Initiating Potential of Centrifugally Accelerated Metal Particles in the Inorganic Synthesis Reactions

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Abstracts

The method of producing clusters of various metals by using self-propagating high-temperature synthesis (SHS) in the conditions of high-speed rotation is presented. The purpose of a study is development of the technology of the acceleration of strong- endothermic reactions and synthesis of ceramic materials and products. The task of a experimental study consists of the observation of the wave of combustion in the effective layer, the determination of the coordinate of its passage in the adiabatic regime and the arrangement here of less effective layer for the purpose of obtaining gradient and composite materials.

The possibility of the output of the process of the combustion of oxide system to the adiabatic regime is shown. The limits of inflammability in the centrifugal-force field come down by the attack of the adiabatic wave of combustion by accelerating the front of combustion with the molten particles of metal, returned into the zone of reaction by centrifugal acceleration.

The potential possibility of using the centrifugal efforts for the production of ceramic materials was demonstrated for the multilayer aluminothermic systems. The speed of motion of metal particles under the influence of centrifugal acceleration is calculated. In the reactor of 30 cm long the speed of particles of tungsten reaches 94 m/s with a frequency of rotation of 3 000 rev/min received accelerated clusters of metals that are considered as possible sources of initiation of the chemical processes having about MJ/mol of activation energy. This method was allowed to produce gradient materials.

Introduction

Undertaken studies of the combustion process performed by the Self-propagating High Temperature Synthesis (SHS) based on the nickel, iron, and molybdenum oxides and affected by a centrifugal acceleration have revealed specific properties and high power capacity [1] of a wave propagating in the reactor. The centrifugal acceleration reduces the underneath combustion concentration threshold and provides a stationary processing mode and separation of the combustion products as well as in the highly diluted mixtures. High velocity of the thermal combustion front advancement is caused by contribution of the rotation kinetic energy in the total energy of the metal clusters motion in the SHS front. A purposeful use of the clusters generated energy is thought to find its practical application.

The objective of this study is to identify kinetic potential of the centrifugally accelerated particles so as to initiate high activation barrier chemical reactions with the purpose to produce unique materials properties.

Experimental

Tungsten has been chosen as a restored metal for the energy vector layer since a heat effect of the WO_3 oxide based aluminum reduction reaction is at the level of iron (III) and nickel (II) and constitutes 2890 kJ/kg, whilst its density is more than twice higher. Considering such initial substance parameters, the combustion behaves like a volume explosion, therefore a stoichiometric mixture of tungsten and aluminum oxides has been diluted using aluminum oxide as one of the synthesis final products. The concentration range of dilution varies from 60% up to 10% above a 100% stoichiometric mixture. Combustion of a separate metal oxide forms both the liquid phase and ceramic components of the combustion products:

$$3Me_xO_y + 2y\,Al \rightarrow 3xMe + yAl_2O_3 \qquad (1)$$

One goal of this study is to create a model of the rotating reactor and study the possibility to develop a new material synthesis trend.

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These studies have been carried out using the unit specially designed to model the combustion process under the centrifugal force effect [2]. This unit includes a shaft installed engine, and a crosspiece with three cylindrical reactors fixed on it in a balanced manner at 1200 angle (Fig. 1). The combustion process inside the reactor is initiated by an electric impulse when set rotation frequency is achieved. The number of the centrifuge revolutions was regulated by changing the electrical motor. The rotation working frequency varies from 500 rpm up to 5000 rpm in accordance with the centrifugal acceleration in the ignition point varying between 25 and 2000 g, correspondingly. Impact of the centrifugal force on the substance placed in the hot zone gradually increases up to 2.5 times with the combustion wave front advancement along the reactor axis of used unit. A metal fraction of the synthesis products is provided by a metal mold. Its size and shape can vary considering composition of an initial components mixture and design shape of a metal ingot. The metal mold wall is provided with holes to remove formed gases.

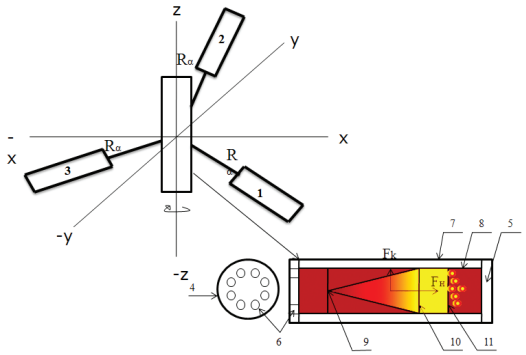


Fig. 1. Layout of the adiabatic wave producing gradient materials: 1, 2, 3 – rotating reactors; 4, 5 – front and rear reactor covers; 6 – gas outlets in the front cover; 7 – steel casing; 8 – a quartz tube; 9 – ignition point; 10 – SHS front; and 11 – adiabatic wave.

The possibility for the oxide system combustion process to be converted to the adiabatic combustion mode as a result of the centrifugal acceleration has been discussed earlier [3]. Motion of a metal particles resulting from reaction (1) is subject to the two following forces, namely centrifugal force F_H and Carioles force F_C.

$$F_H = 0{,}011\ m \cdot n^2 \cdot R_x \qquad (2)$$

$$F_C = 2\ U \cdot \omega \cdot m \qquad (3)$$

where m is a sample mass, ω is an angular rotation velocity of the non-inertial reference system, and U is velocity of a studied physical particles motion in the chosen reference system.

Particles emerging at the moment of ignition and, then, during the combustion front propagation along the reactor axis initially have an approximate size of 10^{-6} m with further coalescence accompanied by certain enlargement. This process can take place in the initial part of the reactor where specified forces render only slight effect on the particle advancement trajectory. However, subsequent growth of R_x radius-vector as well as F_H force results in alignment of the particles trajectory along the reactor axis by their acceleration increment.

Increases of the F_H value causes increase of F_C force that is directed perpendicular to R_x radius-vector and coincides directionally with growing viscosity. This process results in separation of the low density slag movement trajectory from that of the heavier metal particles movement. The particles coalescence process decreases in the reactor part with $R_x > R_a$. Tables 1 and 2 provide mechanical and thermodynamic data of the metal reduction process in the conditions of the centrifugal force effect.

Table 1

Kinetic energy (E_k) and enthalpy depending on a tungsten particle radius and the reactor radius-vector

r·10^{-3}, m	p*10^{3}, kg/m^3	m*10^{-6}, kg	R_x, m	n, min^{-1}	F, m*kg/sec^2	E_k, J	u, m/sec	Q, J
0.0100	19.2500	0.00008059	0.10	3000	0.00000080	0.08	31.4643	0.0000
0.0100	19.2500	0.00008059	0.25	3000	0.00000199	0.50	78.6607	0.0000
0.0100	19.2500	0.00008059	0.30	3000	0.00000239	0.72	94.3928	0.0000
0.1000	19.2500	0.08059333	0.10	3000	0.00079787	79.79	31.4643	0.0393
0.1000	19.2500	0.08059333	0.25	3000	0.00199469	498.67	78.6607	0.0393
0.1000	19.2500	0.08059333	0.30	3000	0.00239362	718.09	94.3928	0.0393
1.0000	19.2500	80.59333333	0.10	3000	0.79787400	79 787.40	31.4643	39.2891
1.0000	19.2500	80.59333333	0.25	3000	1.99468500	498671.25	78.6607	39.2891
1.0000	19.2500	80.59333333	0.30	3000	2.39362200	718086.60	94.3928	39.2891

Table 2
Kinetic energy (E_k) and enthalpy depending on an iron particle radius and the reactor radius-vector

$r \cdot 10^{-3}$, m	$p*10^3$, kg/m^3	$m*10^{-6}$, kg	R_x, m	n, min^{-1}	F, m*kg/sec^2	E_k, J	u, m/sec	Q, J
0.0100	7.8500	0.00003287	0.10	3000	0.00000033	0.03	31.4643	0.0000
0.0100	7.8500	0.00003287	0.25	3000	0.00000081	0.20	78.6607	0.0000
0.0100	7.8500	0.00003287	0.30	3000	0.00000098	0.29	94.3928	0.0000
0.1000	7.8500	0.03286533	0.10	3000	0.00032537	32.54	31.4643	0.0233
0.1000	7.8500	0.03286533	0.25	3000	0.00081342	203.35	78.6607	0.0233
0.1000	7.8500	0.03286533	0.30	3000	0.00097610	292.83	94.3928	0.0233
1.0000	7.8500	32.86533333	0.10	3000	0.32536680	32 536.68	31.4643	23.2516
1.0000	7.8500	32.86533333	0.25	3000	0.81341700	203 354.2	78.6607	23.2516
1.0000	7.8500	32.86533333	0.30	3000	0.97610040	292 830.1	94.3928	23.2516

Though in the natural gravitation conditions the front propagation rate is $U_P = 0.1\ m \cdot s^{-1}$, the U particle velocity depending on R_x value within the range of $0.1 \div 0.3\ m$ varies between 30 and 90 m/s. A typical process time at the front thickness $l = 2 \cdot 10^{-3}$ is as follows:

$$\tau = \delta / U_P = 2 \cdot 10^{-2}\ s$$

The metal particles contact time in the same thickness front is as follows:

$$\tau = l / U = 2 \cdot 10^{-2} / U$$

$$\tau = 6.6 \cdot 10^{-5}\ s \div 2.2 \cdot 10^{-5}\ s$$

These particles cross a narrow combustion front and activate a combustible mixture prior to it. Thus, one can expect certain growth in the metal particles initiating capability with increasing reactor length. Earlier performed study [3] proves that a metal temperature growth with increasing R_x value was exponential. It is clear that specified process acquires an adiabatic propagation mode accompanied by formation of an adiabatic wave (AW).

Considering these SHS process conditions, generated particles moving ahead of the combustion front are able to activate a new process that will most possibly take place in the point of the SHS wave and conversion to the adiabatic wave. The AW chemical and kinetic potential in the course of initiation of the highly endothermic reactions is used in the system of two different and consecutively located reactionary mixtures within one rotating reactor.

The objective of AW application is achieved as described below in Fig. 2. A highly endothermic reaction mixture settles down in the end part of the reactor. Particles that constitute AW tend to attack this mixture and initiate a chemical process.

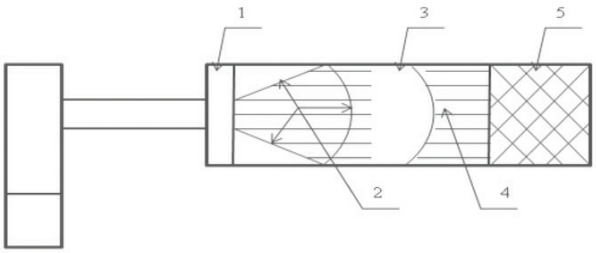


Fig. 2. Technology of AW based material synthesis: 1 – initiation (ignition); 2 – a primary combustion front; 3 – AW emergence; 4 – residue of the initial gas mixture that has not been yet subject to any transformation; 5 – a reactionary mixture attacked by the AW particles.

A high-speed video recording of the process carried out at 400 frames per second (Fig. 3) supports a theoretical conclusion of the combustion wave expansion and temperature elevation.

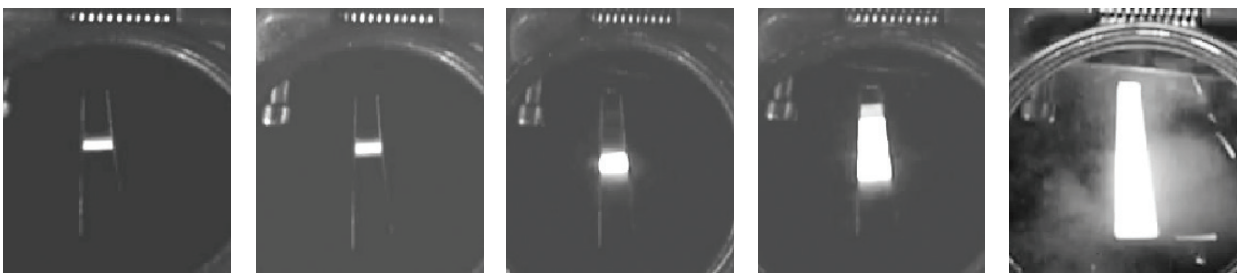
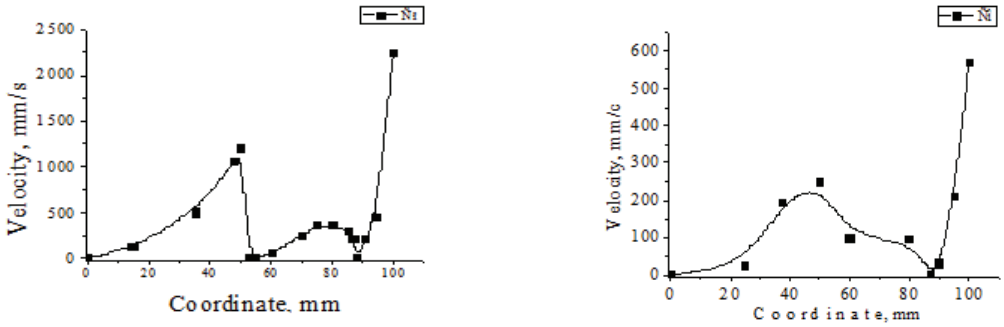


Fig. 3. Video recording of the combustion process in the nickel, aluminum and boron oxides based three-layer system with 2000 rpm rotation frequency.

The results of this analysis testify to increase of the heat energy and allow for identification of a co-ordinate of the wave transition to the adiabatic mode. In this connection, regularities of the WO_2, Co_3O_4 and Fe_2O_3 based oxide systems combustion considering change in the centrifugal acceleration varying between 1 and to 2000 g that have been studied in [4].

A layer of the boric anhydride and aluminum stoichiometric mixtures has been placed on the way of a propagating combustion wave in the field of its transition to the adiabatic mode. Reaction between these components has a high energy barrier and therefore cannot be initiated in usual conditions without their preheating. As well it cannot take place in a single-layer system inside the centrifuge reactor with acceleration up to 2000 g. Attack of this mixture by the reduced metal particles allows to overcome the energy barrier and initiate reaction between B_2O_3 and Al. Based on the video recording, the change in the velocity of the combustion front advancement along the reactor axis (Fig. 4) has been estimated.



a b

Fig. 4. Velocity of the combustion wave front advancement in system (Co_3O_4+Al+Al_2O_3) (B_2O_3+Al): a – 3/1 layer thickness correlation; b - 1/1 layer thickness correlation.

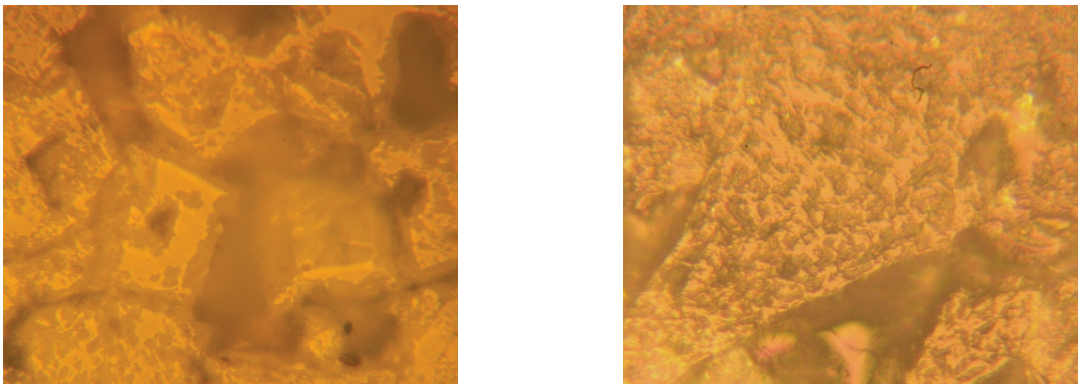
There is initially observed slow velocity increase that subsequently becomes sharply increased. Further displacement of the combustion front results in the wave deceleration at the layers separation border. Obtained study data have been used to identify a co-ordinate of the combustion wave transition to the adiabatic mode. Combustion of similar tungsten oxide based layered systems lead to formation of the gradient materials. Figure 5 illustrates macrostructure of the gradient material in its section along the fractional axis.

Fig. 5. Macrostructure of the gradient material produced as a part of the multilayered system combustion products.

An integrated X-ray phase analysis confirms that the gradient material consists of tungsten and corundum in approximately equal quantities. There have also been found about 1% of tungsten borides and boron-containing phase $Al_{20}B_4O_{36}$ [10]. Presence of these phases leads to formation of the gradient material ceramic area microstructure in the form of cubic shaped crystal grains (see Fig. 6a). The microscopic structure of the material observed herewith differs from the corundum structure characterized by a tetragonal crystal lattice and presence of simple oxide systems in the combustion products that do not contain boron (see Fig. 6b).

The most dense bottom part of the gradient material has a cubic crystalline microstructure that is typical for pure tungsten. The border is characterized by a wide transition layer from metal to ceramics therefore this high-temperature synthesis product is referred to the gradient materials.

The X-ray phase analysis has revealed presence of pure tungsten in the low-calorie layer combustion products. Elementary boron has been found in the bottom layer of the synthesis product. These data testify to authenticity of a physical model of the centrifugal acceleration affected layered systems combustion process currently being developed since they support the assumption of the reduced metal penetration from the high-calorie layer to the low-calorie one and the combustion process initiation in it [4].



a b

Fig. 6. Microstructure (x400) of the (a) combustion product ceramic component in the multilayer system; and (b), simple oxide systems that do not contain boron .

Conclusions

Creation of the sufficient centrifugal acceleration has provided initiation of the adiabatic combustion wave and use of its kinetic properties so as to stimulate chemical processes in the endothermic systems by mass and heat transfer with subsequent synthesis of the high-temperature gradient materials.

The centrifugal accelerated flow of the clusters of metal initiates reactions of the high activation energy, in the limits to 1 MJ. This is shown by the example of interaction of the boron oxide and the aluminum attacked by tungsten particles of high energy. In resultant the formed material possesses composition gradient. The phase $Al_{20}B_4O_{36}$ is characterized by the unpaired spin of an electron. The revealed fact shows the possibility of using the similar connections in the mixture with the nano- and sub-micron materials during the compaction with the ultrahigh pressures.

Thus, the technology of adiabatic wave opens the possibility of produce the new materials with gradient properties.

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