Initiation of the Adiabatic Wave of Combustion for Obtaining the Substances with the Free Valence

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Abstract. According to the task of obtaining substances with the free valence for the linkage of the nano-powders, the procedure of the synthesis of materials under the extreme nonequilibrium conditions is presented. The combustion of multilayer aluminothermic systems in the revolving reactor was investigated. Experiments were carried out in the reactor of high-temperature centrifuge. The initiation of process realizes by electric pulse in the effective layer. Further the wave of combustion was propagated along the axis of the reactor. The particles of the restored metal penetrated the underlayers of fresh mixture under the action of centrifugal acceleration and created the additional centers of ignition. The higher the density of metal, the higher speed and depth of penetration. An increase in the centrifugal acceleration strengthens the activity of process also. The speed of the motion of metallic particles grows. According the theoretical calculations it reaches 90 m/s in the case of tungsten.

1. Introduction
As is known one of the type of combustion is SHS - Self-propagating high-temperature synthesis, which based on the strong exothermic reaction (combustion reaction) in which the heat localize in the layer and spread from one layer to another by conduction. The main purpose of SHS - the synthesis of substances and materials. SHS has a great technological potential, since it includes such features as a high rate of combustion (0.01-0.2 m/s) and temperatures (2300-3800 K) the relative simplicity of the equipment, low energy (heat energy of the process of SHS), the ability to use raw materials of different origin, obtaining a wide range of materials with different properties etc. The above-mentioned advantages makes the SHS process is attractive for implementation in the production of a variety of materials [1].

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 of a wave propagating in the reactor. High velocity of the thermal combustion front advancement cause 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 find its practical application. The main objective is to develop technology based on the energy of an adiabatic combustion wave to obtain the non-trivial material.

2. Formulation of the problem and method of solution
These studies have been carried out using the unit specially designed to model the combustion process under the centrifugal force effect [3] (see figure 1). This unit includes a shaft-installed engine, and a crosspiece with three cylindrical reactors fixed on it in a balanced manner at 120° angle. Inside the
reactor the combustion process 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. There is a narrow cut has been made both in one of the three rotating reactors and in the unit cover to observe advance of the combustion wave front. High-speed video camera is used for supervision [2].

Usually solid-phase combustion in the regime SHS has features of combustion in the gas phase, but without the participation of mass transfer. The thermal wave propagated by means of the thermal diffusivity is supported by high-temperature and high-speed heat emission.

![Figure 1. High-temperature centrifuge](image)

With the combustion of oxide systems, the temperature in the front is 2500 - 3700 K. The melt of products, which the traveling wave leaves after itself, divided (separate) into parts in accordance with the density in the gravitational field, until low viscosity has continued. This effect becomes more intensively under rotation conditions.

The size of the particles of the metal at the time of their formation within the limits of the front of SHS-wave averages 2-3·10^{-6} m. If reaction occurs under the conditions of rest (the natural gravity) then these particles coalesce without difficulty, forming at first amalgamated aggregates, and then ingot. Under rotation, conditions the particles of metal do not remain in the wave of combustion (see figure 2). Their trajectory is directed to the side of fresh mixture with respect to the directivity of the resulting vector of centrifugal force $F_N$ and Coriolis effect $F_K$. It is obvious that the depth $\varepsilon$ of the penetration of hot ($T_c = 2800 - 3500$ K) particles into fresh reaction mixture is increasing with the increase of $F_N$, other conditions being equal. After achievement of a certain critical value $\varepsilon_{cr}$ the process passes into the explosive regime. As opposed to the steady conception, in our case the super adiabatic combustion progresses with the broadening (expansion), of the combustion front, but not with the contraction (narrowness) (see figure 3). It is important that the mass transfer participate in SHS-process under conditions of rotation as opposed to the SHS-process under the conditions of normal gravitation.
Figure 2. Metal clusters distributed in the final product of burning

1,2,3 - rotating reactors; 4,5 – front and rear reactor covers; 6 - gas outflow apertures in the front cover; 7 - steel casing; 8 - quartz tube; 9 - ignition point; 10 – SHS front; 11 – adiabatic wave

Figure 3. Scheme of installation for receiving an adiabatic wave

Stoichiometric mixtures of tungsten, cobalt, and nickel oxides with aluminum was chosen as active layers. These mixtures have been diluted with Al₂O₃. A low calorie layer of the stoichiometric mixture of boron oxide with aluminium [4].

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\begin{align*}
3\text{NiO} + 2\text{Al} &= \text{Al}_2\text{O}_3 + 3\text{Ni} + 2944 \text{ kJ/kg}; \\
3\text{FeO} + 2\text{Al} &= \text{Al}_2\text{O}_3 + 3\text{Fe} + 2810 \text{ kJ/kg}; \\
\text{Fe}_2\text{O}_3 + 2\text{Al} &= \text{Al}_2\text{O}_3 + 2 \text{Fe} + 3455 \text{ kJ/kg}; \\
\text{WO}_3 + 2\text{Al} &= \text{Al}_2\text{O}_3 + \text{W} + 2890 \text{ kJ/kg; (1)} \\
\text{B}_2\text{O}_3 + \text{Al} &= \text{Al}_2\text{O}_3 + 2\text{B}
\end{align*}
\]

Total thermal and kinetic energy of reduce metal flux is enough to overcome the Arrhenius barrier of any exothermic reaction or to break the chemical bonds in the oxides of metals.

A high-speed video filming was used for record of process of combustion in real time. Expanding the video into separate frames, we have identified the combustion wave transition in the adiabatic regime-sharp increase speed of displacement of the front. Here we put less active layer- a mixture of boron oxide with aluminium or pure boron oxide.

Based on this video record we have managed to build up a diagram of the co-ordinate dependent front advance along the reactor axis. Noteworthy that combustion process in the second less active layer develops similarly to the first one. In addition, you can put another layer on the way the second adiabatic waves.
Slow velocity increase is then replaced by its sharp increase. Afterwards the wave slows down at the layers separation boundary. Then the whole process is repeated but with less energy. Therefore, we have placed the third, i.e. the most active layer, in the wave action field (see figure 4).

Actually, the burning process in the three-layer system lasts 0.8 seconds. This time is sufficient for the formation of gradient material. The material structure changes from metal (tungsten) to ceramics (aluminum oxide, corundum). The basic phases take 91.9%. Other involved substances are boron-containing solid tungsten and boron compounds. Similar results have been obtained when used samples active layers are based on cobalt and nickel oxides [5].

If the energy of the metal particle flux is designed to break the chemical bonds in the molecule, the chemical compound with a free valence is formed in the product of synthesis (see figure 5).

![Graph 1](image1.png)

**Figure 4.** The combustion front advance velocity within the (Co₃O₄+Al₂O₃) (B₂O₃+Al) system (a – in two-, b – in three-layer system)

![Graph 2](image2.png)

![Image 3](image3.png)

**Figure 5.** Formation of aluminum oxide macrostructure in boron presence

### 3. Results and Discussion

The combustion wave velocity is not equal to that of the reduced metal particles. According to the experimental data, the flame front moves with 20 m/s velocity. Theoretically, calculated velocity of the particles movement through a loose compacted material reaches 90 m/s at 3000 r/min rotation frequency. In such conditions, viscosity of the synthesized intermediate and final products is not always of any importance for the front advance along the reactor axis. However, viscosity remains a determining factor of the synthesis products structure formation in the cross-section direction. Its importance sharply increases in the direction from the reactor axis to its rather cold walls. Fast
hardening of occurs near the internal surface of the reactor quartz lining, this process resulting in formation smelt of a ceramic tube. Depending on the initial components composition it can have a corundum, spinel, and mullite structure. Consequently, experimental study of the adiabatic combustion wave propagating under the centrifugal acceleration affect in the layer system has led to creation of new materials and products.

An interesting material has been produced at combustion of the three-layer system based on tungsten and boron oxides – an extremely porous aluminum oxide crystallized in its three modifications such as α, δ and γ (see figure 6).

Figure 7 illustrates a sample electron paramagnetic resonance (EPR), data testifying to emergence of a free valence in Al$_2$O$_3$B$_7$ system.

Performed studies allowed for production of materials with various structures and compositions, namely spinels and mullites (see figure 8 and table 1). There have been synthesized materials with both cubic and dendrite-shaped structures [6].

![Figure 6. Results of three-layer system combustion (WO$_3$-Al-Al$_2$O$_3$)-(B$_2$O$_3$)-(WO$_3$-Al-Al$_2$O$_3$)](image)

**Table 1. Phase structure of the products**

| Crystal phase of the product | Mass contents, % |
|-----------------------------|------------------|
| Al$_2$O$_3$                 | 50.6             |
| W                           | 41.3             |
| Al                          | 4.8              |
| Al$_2$O$_3$B$_4$O$_6$       | 1.5              |
| WB$_2$.O                    | 0.7              |
| W$_2$B                      | 0.6              |
| WB                          | 0.4              |

Figure 7. Electron paramagnetic resonance (EPR) of Al$_2$O$_3$B$_7$ system
Thus, sufficient centrifugal acceleration allows initiating of the adiabatic combustion wave and application of its thermal and kinetic properties to start chemical processes or to bond breakage and to formed gradient materials or substance with free valence.

4. Conclusion
The arrangement of the layer of inert substance on the way of the adiabatic wave of combustion leads to a change in its structure. Energy of the adiabatic wave of combustion was used also for the initiation of reactions with the high energy barrier. As a result the complex oxide compound Al20B4O36 was obtained. The presence of free radicals in it is confirmed by the method EPR.

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