolithic structure [1].

When the unit reaches its operation temperature mode, the self-propagating high-temperature synthesis (SHS) in the mortar provides for the temperature that is close to the brick components melting one due to the exothermal reactions. This enables extremely strong binding of the bricks. Following such synthesis the brick joint material acquires physico-chemical and operational characteristics close to those of the brick material.

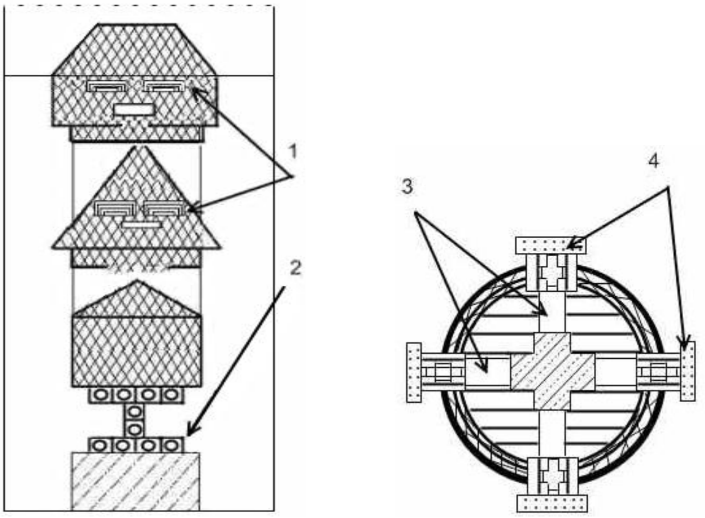

Fig. 1. Layout of the furnace roasting zone: 1 - first and second level air-cooled beams; 2 – water-cooled beam; 3 – gas pipe; and 4 – cyclone burner.

A special exothermal masonry with lower self-ignition temperature has been developed for core laying [3].

Currently available coke based pour furnaces are elsewhere operated using liquid or gaseous fuel. Expertise acquired in the course of the furnaces refurbishment at Nikolayev Alumina Plant as well as the results of the earlier performed and recent studies carried out by Combustion Problems Institute can be of certain use in implementation of the energy-efficient construction materials production "know-how".

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NEW GENERATION OF 2D X-RAY DETECTORS FOR USE IN TRXRD STUDIES WITH NS TIME RESOLUTON

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Developed a two-dimensional x-ray detector with nanoscale time resolution for studies of very fast structural transformations in solid phase, critical for materials science. The detector is made on the basis of three-level GEM (Gas Electron Multiplier) with two-co-ordinate reading plane. GEM detector used in foil is a kapton film thickness of 50 µm with symmetrically positioned holes and covered with a thin layer of copper (10 µm) on both sides.

The active area of the detector is determined by the size of GEM foil and is 100 x 100 mm (fig.1). Camera detector is filled with the gas mixture CO_2/Xe - 85/15 under overpressure 0.5 atm. Reading a plane is a plane of two mutually perpendicular strips of copper, separated by a layer of dielectric thickness 50 microns. The total number of channels in each of the planes is 256. The detector is built on advanced hardware components and allows you to receive and record two-dimensional picture with 4 ns timing resolution.

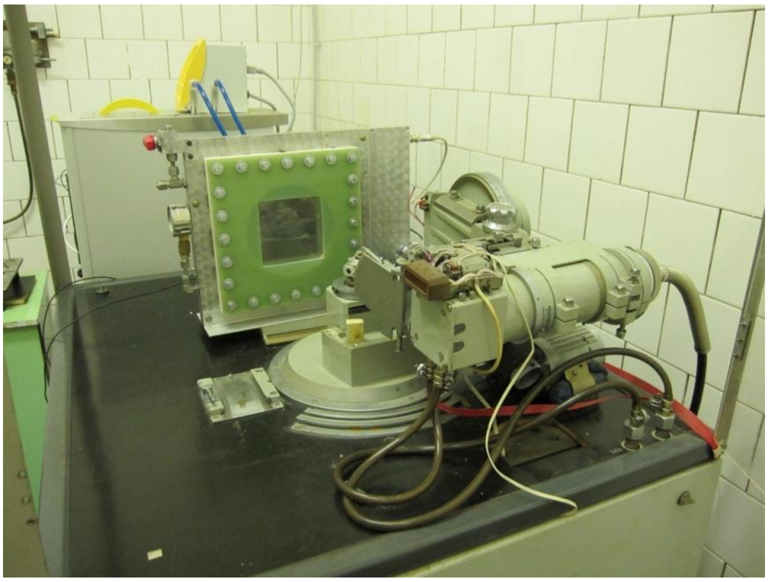

Fig.1 General view of the plants on the base of the a two-dimensional x-ray detector

Basic parameters of the detector:

- sealed with beryllium window	
- working energy	6-15 keV (смесь Xe/CO2)
- sensitive area	100 x 100 mm^2
- spatial resolution	~ 200 micron
- maximum local loading	10^6 imp\s
- expositions of 1 frame	4 ns
- number of frames with continuous recording	unlimited

Tests of the detector using a standard x-ray tube with copper anode are performed. Two x-ray spectra were obtained from several materials with time exposure of 1 ms.

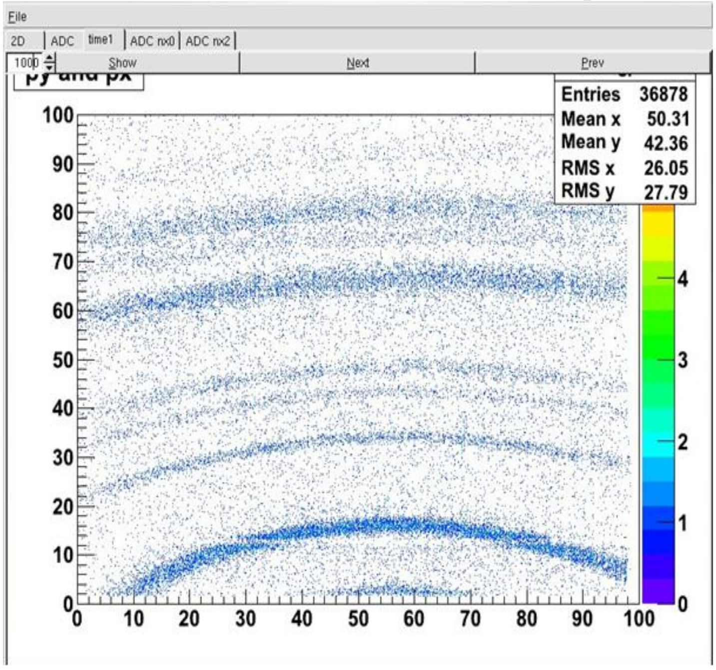

Fig.2 Two-dimensional diffraction pattern of TiO_2 exposure 1 ms, graphite monochromator

A fundamental advantage of this x-ray detector – access lauegramm and nanoseconds time resolution; let's go to the study of elementary transformations of the atomic crystal structure of substances.

NiTi PRODUCED BY SHS WITH TWO DIFFERENT Ti POWDERS

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Shape Memory Alloy NiTi is of high interest as implantable material, as in porous form low apparent elastic modulus can be achieved, comparable to that of bone. This condition, combined with proper pore size, allows good osteointegration [1].

Porous NiTi can be produced by SHS (Self propagating High temperature Synthesis) adopting different procedures depending on the feature of the products. High quantity of secondary phases are formed especially at lowest reaction temperature. On the contrary, at higher reaction temperature, local melting can occur, resulting in the collapse of the porous structure [2]. Addition of hydrated Ti is investigated as a mean to reduce the reaction overheating, and obtain near net shape samples.

Ni powder (99.9% purity, size 3-7 μm, Alfa Aesar), dehydrided Ti powder (99.9%, about

45μm size, Alfa Aesar) and hydrided Ti powder (99.99% purity on metal base, 45μm size, Alfa Aesar) were used to prepare two mixture of approximately equiatomic composition. One mixture was composed by Ni and dehydrated Ti powders (Ni-Ti), the other one by Ni and hydrided Ti (Ni-TiH_X). The mixtures were blended for 12 hours .

Several small cylindrical samples of 10mm diameter and 1-2mm height were compacted in a metallic die with applied pressure of 750 MPa.

Experimental set-up is featured by a laser system (250W) , by which High power densities can be attained. By conveniently regulating the laser power, continuous heating of samples, at different heating rates, and preheating at different temperatures were achieved. Tests have been performed in Ar atmosphere, and the sample temperatures have been measured by Pt/PtRh thermocouples, inserted in the middle of the specimens. Detailed description can be found in [3]. Data were also simulated with a in order to have a better understanding of the phenomena.

Samples were characterised through X-ray diffraction, differential scanning calorimetry (DSC), simultaneous differential thermal analyses and thermogravimetry (TG/DTA), and metallographic inspection.

The thermal histories of Ni-Ti and Ni-TiH_X samples were compared. NiTi powder heated at high heating rates (100°C/s) showed a fast temperature increase starting at about 900°C, associated with the thermal explosion process of NiTi phase formation. Calorimetric analyses confirmed the presence of SMA-NiTi. The reduction of heating rate progressively shifted to higher temperatures the ignition of the reaction: this effect was caused by product formation at the grain interface which also caused a decrease in the following combustion energy as it partially consumes the reactants. The post-combustion exothermic peak in fact decreased with ignition temperature increase.

A different behavior was observed for Ni-TiH_X samples. During fast heating experiments, no fast temperature increase is observed. During heating, endothermic H release from hydrided Ti occurs in the range 480°C – 600°C, as confirmed by TG/DTA measurements on starting hydride Ti powder and on blended Ni-TiH_X mixture, and literature data [4]. TiH_X decomposition probably absorbed reaction heat of Ni with Ti: no sharp reaction peak was observed, high amount of Ti_2Ni was present in samples, no calorimetric evidence of SMA- NiTi was found.

The strong effect of TiH_X endothermic decomposition was confirmed by thermal history of a preheated Ni-TiH_X sample subjected to a first heating up to 520°C and slow cooling to 400°C. During the preheating TiH_X decomposition was allowed, and further heating demonstrated a reaction curve similar to NiTi samples.

Moreover no shape variation was observed for Ni-TiH_X reacted samples, and this reult suggested that this technique could be a promising route to obtain shaped products. Further investigation are required in order to elucidate the effect of hydride Ti on secondary phases content.

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CHARACTERIZATION OF $NiMn_xFe_{2-X}O_4$ FERRITE THIN FILMS FORMED BY ION-BEAM SPUTTERING

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Funtional materials based on nickel ferrites are widely used in electronic components due to their high magnetic properties. The present time perspectives of employment of the NiFe2O4-based ferrites as sensitive components of gaseous sensors are noticeably developing [1, 2]. The mechanism of the oxide material sensitivity is based on the alteration of the electrical conductivity of a thin layer of the material upon adsorption of the molecules of the gas under registration. The possibility of production of the NiFe2O4 material with the predictable properties and stable compositions by the method of ion sputtering of the ferrite powder has been investigated in the present study. At the account made of the above reported problems the present study was aimed at the electroconductivity characteristics of the films deposited on the supports made of glass and silicon and the influence of certain gas concentrations on the electroresistance behavior of the thin ferrite film. In the experiments a green powder of nickel ferrite produced by the method of self-propagating high-temperature synthesis (SHS) was used for the film deposition onto the support [3]. The synthesis was performed according to the following scheme at room temperature under air with the use of simple oxides, metallic iron powder, and sodium perchlorate:

$$\mathrm{NiO + Fe + 0{,}5Fe2O3 + (0{,}2NaClO4) \rightarrow NiFe2O4 + (0{,}2NaCl)} \qquad (1)$$

The target (100×100 mm) was composed of pressed pellets (∅20/5 mm) of the synthesized powder. Deposition of the ferrite films onto the supports of monocrystalline silicon Si (100) was a procedure of ion-beam sputtering. This approach is characterized by an exceptional novelty among the methods of the film deposition onto the silent supports. To determine the temperature dependence of the resistance of the annealed samples R = R(T) measurements were carried out via a triple cycle of heating-cooling within the range of 350-470 K. Measurements of resistance in the NiFe2O4 film carry out under air and in the mixture containing 2.0 vol.% CH4 [4]. Temperature dependence R is seen to have a specific bent at 384 K, which is also retained in the case of air-methane mixture. However, in the course of the temperature elevation the values of Rair and RCH4 keep different up to 421 K. The ratio S = RCH4/Rair exhibits a linear temperature dependence growing up to 403 K followed with a further drop in the range within 403-421 K. The S value in the maximum constituted 1.12. Further investigations are supposed to be aimed at the influence of the manganese content on sensibility of the NiMnxFe2-xO_4 ferrite. This can be important since substitution of the iron ions with those of manganese brings about an extra charge exchange and should excite a stronger response of a sensor material towards the fixed concentration of the detected gas.

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INFLUENCE OF MORA TREE (Maclura tinctorea) FILLER ON THERMAL PROPERTIES OF THE COMPOSITE BIOMATERIAL

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The global market for biomaterials and composites could reach $ 64.7 billion by 2015 [1]. This makes it attractive to develop research in this field and contributes to the search of the new materials to reduce the environmental impacts of its use.

One of the materials of this market is the polyethylene. This material has a global demand that represents around 40% of total polymer industry [2]. An example of this is the industry of Costa Rica, where for the past five years have seen an growth in sales of plastic products of about 60%, of which polyethylene is one of the most widely used polymers [3]. In order to reduce the industrial impact of the polymer, the market of the composite material is growing up, to reduce the consequences of the contamination.

The composite material can be a combination of polyethylene and cellulose that shall meet the market request and be: no toxic, environmental friendly and cheap. One of these cellulose materials is the Maclura tinctoria (L.) or mora tree (Fig. 1), as it is commonly known. This tree belongs to the family Moraceae, and is a wild tree that can be located on the Pacific coast of Costa Rica. This tree has several interesting aspects for research, as a natural dye and plays an effectively roll as a medicinal plant for various purposes including their use to reduce toothache also. [4].

Figure 1. Picture of the Maclura tinctoria (L.) or mora tree.

Given the many properties of this tree, it has been used as a component of polymeric materials composite. The influence of this plant has been evaluated from the thermal properties of composite materials obtained.

In this study was used a mixture of different parts of the mora tree, as a component in the fabrication of composite polymeric material in the matrix of low density polyethylene (LDPE), and its characteristic properties are presented. For this research we used a comertial LDPE grade 15803-020, manufactured by JSC "NefteHimSevilen", Kazan, Russia, was used as the polymer matrix. For this study was selected a load of 30% of the filler material. [5].

The thermal properties of LDPE and the composite film filled with the mora tree particles were investigated by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

RESULTS

The figure 2 shows the TGA curves of low density polyethylene and the compound of low density polyethylene with 30% of aggregate particles of mora tree. The pure LDPE started its weight loss at 320°C and completely decomposed at 480°C. The TGA of the mora tree-LDPE composite show that the incorporation of Mora tree particles in the matrix of LDPE produces an initial mass loss due to moisture loss from the sample and than remained constant up to 200°C, and then decreases . The early degradation of the material relative to the matrix of pure LDPE, is start at 220°C and completely decomposed at about 480°C similar to pure LDPE.

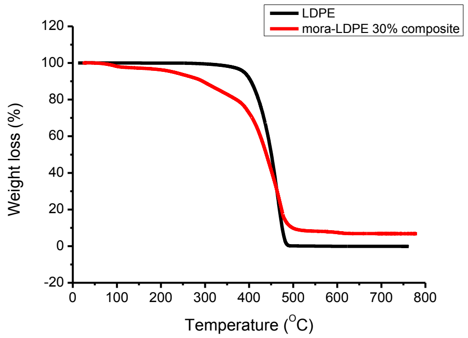

Figure 2. TGA curves of low density polyethylene and the compound of low density polyethylene with 30% of aggregate particles of mora tree.

The composite thermal peak indicates that the increase in the crystallinity of the material is due to the crystal growth process and this begins before the solid particles in the filler material in the pure polymer. The crystallization temperature shows the ability of nucleation in the matrix fiber. However, due to the addition of load lamella thickness increases, causing the increase in melting temperature which generally lowers crystallinity.

We can see in this experiment that mora tree particles in the matrix of LDPE altering the initial mechanism of the first stage of thermal degradation, increasing the rate of degradation.

ACKNOWLEDGEMENT:

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EFFECTS OF CRYSTALLINITY AND MORPHOLOGY OF SOLUTION COMBUSTION SYNTHESIZED Co_3O_4 AS CATALYST PRECURSOR IN HYDROLYSIS OF SODIUM BOROHYDRIDE

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In general suitable catalyst materials for $NaBH_4$ hydrolysis are precious metals such as Pt or Ru [1, 2]. Due to their cost, increasing attention has been given to cobalt and cobalt based catalyst precursors as alternatives [3]. Cobalt based materials are often labeled catalyst precursors in hydrolysis systems as they become reduced *in-situ* by $NaBH_4$ to form the active catalyst, identified in many cases to be Co_xB [3]. Despite the many attractive features of Co as an alternative to precious metal catalyst, drawbacks include lengthy and involved synthesis methods and the pyrophoric nature of elemental nano-sized cobalt in air to rapidly form cobalt oxide.

Recently, results using the stable in air cobalt oxide (Co_3O_4) as a catalyst precursor for hydrolysis of $NaBH_4$ solutions and $NaBH_4$/NaOH solutions appear promising. For example, Simagina *et al.* [[4]] reported a hydrogen generation rate (HGR) of 0.57 L $min^{-1}g_{cat}^{-1}$, at 20°C, using Co_3O_4 with a specific surface area of 16 m^2/g as the catalyst precursor at 20 wt% loading. Krishnana *et al.*[5] demonstrated that increased crystallinity of Co_3O_4 improves catalytic behavior (surface areas were not reported.

Several synthesis methods for Co_3O_4 have been reported in recent years such as thermal decomposition of solid phase cobalt based salts or sol-gel methods. These methods can take on the order of several hours to several days. An alternative, rapid synthesis method would be advantageous if Co_3O_4 is to be employed as a catalyst precursor for $NaBH_4$ hydrolysis systems. Solution combustion synthesis (SCS) can rapidly synthesize large quantities of materials and has been studied widely for the synthesis of various oxides [6,7], though there are only a few reports of cobalt oxides formed via this method [8,9]. Results reported by Toniolo *et al.* indicate surface areas of 36 m^2/g for Co_3O_4 using glycine as fuel with cobalt nitrate [8]. However, to the author's knowledge these powders have not been extensively studied or optimized for use as a catalyst precursor for $NaBH_4$ hydrolysis.

In this work, solution combustion synthesized (SCS) cobalt oxide (Co_3O_4) powder has been studied as a catalyst precursor for the hydrolysis of sodium borohydride ($NaBH_4$). Results indicate SCS is capable of reproducibly synthesizing 98.5-99.5% pure Co_3O_4 nano-foam materials. SCS materials demonstrate an as-synthesized specific surface area of 24 m^2/g, a crystallite size of 15.5 nm, and fine surface structures on the order of 4 nm. Despite having similar initial surface areas and sample purities, SCS-Co_3O_4 outperforms commercially available Co_3O_4 and elemental cobalt (Co) nano powders when used as a catalyst precursor for $NaBH_4$ hydrolysis.

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MECHANICAL PROPERTIS OF TITANIUM, PRODUCED BY SINTERING OF TITANIUM HYDRIDES

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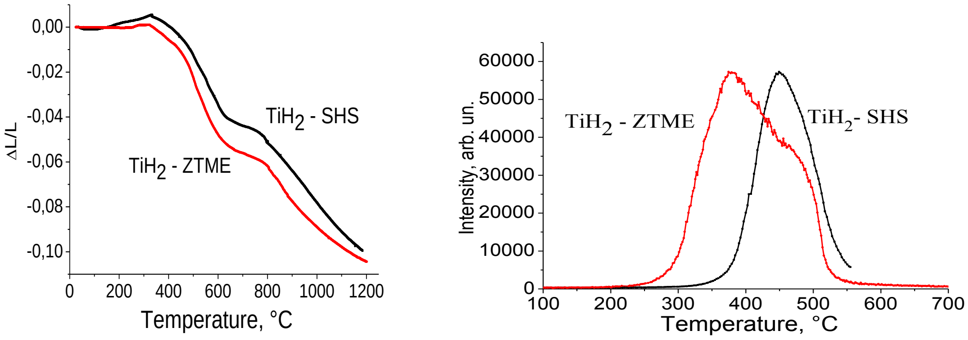
The results of titanium hydrides (TiH_2) sintering have been considered in present work. These hydrides were obtained from titanium sponge by two different methods. The first of them is a self-propagating high temperature synthesis (SHS) in hydrogen atmosphere [1] and the second is a standard method of heating titanium in hydrogen atmosphere (Zaporozhye Titanium-Magnesium Enterprise – ZTME). Hydrides were reduced to powder before sintering then pressed at pressure 300-400 MPa in fillets (the length by 50 mm and cross section by 10×10 mm) and then were subjected to heat treatment from 620 K to 970-1070 K with the heating rate 20 K per min. up to total yield of hydrogen. Final sintering was performed at 1520 K during 4 hours in vacuum to residual porosity 1-4 bulk per cents. Mechanical tests by tension have performed on the ASTM E8-M. The features of pure titanium samples obtained after sintering and tension have shown at Table 1.

Table 1.

Hydrides modification	Ti density after sintering, G/cm^3	Oxygen content, Mass per cent	Yield point, MPa	Ultimate strength, MPa	Elongation, per cent
TiH_2 CBC-4	4,442	0,28	446	532	18

TiH_2 CBC-5	4,445	0,23	440	500	24-26
TiH_2 3TMK	4,444	0,22	465	560	21-26
TiH_2 3TMK	4,437	0,15	445	537	35

The samples produced from different TiH_2 had in fact the same final density and varied by oxygen addition content. Dilatometric analysis showed that the ways to achievement of final density for the different modifications of hydrides were found the different (Figure 1). At heating in vacuum with rate 7 K per min. consolidation of TiH_2 SHS is late in compare with consolidation of TiH_2 ZTME. The difference in linear dimensions can be explained by greater thick of oxide film on the TiH_2 SHS surface. It is a reason of hydrogen dragging output on temperature in compare with TiH_2 ZTME.



a) b)

Figure 1. a) dilatometric curves of consolidation in dependence of temperature,
b) comparison of temperature intervals of hydrogen output from hydrides
TiH_2 ZTME and TiH_2 SHS.

Different oxygen addition content in materials has an influence on the equilibrium vacancy concentration. It in turn affects on titanium self-diffusion coefficient. That is why in the beginning of heating TiH_2 SHS drops behind from TiH_2 ZTME in consolidation rate but higher than 1120 K it is compressing most active achieving the same final density as TiH_2 ZTME. Oxygen content is the most important factor of influence on mechanical properties of titanium, sintered from titanium hydrides powders. The less oxygen has titanium the more it is plastic and therefore manufacturable. However as it seen from Table 1 titanium sintered from TiH_2 SHS though the higher oxygen content is shown near the same plasticity as titanium sintered from TiH_2 ZTME with the less oxygen content. The most probable explanation of this fact can be the suggestion that titanium sintered from TiH_2 SHS has the less content of other additions, which are negatively influenced on plastic properties, for example, carbon embrittling titanium as oxygen.

Probably, TiH_2 SHS has appeared more pure on carbon owing the fact that argon displaces the air from reactor. Moreover, at synthesis in SHS regime the refinement can take place from the other additions also in first turn adsorbed and gasifiable in combustion wave due to the known “self-refinement” effect [2]. In standard hydrogenation method the carbon can appear by the reason of oil pumps used for vacuum.

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SH-SYNTHESIS OF NANOCOMPOSITION MATERIALS BASED ON THE SYSTEM SiO_2+Al+$CaSiO_3$ WITH WOLLASTONITE AFTER ULTRASONIC TREATMENT

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When obtaining nanocomposition materials with high indices of strength, crack resistance and other physico-chemical properties under the conditions of self-propagating high temperature synthesis (SHS), nanopowders of oxide compounds are introduced into the composition of the charge mixture. Mechanochemical treatment in the mills of a dynamic action is one of the methods that allows obtaining ultradisperse powders with particles of nanocomposition structure [1]. Another rather effective method to change both dispersity and the structure of the surface layer of particles is ultrasonic treatment of powders in an aqueous medium. Wollastonite is one of the promising materials, when obtaining different composition systems containing objects of a nanoscale level.

This paper presents the results of a complex study of the structure and properties of wollastonite after ultrasonic treatment (UST) and its effect on the development of the process of technological combustion (SHS) of systems based on quartz, the structure and properties of synthesized composition materials. Ultrasonic treatment of wollastonite of the brand FW100 was carried out in water and 5% aqueous solutions of different alcohols and acids at 40 and 100 kHz as well as at simultaneous US action of 40 and 100 kHz during 20-60 minutes. After US treatment we determined dispersity, bulk density of the powder, carried out electron-microscopic investigations on the particles and measured their dielectric permittivity. Dispersity of the powder, accumulation and redistribution of defects increase depending on both time and frequency of US action, the greatest effect being registered at simultaneous action with frequencies of 40 and 100 kHz. In the presence of different organic modifying additives during UST there takes place not only milling of wollastonite particles and erosion of their surface but also different complex structural changes on the surface of particles and their capsulation into colloidal conglomerates. Structural changes of wollastonite considerably effect the dielectric permittivity of the powder. It is shown that this index can serve as a quite sensitive characteristic of the new state of particles after US treatment.

All the structural changes taking place in wollastonite particles under the conditions of UST result also in the change of the chemical activity of the material, this effecting the thermodynamic characteristics of the combustion process (SH-synthesis) of systems containing modified by UST wollastonite in the charge mixture. Introduction of wollastonite in the amount of 10% into the charge mixture contributes to the decrease of the induction period of the mixture ignition, the increase of the combustion rate and temperature as well as the change of temperature at the stage of post processes. The samples containing wollastonite after UST during 40 minutes at simultaneous US effect of 40 and 100 kHz showed maximum combustion temperature, more than 1600 °C (Figure 1).

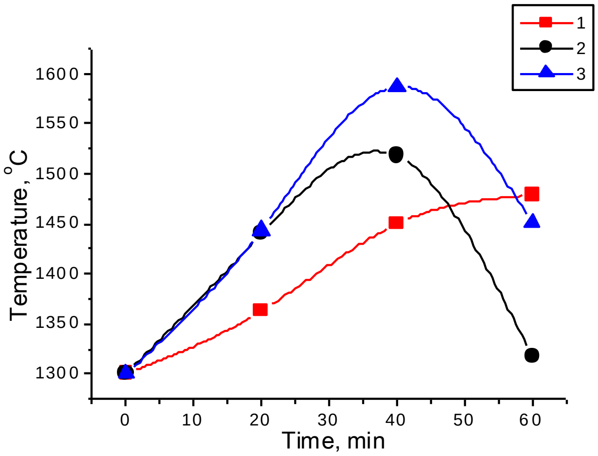

Figure 1 – The dependence of maximum combustion temperature of SHS-samples with 10% of wollastonite after US treatment in water on time at the frequency of 40 (1), 100 (2) and simultaneous effect of 40 and 100 kHz (3)

It is stated that, when introducing wollastonite after US treatment into SHS-charge, there takes place a more complete conversion of initial components in the combustion process of the samples. The greatest amount of corundum and nanocrystalline silicon is formed, when using wollastonite treated in water, aqueous solution of polyvinyl alcohol and acetylsalicylic acid. The synthesized samples are characterized by high stable values of strength (up to 73 MPa) and indices of electric insulation properties.

Thus, US treatment of wollastonite powder being introduced into the composition of the charge mixture is an effective method of purposeful changing properties of SHS-material being synthesized.

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SHS - HEAT INSULATORS OBTAINED ON PREACTIVATED MINERAL RAW MATERIALS

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At present, there is a wide choice of developed heat shield porous and refractory materials obtained under the conditions of sell-propagating high temperature synthesis (SHS), in the range of densities 0.2 – 1.2 g/cm^2. They are used on different objects of metallurgical and machine building industries and, most of all, on different thermal sets in heat power industry. Aluminosilicate refractory and heat insulation SHS-materials the main components of which are aluminum and silicon dioxide, being cheap and widely distributed, rank high among this category of heat insulators [1].

When producing high temperature heat insulators, the range of the initial mineral compound being used gets widened. The system $CaO-SiO_2-Al_2O_3$ for synthesis under the conditions of SHS is of especially great interest as it allows obtaining composites containing wollastonite, anorthite and helenite which provide the increase in strength and thermal stability of the material with its quite high porosity, and, hence, low thermal conductivity.

Quartz, marble and wollastonite were used as initial raw material in the work. Preliminary mechano-chemical treatment (MCT) of the charge components was carried out for directed synthesis of SHS-composition materials. Activation and modification of the surface of the charge mixture parcticles change the kinetic parameters of technological combustion directed to formation of nanosize components of the structure of SHS-composites determining a high level of strength and thermal physical properties [2].

The results of the carried out experiments allowed to state that introduction of wollastonite into the charge mixture provides the procedure of site combustion along the volume of the sample on the background of the general wave of combustion. In the course of site combustion there takes place formation of ultradisperse compounds uniformly distributed along the volume of the sample being synthesized and formation of micropores. The indices of thermal conductivity of the synthesized material considerable charge depending on the time of MCT and the kind of modifier (Figure 1).

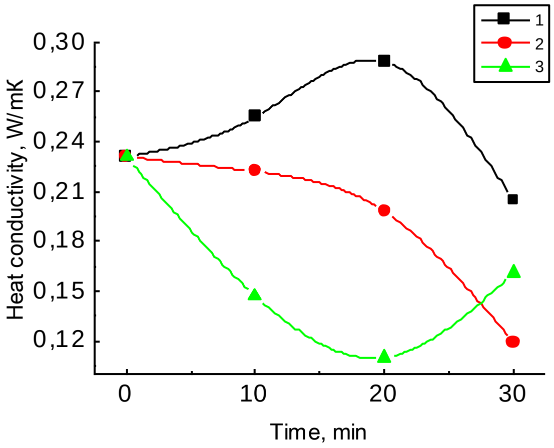

Figure 1 – The change of thermal conductivity of SHS-samples depending on the time of MCT of the charge obtained on the basis of systems: [SiO_2+5% $CaSiO_3$] (1), [SiO_2+5%$C_4H_6O_4$+5% $CaSiO_3$] (2), [SiO_2+5% $(C_2H_2OH)_n$+5%$CaSiO_3$] (3)

The use of alcohols as a modifying additive during MCT of the charge as well as the content of calcium carbide in the mixture enhance the role of gas phase reactions in the activated system combustion process due to formation of synthesis gas which takes an active part in the process of the system combustion changing its thermokinetic characteristics and increasing porosity of the samples. It is stated that MCT of the charge contributes to the increase in the strength of SHS-samples. The increase in the strength of the samples correlates with the growth of the amount of helenite, formation of aluminium nitride and $FeAl_3SiO_2$ in synthesis products.

In order to provide the multifunctional action of the material: heat insulator and a strong compound with a metallic basis – the compositions of the charge were chosen by layers. We determined the most effective conditions of MCT for charge mixtures of every layer which allow purposefulyl controlling thermokinetic characteristics of the combustion process and phase formation, when obtaining ceramic composites with enhanced thermal and mechanical stability. On the basis of the developed charge mixtures, coatings on the metal surface with thermal conductivity up to 0.028 W/mK were synthesized. The obtained values characterize the synthesized material as a good heat insulator which provides small losses of heat from the heated surface comparable to indices, when using expanded pearlite as heat insulator.

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ENERGY AND MASS SAVED SPACE EXPLORATION AIDED BY DIMENSIONALLY-CONTROLLED SHS TECHNOLOGIES

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The International Space Station(ISS) has been used not only as an in-orbit research laboratory but also as a training base for deeper space exploration, which will finish its existence around 2020. Although it has still been under discussion to formulate a vision for space exploration beyond low Earth orbit(LEO), continuous efforts have been undertaken toward human space activities and presence in space. They include the participation in the ISS and future exploration of Moon with construction of a lunar outpost. Furthermore, under participation in international manned space exploration with construction of lunar base, “extended stays of humans in space" are aimed with necessary steps in realizing such as robotics, nano- and micromachine technologies, space solar energy, and multiple resource utilizations of which energy and mass loss should be reduced. Specially, the availability of renewable or self-sustaining energy is prime for space exploration

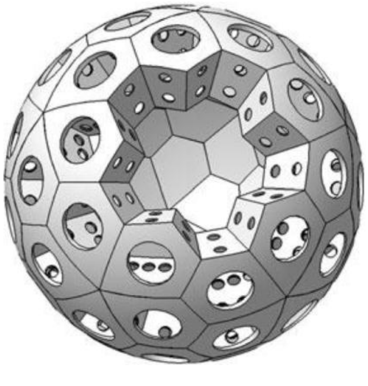

Fig. 1 The shape of the assembly using the designed units [1]

and essential for space utilization, and it plays a critical role in the design and implementation for human space access in space exploration beyond LEO. Self-propagating high-temperature synthesis(SHS) technologies have been applied to the R&Ds for such requirements as “in-situ resource utilization(ISRU)” and “thermal wadis” applicable to both the Moon and Mars; the SHS technology is a rapid, versatile and near net shaping one that can operate under various conditions such as centrifugal-force, low-gravity and high vacuum. Recently developed two SHS-related technologies also promise to fulfill highly efficient space exploration in energy and mass; (1) SHS-joinings applied to “stereo fabrication of large-sized matters with hollow ceramic units assembling” and (2) SHS-capsulatings applied to “large-sized light and tough aggregate fabrication with metal and/or

ceramic hollow spheres”. (1) Stereo Fabrication of Large-sized Matters with Hollow Ceramic Units Assembling The R&D has been performed as a part of “Innovative Development of Ceramics Production Technology for Energy Saving” project with the Stereo Fabric Research Center. The main concept of the stereo-fabric is as follows; for example, when a large-sized ceramic container with high thermal insulation and light mass is required by designing the shape in spherical, large-sized spheres can be regarded as an assembly of uniform polygons divided into small segments made of ceramic that are hollow as shown in Fig. 1, the segments can be manufactured and assembled to produce the large-sized sphere, where each ceramic unit was fixed and joined using an alumina-based SHS-joining. Al_2O_3 ceramic ceramic joinings in the present work as shown in Fig. 2 have been performed by the controls in process and chain reaction dimension with changes of reactant component characteristics, which is of great interesting in order to establish highly efficient joining technology.

Fig. 2 SHS-joining of Al_2O_3 pipes with 160 mm in diameter and 2,000 mm in length

(2) Large-sized Light and Tough Aggregate Fabrication with Hollow Spheres

Mesoscopic scaled metallic/ceramic hollow spheres were fabricated with small sized hierarchic structures such as hollow spheres and capsules. The assembled aggregates could show high mechanical properties and much in light. Hollow spheres and capsules are attractive owing to their wide applications in low dielectric constant substrates, sensing and labeling, optoelectronics, catalysis, wave scattering, lasing, photonics, etc. The group of the JFE Techno-Research Corp. has developed a sintering process performed mainly with the reduction of iron oxides.[2]

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PATTERN FORMATION BY SHS AND SIMILAR PROCESSES

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SHS and similar processes (such as optical discharge in optical fiber) let to obtain products with remarkable properties. Between them, gradient materials achieved due to periodical modes in propagation of reaction waves. In the case of laser irradiation through optical fiber, the breakdown is observed. The discharge plasma (small star) moves toward input. Behind it, periodical structure of cavities or bubbles rests. Such a phenomenon can be used to produce laser superlattices having wide applications in electronics, optics and other fields.

When chemical reactions are responsible of pattern formation, various modes can be established as result of different reaction ways. Firstly, reaction diffusion was considered. However, diffusivity in solids is too weak. If the melt forms in reaction front, the spreading of liquid towards initial mixture is possible. There in cold pores the melt solidification may occur. This results in critical value of heat power. For supercritical heating the wave moves uniformly, while subcritical one leads to periodical regime. When the melting temperature appears to be larger than that of combustion, the fracture of grains due to thermal stresses provides increase in the reaction rate. The thermal expansion of grains generates stresses, activation energy drops (effect of S.N. Zhurkov), the fracture takes place, and we have rapid diffusion on new surfaces.

APPLICATON OF A RESISTOMETRIC METHOD AND IMPEDANCE SPECTROSCOPY TO STUDY MICRON-SIZED AND NANODISPERSED SHS MATERIALS

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The presentation gives an overview of different approaches to measuring DC [1-8] and AC [9] conductivity in order to study interrelation of conducting structure of powder materials with their behavior in SHS compositions including solution of specific applied problems in SHS technology. Major emphasis is placed on comparison of the structure and conducting properties of micron-sized and nanodispersed components with similar material composition which enabled to clear up the features of their behavior in SHS compositions at various stages of working cycle and application.

DC measurements resulted in ascertaining of a number of distinctions in the kind of properties of nanodispersed metallic powders as against powders with micron-sized particles. Resistivity vs. degree of compaction dependences (Fig.1) show that nanodispersed metals do not exhibit abrupt change of impedance near conductivity threshold typical for micron-sized powders [1]. This fact gives evidence about invariable nature of conducting structure of these materials in a wide range of compaction degrees starting from free loose state.

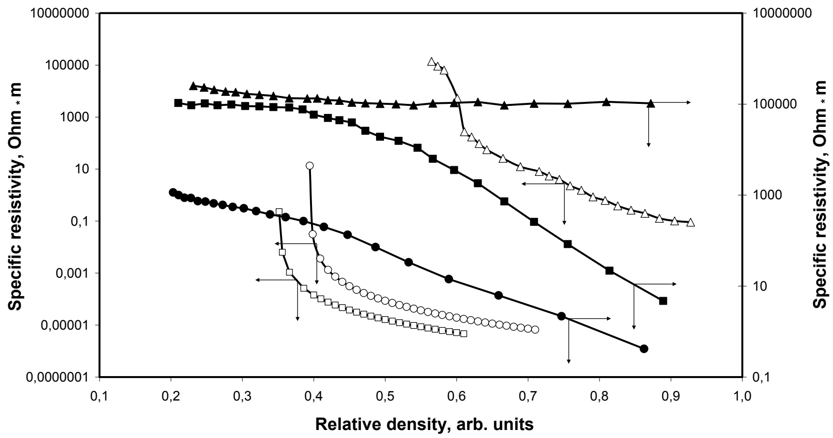

Fig.1 Resistivity for nanodispersed powders of aluminum (▲), titanium (●), tungsten (■) and micron-sized powders of aluminum (Δ), titanium (○), tungsten (□) as a function of compression degree

Impedance spectroscopy data prove information on an invariable nature of conducting structure of nanodispersed metals caused by integrity of oxide films in the points of contact of particles which, in particular, is evident from typical invariance of the mode of impedance loci from compaction degree (Fig.2, d).

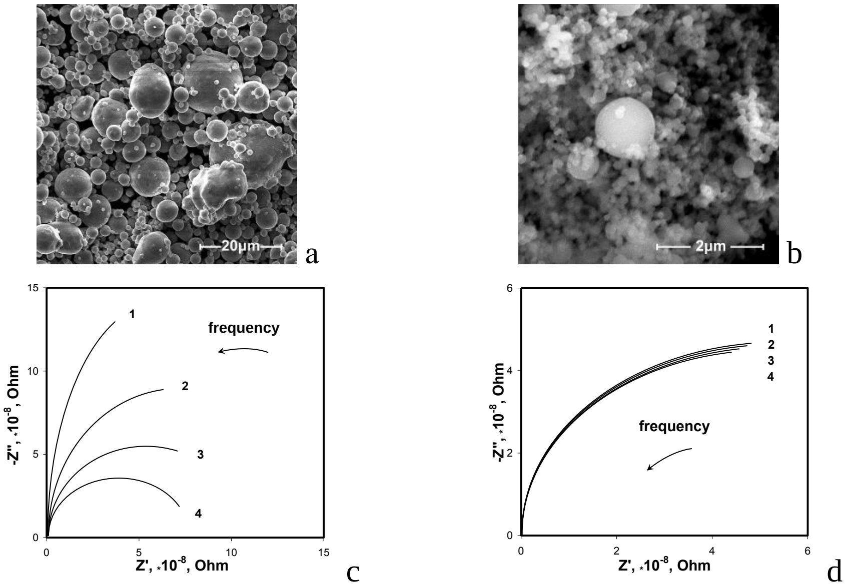

Fig.2 Electron microscope images and impedance loci of micron-sized (a, c) and nanodispersed (b, d) Al powders (sample's density increase from 1 to 4)

These and other examples of resistometric analysis and impedance spectroscopy together with improved methodological approaches and integrated knowledge related to interrelation between conducting structure and behavior of materials in SHS processes enabled to work out experimental techniques to control their quality including industrial applications.

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A STUDY OF SELF-REFINING OF A REACTION SYSTEM DURING SHS

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It is known that as a result of SHS many refractory compounds undergo self-refining from impurities: concentration of a number of gaseous and volatile impurities in the end product is significantly lower than in source components [1, 2].

This presentation gives the insight of studying the possibility of self- refining of Ti-H reaction system from oxygen and nitrogen impurities in the process of titanium hydride SHS.

Two types of cylindrical samples were used for titanium hydride preparation: open (as a set of the pellets) and closed (source material was pressed into a gas-tight tube with one open end). Synthesis was carried out using titanium powder of various grades at hydrogen pressure of 40-60 atm inside a metal reactor which, prior to SHS, was evacuated down to the pressure not more than $5 \cdot 10^{-2}$ Pa. Hydrogen for synthesis was produced by thermal decomposition of vanadium hydride in hydrogen gas generator. SHS was initiated by a filament made of nichrome wire. The process was controlled by monitoring the change of hydrogen pressure in the system.

ELTRA ONH-2000 type analyzer was used to determine the concentrations of oxygen and nitrogen impurities in source and synthesized materials. The quantity of hydrogen in the samples was determined volumetrically.

Obtained data enable to draw a conclusion that self-refining of titanium hydride occurs during SHS: concentrations of oxygen and nitrogen impurities in titanium hydride are lower as against source titanium powder. Separation efficiency depends on SHS conditions. In addition, these impurities are re-distributed through the volume of sample, moreover the change in oxygen and nitrogen concentrations is in correlation with distribution of temperature in titanium hydride sample when it cools down after SHS. The least values of concentrations of tested impurities were obtained in the center of samples.

Mass spectrometric analysis of reaction gas conducted after synthesis revealed that oxygen impurity was removed from the reaction system in the form of water vapors which well correlates with [3], whereas nitrogen impurities are removed in the form of ammonia. It is ascertained that degree of self-refining when the main stage is, presumably, a withdrawal of newly produced water vapors and ammonia into available “free” volume depends on the area of open surface of titanium hydride sample.

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COMBUSTION VELOCITY DEPENDENCE FROM SIZE OF THE SAMPLE IN THE Ni+Al SYSTEM.

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In the Ni+Al system experimentally explored was the combustion velocity dependence from sample diameter for initial mixture and for mixture after mechanical treatment in the argon atmosphere and then in the water. In spite of the fact, that samples, pressed from the mixture after mechanical treatment, became longer during combustion and samples, pressed from initial mixture did not change the size, combustion velocities dependence from diameter of the sample are similar for both mixtures. With increasing diameter of the sample from 8 to 12 mm combustion velocity pass through the maximum. On the rising dependence branch the main factor, affected on the combustion velocity, is heat loss decreasing. On the descending dependence branch dominating factor became increasing of pressure of impurity gases, that releasing before combustion front and were an obstacle to combustion wave propagating.

It was fond, that combustion velocities of films with thickness 270-360 mkm, obtained by rolling from the initial, mechanically activated and additionally activated in water (dispersed) mixtures Ni+Al, increased combustion velocities of the samples with diameter 8-12 mm, pressed from the same mixtures, 4-20 times.

Data, obtained in the work, explained by convection-conductive combustion wave propagating model [16].

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SYSTEM Ni+Al COMBUSTION. Al POWDER PARAMETERS INFLUENCE.

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Explored was the reason of combustion velocities difference between Ni+Al mixtures with two Al powders of the same brand (ASD-4), but from different lots, with different average particle size and O content. One Al powder has maximal particles mass contain in the range 6.31-8.31 mkm, and other has maximal particles mass contain in the range 8.31-11 mkm. Oxygen contain in this powders (due to the presence of oxide films on the surface of Al particles) was 1.9 and 1.75 mass % respectively. Powder mixture Ni+Al with each of this two Al, sticking to the drum walls and milling bodies during mechanical activation was explored. Mixture Ni+Al with smaller and more oxidized Al stuck to the walls of the drum and milling bodies to a lesser extent and burned at a higher velocity as compared to a mixture Ni+Al with larger and less oxidized Al. After mechanical activation, the burning velocity of the both mixtures became nearly the same.

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STRUCTURE FORMATION OF PRODUCTS IN MULTIWAVE COMBASTION OF THE Me1 – Me2 – N_2 SYSTEM

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As suggested in [1, 2], SHS reactions in Me1–Me2–N_2 systems (where Me stands for a metal) take place in the liquid–solid suspensions formed upon heating starting Me1–Me2 mixtures to some temperatures within a narrow range between the solidus (S) and liquidus (L) temperatures. In this work, we characterized the macrostructure of combustion products formed in Me1–Me2–N_2 systems (Me1 = Ti, Al, Me2 = Mo, Cr, Co, Al) and attempted to explain the origin of bright high-temperature traces visually observed during the combustion process.

EXPERIMENTAL

Combustion was carried out in a constant-pressure reactor under a pressure of high-purity nitrogen gas acting also as a gas reagent. Commercially pure powders of Ti, Al (used as Me1) and Mo, Cr, Co, Al (as Me2) contained an impurity of oxygen so that the system under study is better represented by the formula Me1–Me2–N_2(O_2). Cylindrical powder compacts were ignited with a heated tungsten coil. In experiments, the Me1/Me2 ratio of green mixtures was varied within the range 15–95 wt %.

RESULTS AND DISCUSSION

Visually we observed a sequence of bright flashes appearing on the sample surface during propagation of a combustion wave. Depending on starting conditions, the flashes moved along different trajectories—such as tilted spirals, vertical rows, upward or downward oriented cupola, etc.—arising in various sample areas in different order. Burned samples exhibited a number of craters with fritted edges on their surface. The craters were formed by the hot gaseous jets (torches) erupted from the sample bulk through hollow channels. It was the bright glow from these jets that was visually observed upon their output from the sample bulk. The sample macrostructure is a result of passing several combustion waves with their own onset time, spatial configuration, and trajectory of motion. For instance, some part of green mixture at the center either burns later or remains unburned, thus forming a ′finger′ (indexed as **1** in Figs. 1) [3, 4].

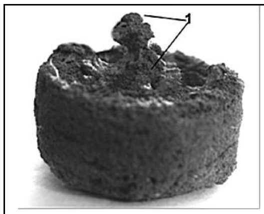	Fig.1. The burned sample with a finger 60 вес% Ti +40 вес% Mo		Fig.2 view of fragmented burned samples. d - 28вес%Ti+72вес%Al, e – 95 вес%Ti + 5 вес% Al

Figure 2 shows fragmented burned samples. The cupola-like bodies were formed due to periodic narrowing/expanding of the combustion front. The material inside the cupolas burns out later on. Gaseous combustion products are gathered in a space between the combustion waves, so that the burned samples easily defragment into the parts shown in Figs. 2.

CONCLUSIONS

SHS reactions in the Me1–Me2–N_2 system within the L–S temperature range proceed by the mechanism of catalytic combustion, without formation of planar combustion front, but via numerous combustion waves with different spatial configuration and phase shift. The process of afterburning involves formation of new waves or warm-up with the torches of burning gaseous products. The latter ones form outlet craters on the surface of burned samples.

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