Research of products of high temperature synthesis flowing in the rotation conditions

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Abstract. The method of production of materials by out-furnace process of self-propagating high temperature synthesis (SHS), flowing in the conditions of action of centrifugal force, is developed presently. The primary purpose of working is achievement high level of generating of energy and use of it for forming of steady meta-stable crystalline phases with an uncommon set of physical and chemical properties.

1. Introduction
To study the Self-Propagating High-Temperature Synthesis (SHS) processes under the centrifugal forces effect there has been created a unique installation i.e. a high-temperature centrifuge [1]. Three steel reactors with internally installed quartz tubes stuffed with two-layer or multilayer powder reaction mixtures are rotated around a vertical axis. Ignition occurs from the centre after the engine is started and the installation is operated using routine mode. Further the combustion wave front spontaneously propagates along the reactor axis (Figure 1).
2 Experiments

The installation rotates with frequency ranging from 500 up to 3000 RPM corresponding to the centripetal acceleration up to 2000 g. According to (1), it is the angular velocity, quadratic dependence as a varying value, allows for modification of the experiment conditions in the best way. Therefore there is no point to change initial radius of the combustion wave front position. It is about four centimeters.

The total process time is 0.2-0.4 seconds, and temperature inside the reactor is 2500-3500 K.

\[ F_C = m \omega^2 R \] (1)

An attacking layer is ignited the first. There occur the processes of metal reduction from the oxide and formation of the adiabatic combustion wave [2]. This system can be considered adiabatic starting from the point when the heat release rate becomes considerably larger than the rate of heat loss to the environment. In the stationary conditions when the reaction mixture is affected only by the gravity force, molecules of the reduced metal oxide come together as particles and form an ingot outside the combustion wave front. Under the centrifugal forces effect the picture cardinally changes [3]. The metal particles come together to form larger clusters, they form an accelerated flow that overtakes the combustion front, and hits the nearest fresh mixture layer resulting in a heat-and-mass transfer to the pre-reaction zone (Figure 2). This effect is a key distinctive property of the described method. At the moment of collision kinetic energy of the clusters turns into the heat energy thus adding one more component to the heat balance of the system. Considering that the powder mixture is a porous medium and the metals clusters’ temperature significantly exceeds melting temperature, non-viscous melted particles penetrate through the surface layer and go down the mixture to a certain depth. Once metal gets to the borders of the opposite charge powder grains it forms additional micro-centers of ignition. The combustion wave front is constantly extended and accelerated. All these factors lead to a continuous temperature increase before the combustion wave front, the rate of the latter’s propagation along the reactor axis accelerates and the front is expanded. There takes place the so-called non-chain autoacceleration of the SHS wave. The figure below also illustrates velocity decrease at the border with the attacked layer.

![Figure 2](image)

**Figure 2.** The SHS process mechanism within the centrifugal forces effect field

a – flow of accelerated centrifugal clusters of the reduced metal; b – expansion of the reaction wave front observed on the time-lapse snapshots, their velocity and relocation plots
3. Results and Discussions

When the active layer is fully burnt down the metal forms are ingot in the reactor bottom, while lighter slag (aluminum oxide) stays on the ingot surface and partly on the quartz tube walls. In the two-layer or multilayer system the total mass of the metal reduced in the attacking layer falls down onto the second - «cold» attacked layer. It is this thermo-mechanical effect that is a key purpose of the experiments. Attacked layers differ in their configuration. These can be low-calorie powder reaction mixtures that cannot be otherwise ignited, e.g. either mixtures based on the rare earth elements (REE), boron and barium oxides, or the oxides powders. One of the most attractive attacked layers is the carbon powder layer. The other versions of the attacked systems are various particle entrapping screens such as plexiglass, grain quartzite, and pressed graphite. If the reactor has a hole in its cover like a nozzle, the metal particles flow can be taken out to the external screen and then covered with any necessary substances. Figure 3 illustrates the results of the copper clusters flow effect on the installation parts. One can estimate its intensity by numerous burns and thermo-mechanical damage. In certain cases the metal is dispersed covering any available surfaces with a thinnest layer whilst in other cases it forms a film locally.

Striking and thermal strength of the attacking clusters flow is able to initiate highly-intensive high-temperature processes. The reaction duration at each cross-section does not exceed $10^{-4}$ seconds. Subsequently the adiabatic mode is interrupted, obtained products get cold rapidly, natural processes of the chemical reaction do not have any more time to be completed and there occurs instant “freezing” at the intermediate stages.

![Figure 3](image)

Figure 3. External attacked layer

a – a plot of the combustion products outflow to the external screen; b – the result of the copper clusters flow effect outside the reactor.

This explains abundance of the free valency substances received during the experiments. Figure 4 illustrates a list of particularly interesting compounds that, according to the X-ray analysis, are contained in the food stuff.

There are found tungsten and molybdenum carbides, various silicides, borides, aluminates, and intermetalldies; on the ERP most of these substances give peaks corresponding to the presence of the free valency, moreover most of them exist only in our laboratory. The most well-known ones are as follows: CuBO$_2$ – transparent conductive p-type oxide with high individual electric conductivity called delafossite, MgB$_2$ – magnesium diboride, a superconductor with high temperature transition (40 K), and CuAlO$_2$ – a semiconductor. Synthesis of these free valency substances and their extraction from the solid solutions gives a great variety of the possibilities. The most obvious possibility is to modify metals, as well as modify a crystal lattice during its solidification [4, 5]. Besides, the other possibilities are to provide additives for rocket fuel, high-temperature superconductors, superconductors [6], semiconductors, paramagnetic materials, and affect the biological processes occurring with formation of the free valency.
One more illustration of the possibilities given by this method is the result of attack of the common graphite powder by the copper clusters. Figure 5 illustrates a diagram of the reactor charging and a picture of the products. The picture shows that the product has a slag pellet in the bottom whilst on the top there is an ingot covered with a powder layer. According to the comparative analysis of the compensatory laser spectroscopy data, the copper ingot surface is covered with graphene but not with graphite. Such experiments often reveal diamond carbon structures testifying to the presence of serious flow shock impacts, however researchers are much more interested in obtaining nanocarbon films.

Figure 4. A list of nontrivial substances detected in the combustion products by the X-ray phase analysis

| Substance          | Percentage |
|--------------------|------------|
| Al₂O₃              | 11.2%      |
| Al₃Cu              | 5.9%       |
| Al₃Mo₃Si₃         | 21.5%      |
| MgB₂              | 55%        |
| Al₄B₃O₉          | 3.1%       |
| Cu₃Si₄            | 0.8%       |
| Al₃Mo              | 5.9%       |
| W₂C              | 74.4%      |
| Ba₂Al₂Si₂O₈       | 5.4%       |
| Cu₃BiSi₈         | 13.4%      |
| MoB₂              | 0.4%       |
| W₂C₀.₃5          | 5.2%       |
| Ba₉₃₄Al₄O₁₇²₂₂     | 32.6%      |
| Cu₃₀₉Si         | 100%       |
| Mo₃Si            | 1.1%       |
| WC              | 5.3%       |
| Mg₃O₄           | 4.7%       |
| Cu₃₀₉Si         | 24.6%      |
| Mg₃O₄           | 4.7%       |

Figure 5. Attack of a common graphite layer by the copper clusters
a – diagram of reactor charging; b – ingot picture; c – the result of the sample study from the ingot surface by the compensatory laser spectroscopy; d – the result of a similar study of the graphene sample

4. Conclusion
There is still a task to identify a bond between concentration of necessary substances in the combustion products and rotation frequency of the installation. Apart from that, it is important to find efficient methods to be used for extraction of these compounds in their pure form. To execute this project the chemical and analytical studies are being currently carried out and a higher intensity installation is being started-up.
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