Obtaining Radiation-resistant Material by SHS Method

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Abstract. All the first results of obtaining radiation-resistant material by the SHS method are presented in the article. Synthesis of material based on the system Fe₂O₃-Al-Cr₂O₃-MoO₃-Ti. The resulting material was irradiated with an electron beam of 1.8 MeV. The synthesis process was filmed by an action video camera. Fourier image analysis revealed the instability of combustion regimes and predicted the quality of reaction products. A comparative analysis of the microstructure of the samples before and after irradiation with electrons confirmed the results of the FFT. Despite the relatively low quality of the synthesis products, the embrittlement occurred at the absorbed dose of 70 Mrad. In the future, it is planned to improve the methodology for identifying unstable synthesis modes and adjusting the percentage ratio of the charge components.

1. Introduction
The problem of providing radiation-resistant materials has been relevant for several decades, and now it will remain important. There are the following areas of technology in which such materials are necessary to ensure long-term operation of measuring instruments and structures. Self-propagating high-temperature synthesis (SHS) is an efficient, economical, energy-saving and energy-saving synthesis method for materials with desired properties [1-3]. The advantages of self-propagating high-temperature synthesis, compared with traditional methods, are speed, low power consumption, unique structure and properties of synthesis products. In the wave of synthesis, purification from harmful impurities occurs. Due to this, SHS products are distinguished by high purity. However, there are unsolved problems. You cannot get steel or alloy, which includes a large number of ingredients. A large number of metal ligaments and alloying additives, which are inert, worsens the exothermicity of the mixture. This leads to incomplete recovery of elements from oxides. Replacing alloying additives with finished metals makes the process uneconomical. At the same time, it is known that the size of the inert additive can be up to 30% by weight of the reactants. Thus, the relevance of research is maintained. We attempted to obtain a radiation-resistant material by the SHS method. The purpose of this article is to describe the first results.

Temperature and speed of processes affecting the properties of synthesis products. The method of monitoring the thermal imager allows not only to estimate the average speed and temperature of the reaction, but also to observe their dynamics in the area of interest, to monitor the movement and the evolution of regions from temperature. Therefore, the control of the main thermophysical parameters is carried out using the method of high-speed video.
2. Research Methodology

SHS cast refractory materials - a complex multi-step process. There are three basic steps: burning, phase separation and cooling of combustion products. Combustion takes place in two stages: the reconstitution of the elements of an oxide (metallothermy) and reacting the recovered elements. Prevalence of iron oxides cheapness and high calorie thermite mixture (8400kDzh / kg) allows its use for the synthesis. The composition of the mixture of powders must satisfy the equation [1-3]:

\[
\sum_{i=1}^{N_{M_{oj}}} v_i (M_{oj}) + A T \left[ \sum_{j=1}^{N_{X_j}} v_j X_j = \sum_{j=1}^{N_{P_i}} v_i P_i + A T \right] O_3,
\]

where \((M_{oj})\)-oxides; \(X_j\)-metallic or non-metallic reagents; \(P_i\)-solid phase products, coefficients before exponential factor, \(v_i\)-stoichiometric coefficients.

The adiabatic combustion temperature, chemical and phase composition of products depend on the ratio of reactants in the starting mixture, their initial temperature, the size of the reaction volume and the pressure of the surrounding gaseous medium. The composition of the equilibrium final products of synthesis is determined by minimizing the thermodynamic potential of the system. Vapors and suboxides released in the melt during combustion, lead to scatter of the melt. After passing through the combustion front, a two-phase melt is formed, in which the metal oxide – reducing agent (oxide phase) forms a continuous medium. Drops of the refractory compound of the reduced metal (metal phase) are distributed in it. Due to the difference in the densities of the phases under the action of the field of gravity, the mutual movement of the phases occurs. The motion occurs in the cooling melt under conditions of increasing viscosity of the oxide phase. Termination of phase separation occurs either at the time of complete release of drops into the "metal" ingot from the melt (full phase separation), or at the time of crystallization of the oxide phase (incomplete phase separation). Expression for the dependence of the completeness of phase separation on the main parameters [1-3]:

\[
\eta_F = A \frac{d_k g}{\alpha \mu_0 r + L_0} \exp \left( -\frac{E_v}{R T_a} \right) \left[ 1 - \exp \left( -\frac{E_v (T_g - T_F)}{R T_a^2} \right) \right],
\]

where \(g\) is the acceleration of free fall; \(T_F\) is the temperature at which phase separation ends; \(T_g\) is the burning temperature, \(d_k\) is the droplet diameter; \(\mu_0\) is the pre-exponential viscosity of the oxide phase, \(E_v\) is the activation energy of a viscous flow, \(r\) is the radius of the sample, \(L_0\) is the height of the sample, \(\alpha\) is the heat transfer coefficient from the sample.

Obviously, the strongest parameter that allows you to adjust the completeness of phase separation \(\eta_F\) is the combustion temperature. Under conditions of intense cooling, complete melt separation requires substantial overheating of the melt above the melting point of the oxide phase. To maintain the required combustion temperature, the spatial and temporal uniformity of the emergence of new combustion centers is needed. If we supplement the optical part of the system with a microscope, we can measure the brightness temperature with a high spatial resolution. To study the process of phase separation, you can use optoelectronic micropyrometric systems. Trace-analysis [] and FFT video recording of the wave propagation process of SHS. Video filming converts the synthesis process into a sequence of images, each pixel \((x, y)\) of which has a brightness proportional to the instantaneous temperature value of the corresponding element of the reactant:

\(g (x, y, T) = T [f (x, y, I)],\)

where \(f (x, y, T)\) is the original object, \(g (x, y, I)\) is the image, \(T\) is the transfer function of the optoelectronic system. Next, you need to find the interframe difference of the video sequence \(\Delta X (t, y, I) = X (t, y, I) - X (t - \Delta t, y, I)\) and set the mask that limits the phase separation temperature.

The Fourier transform of a discrete function in one variable \(f(x)\), \(x = 0, 1, 2, ..., M-1\), is given by

\[
F(u) = \frac{1}{M} \sum_{n=0}^{M-1} f(x) e^{-2 \pi i n u / M}, x = 0, 1, 2, ..., M - 1.
\]

The power spectrum of the recorded signal can be estimated from the amplitude of the transformed Fourier data. Comparing the power spectra for the beginning, middle and end of the reaction, one can understand whether the concentration of alloying additives was critical.
3. Experimental equipment

To apply optical pyrometry, the radiation of a heated body must obey Kirchhoff’s law. Usually solids and liquids when handling this requirement. Brightness pyrometry uses the equality of the brightness of the object under study and the brightness of an absolutely black body at the same wavelength \( \lambda_0 \).

For calibration, we used the TRU 2350 temperature lamp as a reference. The radiation of real bodies is different from the level of a black body. The formula relating the brightness and true temperature of a real body through the spectral emissivity (monochromatic degree of blackness) \( \varepsilon_{\lambda,T} \):

\[
\frac{1}{T} = \frac{1}{T_b} + \frac{\lambda_0}{c_2} \ln \varepsilon_{\lambda,T},
\]

where \( c_2 = (1.43880 \pm 0.00019) \cdot 10^{-2} \text{ m} \cdot \text{K} \).

After calibration, you can use a video camera as a bright thermal imager. For a detailed study of the processes occurring in the wave of combustion of SHS [8-9], a microscope objective was used. The lens was mounted on a digital electronic video camera "ASI120MC Camera". The resolution of the video camera is 1.2 megapixels 1280 × 960, pixel size: 3.75 microns. The result is a digital microscope that is directly connected to a computer. Video recording is carried out at a speed of 30 frames per second. Working distance 100 mm. The digital electron microscope is used to measure speed and local temperature, the viewing area is 1.5x1.5 cm. The additional sports video camera “Soocoo S70” is designed to monitor the temperature and speed of the combustion process as a whole.

On both video cameras, welding glasses were used as additional filters. A general view of the experimental setup, video footage of the combustion process, filmed «Soocoo S70», they are shown in figures 1 and 2 respectively.

**Figure 1.** These two figures have been placed side-by-side to save space. Justify the caption, experimental setup.

**Figure 2.** Video frame examples of a typical synthesis process taken by a sports camera «Soocoo S70».

The experiments were carried out using several variants of the elemental composition of the powder mixture. Here we present the results of the synthesis without carbon and nickel. For the synthesis, PA4 aluminum powder, molybdenum oxide and chromium oxide with three valence dispersions up to 50 microns, iron oxide with dispersions up to 300 microns and titanium powder up to 100 microns were used. The powders were mixed in mass percent: Fe₂O₃-57.77 wt.%; Al-30.13 wt.%; Cr₂O₃, 9.09 wt.%, MoO₃-1.05 wt.%; Ti-2.03 wt.% The mixture of powders was placed in a quartz open-type reactor (test tube). The quartz reactor with the charge was mounted on a tripod, set so that the edges of the test tubes were flush with the refractory disk. Then all the smoke and sparks flew into the pipe. Combustion was initiated by the tungsten coil. After cooling, the synthesis products were separated from the slag. Next, prepare the thin sections. The microstructure of the samples was studied on an Axiovert-200 metallographic microscope using an image processing system. Structure VideoTest-5.
Each sample was divided into two parts. One part was sent to Dimitrovgrad for irradiation, the second was given for X-ray analysis. Irradiation was performed on a pulsed linear accelerator ILU-6. Irradiation occurred at room temperature; pulse frequency - 12.5 Hz; current 0.39A; electron energy 1.8 MeV in an atmosphere of oxygen and ozone; irradiated area 20 × 10 cm. X-ray diffraction analysis was performed on an ARL X’TRA diffractometer.

4. Results and discussion
Experience shows that when a combustion wave moves in a sample volume, a substance is transformed. This leads to a change in a number of properties: density, thermal conductivity, heat capacity, etc. On this basis, the entire sample can be divided into three zones. In zone 1, the cooling process is in progress, in zone 2 (the reaction zone) there is a combustion process with a large release of thermal energy, which goes to support the combustion reaction and heating zone 3 (preheating zone). In accordance with the methodology used to obtain high-quality samples, the distribution in space and time of new high-temperature combustion centres should be uniform. To verify the fulfilment of this condition by the method of brightness micropyrometry, the dynamics of temperature fields was obtained. The emergence of new foci of combustion of a given temperature was watched by interframe difference. Fast Fourier transform was done in the programs Fiji, OriginPro19. The results are presented in Figures 3, 4.

![Figure 3](image1.png)  ![Figure 4](image2.png)

**Figure 3.** Fourier spectrum of temperature fields corresponding to the beginning, middle, and synthesis process.

**Figure 4.** These two figures have been placed side-by-side to save space. Justify the caption.

A comparative analysis of the Fourier spectra of the temperature fields corresponding to the beginning, middle, and completion is observed by a noticeable decrease in temperature at the end of the reaction, and also new highly exothermic regions are reduced. Perhaps for this reason unreacted powder of refractory oxides will be found in the reaction products. Two-dimensional Fourier analysis [7-9] of the entire reaction shows its multistage. So, you can expect in the reaction products the appearance of lower oxides. The lack of highly exothermic foci leads to a slower reaction and its cessation. Metallographic studies of the initial samples showed a non-uniform distribution of the phase composition, the presence of pores of various sizes. This is a disadvantage in mixing the components of the powder. The reaction of SHS proceeded in a reactor with a diameter close to the critical one. After synthesis, the sample is rapidly cooled due to the large amount of heat sink through the side surface and its small mass (20 g). Melt viscosity increased rapidly with cooling. Gases that did not have time to go out during the phase separation formed large closed pores. The radiograph and microstructure of the sample after the synthesis are presented in Figures 5, 6.
The structure of the multicomponent system after SH-synthesis is a solid solution based on \(\alpha\)-Fe with inclusions of unreacted molybdenum oxide and particles obtained as a result of a chemical reaction between reduced iron and molybdenum. Aluminium and titanium are \(\alpha\)-stabilizers, easily soluble in \(\alpha\)-Fe and Cr, forming wide areas of solid solutions with a bcc structure. Thus, the solid solution has an increased hardness \(H_s = 400\) MPa due to the dissolution of the atoms of the reduced elements in the iron lattice.

To check the obtained material for radiation resistance, the samples were irradiated with an electron beam. After irradiation with a 1.8 MeV pulsed electron beam, the temperature of the samples remained almost unchanged. The phase composition of the samples after irradiation changed (Figure 7, 8), but the main phase remained a solid solution of \(\alpha\)-iron.

With an absorbed dose of up to 20 Mrad, the microhardness of the samples remained almost unchanged. When an electron beam of more than 1.8 MeV interacts with metals, the main contribution to radiation damage is made by the mechanism of atom ejection and the creation of Frenkel pairs. The calculated migration energy of vacancies in Fe, Cr is from 0.8 to 1.3 eV [10]. The atoms of aluminium and
molybdenum interact with iron and chromium and form complex oxides. The roentgenogram showed presumably Fe (Cr, Al)₂O₄, FeMo₃O₈ or FeO * Cr₂O₃. Phase analysis of a sample containing several phases is complicated by the fact that reflections of different phases overlap each other. This means that the same reflex on the diffractogram can belong simultaneously to several phases. At the absorbed dose of 30 Mrad, a small accumulation of pores appears along the grain boundaries. On the surface of the sample, grain sections are well distinguished; their microhardness is \( H_\mu = 421.6 \) MPa. The crystalline inclusions did not change in size, but the hardness values increased (\( H_\mu = 549 \) MPa). With increasing doses up to 60 Mrad, pores appear in the volume of crystals of the solid solution, previous samples. The crystalline inclusions also increased to 35 µm, and the microhardness values decreased to \( H_\mu = 483.9 \) MPa. The hardness of the main stages decreased to values of \( H_\mu = 404.1 \) MPa. A sample with an absorbed dose of 70 Mrad was too fragile.

The results discussed may be that the samples withstand electron irradiation. Results can be improved. The distribution of the phase composition in the volume of synthesis products is uneven due to poor charge mixing and incomplete reduction of oxides. Fourier analysis showed that the frequency of occurrence of areas with high heat transfer is insufficient. Although at the beginning of the reaction, refractory elements were recovered from oxides. This is confirmed by x-ray analysis. Thus, an increase in the cost of aluminium should lead to a more complete recovery. Unfortunately, the results of the analysis of the chemical elemental composition are still missing.

5. Conclusion
The alloy was synthesized based on the Fe₂O₃-Al₂O₃-MoO₃-Ti system. During the research it was found:

1. Fourier analysis of the temperature field of the reaction showed its multistage. the need to increase the mass fraction of thermite mixture.
2. The synthesized material consists mainly of solid solution phases with a bcc lattice based on iron and chromium.
3. Tests of samples for radiation resistance have shown that an increase in the absorbed dose to 30 Mrad leads to the appearance of pores along the grain boundaries.
4. An increase in the absorbed dose to 60 Mrad pores appear in the volume of crystals. In areas rich in chromium, the solid solution disintegrates with the formation of a eutectoid in the chromium-aluminium system.
5. At the absorbed dose, crystalline inclusions increased to 35 µm, and the microhardness values decreased to \( H_\mu = 483.9 \) MPa. The hardness of the main phase decreased to values of \( H_\mu = 404.1 \) MPa.

The results indicate the need for further research to improve the method of using Fourier analysis to control phase formation and to establish the optimal ratio of the components of the powder mixture. Each figure should have a brief caption describing it and, if necessary, a key to interpret the various lines and symbols on the figure.

6. References
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