Synthesis of magnesium aluminate spinel in the MgO-Al₂O₃-Al system using the SHS method

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Abstract. Magnesium aluminate spinel is obtained in the MgO-Al₂O₃-Al system using the method of self-propagating high-temperature synthesis. The leading SHS reaction is the oxidation of aluminum in an oxidizing environment. The composition and structure of spinel were studied by X-ray diffraction (DRON-UM-1), infrared spectroscopy (Nicolet 5700) and scanning electron microscopy (Philips SEM 515). The mineralizer NaCl used in the amount of 1 wt.% increases the conversion depth during SHS. Initial components are ground in a M3 planetary mill for 60 s results to obtain MgAl₂O₄ that does not contain impurities of initial oxides. The grain size of magnesium aluminate spinel obtained is ≤1 microns.

1. Introduction
Magnesium aluminate spinel (MgAl₂O₄) is an excellent refractory material and widely used as a structural material in modern engineering. The absence of low-melting eutectics in the MgO-Al₂O₃ system, high melting temperature, chemical resistance to mineral acids, good dielectric characteristics and Mohs hardness of 7.5–8 make it one of the most important high-refractory materials in industry [1].

In addition, synthesized spinel has excellent optical characteristics and is used as optical transparent ceramics in the military industry [2]. Spinel is also used in the manufacture of catalysts and stable ceramic paints [3, 4]. However, its manufacture is associated with a number of difficulties caused by the development of solid-phase reactions at high temperatures.

MgAl₂O₄ is obtained by different methods: chemically (from sodium aluminate and magnesium salts), mechanochemically (grinding the magnesium and aluminous components), plasma-chemically, melting in electric arc furnaces, furnace roasting (annealing temperatures of 1200 -1400°C) and using a sol-gel method followed by calcination [1, 5-9]. A polymer-gel process refers to the sol-gel method when gel is formed by adding a water-soluble polymer to a solution, followed by evaporation and the Pechini method (citrate-gel). Drying of polymer gels with further heat treatment is conducted at a temperature of 1100°C [10, 11].

Despite the fact that the sol-gel method produces high-quality products, this method has disadvantages such as the long time of synthesis to obtain spinels and the presence of wash water that requires purification.

Electric melting and reaction sintering are widely used methods for the synthesis of synthetic magnesium-aluminate spinel. At present, electric melting is applied to produce spinels in large volumes in China, Hungary, the USA and Brazil, but some large companies use solid-phase reaction sintering, for example, White Circle Oxides Ltd (WCO), India [5]. The growth of ferrous metallurgy in Asian countries requires an increase in the volumes of high-quality refractories and raw materials for their production, so the demand for magnesium aluminate spinel will only increase in the nearest future. However, the above methods require high power and time consumptions, as well as expensive equipment, which affects the cost of spinel.
The problem of energy saving in the production of refractory materials is urgent and important. In this regard, self-propagating high-temperature synthesis (SHS) is a promising energy-saving method for the obtaining of magnesium aluminate spinel. Based on exothermic interaction of two or several chemical elements (compounds) taking place in the mode of controlled combustion, SHS reduces the cost of refractory materials. High speed of processes, simple equipment and non-waste production are the advantages of this method. An unconventional method of the synthesis of ceramic materials is used to synthesize MgAl_2O_4 finely dispersed magnesium aluminate spinel in the combustion wave. As a result, it can be used further as a precursor for the production of refractory ceramic products.

2. Experimental procedure
The powders of MgO and Al_2O_3 were used as initial reagents and aluminum (ASD-4) with a dispersion of less than 30 μm was used as fuel. Hexahydrate magnesium nitrate Mg(NO_3)_2·6H_2O was used as an oxidizing agent. Metal mesh cups and gradient furnace were used for synthesis. Reaction was performed in air at the atmospheric pressure. The stoichiometric mixture of magnesium oxide (including magnesium nitrate) and aluminum oxide was used to obtain MgAl_2O_4. The grinding of the initial components was conducted for 60 s in the M3 planetary mill with an acceleration of 45g.

For the synthesis of spinel, the bulk samples were ignited starting at the top, where the furnace temperature was maximal. Heat of the spiral initiated a chemical reaction, resulting in a combustion wave. Temperature-time profiles during SHS of spinel were measured using a tungsten-rhenium thermocouple placed in the center of the sample.

The synthesized products were analyzed by X-ray diffraction, using a diffractometer «DRON-UM-1» and filtered Co Kα-radiation. Structural characterization was done using IR spectroscopy (Nicolet 5700FT-IR spectrometer).

The microstructure of the obtained samples was studied by scanning electron microscopy (Philips SEM 515). The dispersed composition of spinel was determined by the analyzer DelsaMax PRO.

3. Discussion of results
Aluminum is widely used as a fuel to obtain refractory compounds. The high heat release during its oxidation, availability and low cost make aluminum attractive for SHS processes.

This method can be used to synthesize refractory finely-dispersed MgAl2O4 directly in the combustion wave. It is known that only one compound MgAl_2O_4 with a melting point of 2135°C is formed in the MgO-Al_2O_3 system [1]. There are two eutectics, the melting points of which are given in Table 1.

| Spinel  | T_melt, °C | Radius of cation, Å | Eutectics | Amount of Al_2O_3, wt.% | T_melts, °C | Amount of Al_2O_3, wt.% | T_melt, °C |
|---------|------------|---------------------|-----------|------------------------|-------------|------------------------|-----------|
| MgAl_2O_4 | 2135       | 0,65                | 0,5       | 18±55                  | 1995        | 92,5±98                | 1920      |

Figure 1 shows the temperature-time profile during the SHS of magnesium aluminate spinel.

During the heating of the mixture, magnesium nitrate decomposes. The reaction can be described by the equation:

2Mg(NO_3)_2·6H_2O=2MgO+12H_2O↑+O_2↑+4NO_2↑  \quad (1)
Figure 1. Temperature-time profile during the SHS of magnesium aluminate spinel; the reaction mixture consists of MgO, Al$_2$O$_3$, Mg(NO$_3$)$_2$·6H$_2$O, Al.

A mixture of nitrogen oxides, water vapor and oxygen formed during the decomposition of hexaquamagnesium nitrate is an oxidizing and highly reactive environment, causing the ignition of samples. As can be seen in Figure 1, ignition occurs at a temperature of ~ 900°C and reaches a maximum temperature ~ 1500 °C, and the synthesis proceeds in the layer-by-layer combustion mode. Oxidation of aluminum is accompanied by heat release, resulting in the synthesis of spinel.

\[
4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3 + \text{Q}_1 \tag{2}
\]

\[
\text{MgO} + \text{Al}_2\text{O}_3 = \text{MgAl}_2\text{O}_4 + \text{Q}_2 \tag{3}
\]

Fig. 2 shows the X-ray diffraction patterns of synthesized magnesium aluminate spinel. The initial reaction mixture consisted of MgO, Mg(NO$_3$)$_2$·6H$_2$O, Al$_2$O$_3$, Al.

Figure 2. X-ray diffraction patterns of synthesized magnesium aluminate spinel: (1) M-3 pigment (without MA of reaction mixture), (2) M-3 pigment with a mineralizer NaCl, (3) M-3 pigment (with MA of the reaction mixture for 60 seconds in the planetary mill M3), where 1 is 1 MgAl$_2$O$_4$ (Cubic), 2 is $\alpha$-Al$_2$O$_3$ (Rhombohedral), 3 is MgO, 4 is MgAl$_2$O$_4$ (Orthorhombic), 5 is Al$_2$O$_3$ (Hexagonal).
The mineralizer NaCl in the amount of 1 wt.% increases the depth of conversion during SHS, as evidenced by the disappearance and reduction of the diffraction maximum of MgO and Al₂O₃ oxides. Two modifications (cubic and orthorhombic) of MgAl₂O₄ are formed during the high-speed SHS process (curve 1, Fig. 2). The main phase is magnesium aluminate spinel with a cubic structure. It is known that larger Mg²⁺ cations have a lower mobility than Al³⁺ [1], the radius of which is given in Table 1. The presence of a low-melting salt NaCl in the reaction mixture simplifies diffusion processes. The melting point of NaCl is 801 °C, and the boiling point is \( T_{\text{boil}} = 1465 \) °C. During the melting process, the mineralizer weakens the crystal structure of substances, resulting in its activation, and accelerating the formation of synthesis products. The best results of the MgAl₂O₄ synthesis were obtained using the mechanical activation of reaction mixtures. Thus, grinding of initial components in a M3 planetary mill for 60 s is conducted to obtain MgAl₂O₄ spinel without oxide impurities by the SHS method (curve 3, Fig. 2).

Fig. 3 shows the microstructures of magnesium aluminate spinel synthesized by SHS. It can be seen that spinel consists of round grains and whisker crystals which also confirm the presence of two modifications of MgAl₂O₄ (Fig. 3-a). According to the literature data [1], whisker-shaped spinel MgAl₂O₄ can be formed by condensation from the gas phase. It is known that at high temperatures, over the mixture of Al₂O₃ and Al components, aluminum suboxides Al₂O₃(g), AlO(g) and Al(g) [12] are contained, during the precipitation of which whisker crystals are formed. Crystal growth depends on the temperature and concentration of chemical compounds in the gas phase. The maximum temperature of magnesium aluminate spinel synthesis are above the boiling point of sodium chloride \( T_{\text{boil}} = 1465 \) °C, therefore it is not detected in the products, as it evaporates.

Reannealing in a furnace at 1200 °C leads to the disappearance of MgAl₂O₄ (Orthorhombic), and the mechanical activation of the initial reaction mixture results in the formation of MgAl₂O₄ with a cubic structure (Fig. 3-b).

IR spectroscopy showed that the product had a spinel structure (Fig. 4). The vibration of bond is manifested at 693.4 cm\(^{-1}\) for tetrahedrally coordinated magnesium [MgO₄] and at 555 cm\(^{-1}\) for octahedrally coordinated aluminum [AlO₆]. The vibration of the \( v(\text{Al-O}) \) bond with a frequency of 459.8 cm\(^{-1}\) is typical for the \( \alpha-\text{Al}_2\text{O}_3 \) phase. The diffusion of the spectrum in the range of 500–550 cm\(^{-1}\) indicates the disorder in the lattice of AlO₆ [13, 14].

**Figure 3.** Micrographs of magnesium aluminate spinel synthesized by SHS. The initial reaction mixture consists of MgO, Mg(NO₃)₂·6H₂O, Al₂O₃, Al and NaCl as a mineralizer: (a) without mechanical activation of the reaction mixture, (b) with mechanical activation of the reaction mixture for 60 s in the M3 planetary mill; \( \times 10,000 \), Philips SEM 515.
Figure 4. IR spectra of magnesium aluminophosphate spinel obtained by the SHS method; the initial reaction mixture consists of MgO, Al₂O₃, Mg(NO₃)₂·6H₂O and Al, where 1 is spinel MgAl₂O₄; 2 is spinel MgAl₂O₄ synthesized using a NaCl mineralizer (1 wt.%); Nicolet 5700 FTIR spectrometer.

The presence of two modifications of magnesium aluminophosphate spinel with similar interatomic distances is accompanied by a change in the bonding force in the lattice, which leads to the appearance of almost identical frequencies. The absorption band at 912.7 cm⁻¹ is typical for Al₂O₃. SHS of MgAl₂O₄ with the mineralizer NaCl (1 wt.%) leads to the ordering of the structure of spinel.

The diffusion of IR spectrum decreases in the region of octahedrally coordinated aluminum [AlO₆] vibrations, and the absorption band typical for the α-Al₂O₃ phase disappears at 459.8 cm⁻¹ [14, 15].

Finely dispersed magnesium aluminophosphate spinel was obtained, and the grain size was ≤1 μm (Fig. 5).

Figure 5. Histogram of the dispersion of magnesium aluminophosphate spinel; the initial reaction mixture consists of MgO, Al₂O₃, Mg(NO₃)₂·6H₂O and Al with the mineralizer NaCl (analyzer DelsaMax PRO).
4. Conclusions
Magnesium aluminate spinel was synthesized by the SHS method. The mineralizer NaCl (1 wt.%) contributes to the completion of the reaction forming MgAl$_2$O$_4$ spinel.

The best results of MgAl$_2$O$_4$ synthesis were obtained using mechanical activation of the initial reaction mixture. Grinding of initial components in the M3 planetary mill for 60 s was conducted to obtain MgAl$_2$O$_4$ spinel without oxide impurities by the SHS method.

Finely dispersed magnesium aluminate spinel was obtained, and the grain size was ≤1 μm.

Magnesium aluminate spinel obtained by the SHS method can be used as a precursor to obtain fire-resistant ceramic products.

References
[1] Horoshavin L B 2009 Spinel nano-refractory materials. Ekaterinburg: UrB RAS, p 600 (in Russian)
[2] Lemeshev D O, Senina M O and Pedchenko M S 2018 Transparent ceramics made from armored magnesium aluminate spinel Proceedings of the IV Intern. Scie. Forum “New materials and promising production methods”. (Moscow: Viki Vedi) p 735
[3] Zaychuk A and Iovleva Ju 2013 The study of ceramic pigments of spinel type with the use of slag of aluminothermic production of ferrotitanum Chemical Technology 7(2) 217-25
[4] Karanasios K, Xanthopoulou G, Vekinis G and Zoumpoulakis L 2014 SHS-Produced Cobalt-Alumina Catalysts for Dry Reforming of Methane Int. J. SHS 23(4) 222-31
[5] Ramana Rao M V 2006 Magnesia-alumina spinel in action Industrial Minerals 1 51-3
[6] Vinnik I B, Sirotyuk M M, Koval’skii P M and Uvarova I V 1998 Refractory and ceramic materials Powder Metallurgy and Metal Ceramics 37(5-6) 287-90
[7] Senina M O, Lemeshev D O 2017 Production of magnesium aluminate spinel powders by the coprecipitation method Journal Advances in Chemistry and Chemical Technology Successes 31(1) 75-6
[8] Wu Y, Bandypadhyay A and Bose S 2004 Materials Science and Engineering A 380 349-55
[9] Naskar M K and Chatterjee M 2005 Magnesium aluminate (MgAl$_2$O$_4$) spinel powders from water-based sols J. Am. Ceram. Soc. 88(1) 38-44
[10] Hui Li, Heng-Yong Wei, Yi Cui, Rong-Li Sang, Jing-Long Bu, Ying-Na Wei, Jian Lin and Jun-Hong Zhao 2017 Synthesis and characterization of MgAl$_2$O$_4$ spinel nanopowders via nanhydrolytic sol-gel route J. of the Ceram. Society of Japan 125(3) 100-4
[11] Candeia R A, Bernardi M I B, Longo E, Santos I M G and Souza A G 2004 Synthesis and characterization of spinel pigment CaFe$_2$O$_4$ obtained by the polymeric precursor method Materials Letters 58 569-72
[12] Gromov A A, Habas T A, Ilyin A P et al. 2008 Combustion of metal nanopowders (Tomsk: Deltaplan)
[13] Muller U 2007 Inorganic structural chemistry (John Wiley & Sons) p 280
[14] Barabanov V F 1990 Modern physical methods in geochemistry (L.: LSU) p 245 (in Russian)
[15] Chernyakova K V, Vrublevsky I A, Ivanovskaya M I and Kotikov D A 2012 Impurity-defective structure of anodic aluminum oxide formed by the method of two-step-anodization in a solution of tartaric acid Journal of Applied Spectroscopy 79(1) 83