Study of the formation of the phase composition and structure of magnesium-aluminate spinel obtained by the SHS method

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Abstract. Magnesium-aluminate spinel was obtained by self-propagating high-temperature synthesis. Magnesium and aluminum oxides were used as initial components, and aluminum (ASD-4) with additives of amorphous boron was used as fuel. The structure and phase composition of the initial substances and reaction products were studied by means of X-ray diffraction, infrared spectroscopy, and scanning electron microscopy. The synthesis products are shown to contain \( \text{MgAl}_2\text{O}_4 \) as a main phase and a small amount of \( \alpha\)-\( \text{Al}_2\text{O}_3 \) corundum as an impurity. Partial substitution of \( \text{Mg}^{2+} \) by \( \text{Co}^{2+} \) and of \( \text{Al}^{3+} \) by \( \text{Cr}^{3+} \) leads to a shift of X-ray diffraction peaks towards smaller angles, increasing a parameter of the crystal lattice of spinel \( a \), which indicates the formation of solid substitutional solutions. The colour of spinels becomes bright-blue and pink, respectively. A small amount of boron used as energetic additive forms boron oxide, low-melting borates, and eutectics in the \( \text{MgO-B}_2\text{O}_3 \), \( \text{CoO-B}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3\text{-B}_2\text{O}_3 \) systems during combustion, which leads to the appearance of a liquid phase and the formation of skeletal crystals with the size of \( 1\div10 \mu\text{m} \) during the high-speed SHS process.

1. Introduction
Magnesium-aluminate spinel with a high melting point of 2135°C is widely used as a refractory material operating at temperatures of 1500-1750°C in corrosive media [1, 2]. Coloured spinels are used in jewelry. Optical ceramics based on \( \text{MgAl}_2\text{O}_4 \) is material with transparency in a wide spectral range and high strength characteristics [3]. The ability of spinels to form solid coloured substitutional solutions is used in the production of ceramic pigments [4]. Spinel pigments have a number of advantages: thermal and chemical resistance, light resistance, ecological compatibility, and intensive colouration of glaze with a small amount of pigments. They are widely used in colouration of ceramic and porcelain products, in the manufacture of enamels and coatings for metals, vitreous enamels and glazes.

Usually, pigments based on magnesium-aluminate spinel with additives of coloring cations are obtained by a ceramic or sol-gel method followed by heat treatment [4-6]. The disadvantages of these methods are significant power and time consumption. At present, different types of water-based SHS combustion are widely used [7, 8]. However, they have some disadvantages associated with the use of only water-soluble components, which limits their application.

Using self-propagating high-temperature synthesis (SHS) and mixed aluminum and magnesium oxides containing aluminum powder (ASD-4) with additive of amorphous boron as fuel and magnesium nitrate as an oxidizing reagent, we obtained magnesium-aluminate spinel [9]. The
synthesis proceeded at high temperatures and high rates. Coloured spinels were obtained in MgO-CoO-Al₂O₃ and MgO-Cr₂O₃-Al₂O₃ systems. For this purpose, chromophores of transition metals, cobalt and chromium cations in the form of salts and/or metal oxides, were added to the reaction mixture. In this regard, the goal of this work is to obtain magnesium-aluminate spinel coloured with cobalt and chromium cations by the SHS method and to study its phase composition and structure.

2. Materials and procedure
The pure powders of MgO, Al₂O₃, Cr₂O₃ and aluminum (ASD-4) with a dispersion less than 30 microns and additive of amorphous boron (B-99A-TU 6-02-585-75) with a particle size of 1-5 microns, as well as magnesium nitrate Mg(NO₃)₂·6H₂O and cobalt chloride CoCl₂·6H₂O were used as initial components.

Metal mesh cups and a gradient furnace were used for the synthesis of spinel. The reaction was performed in air at the atmospheric pressure. For the synthesis of spinel, the bulk samples were ignited starting at the top, where the furnace temperature was maximum. 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 products obtained were ground to conduct structural studies. The initial substances and the synthesized products were analyzed by means of the X-ray diffraction technique, using a diffractometer «DRON-UM-1» and filtered CuKα-radiation. Structural characterization was done using IR spectroscopy (Nicolet 5700 FTIR spectrometer). The microstructure of the obtained samples was studied by scanning electron microscopy (PhilipsSEM 515). The parameter of the crystal lattice for the elementary cell of spinel for cubic syngony (a) was calculated using the MathCad software by the formula:

\[ a = \frac{\lambda}{2\sin \theta} \sqrt{H^2 + K^2 + L^2} \]

where \( \theta \) is the angle of X-ray reflection; \( H, K, L \) are the reflection indices.

3. Results and discussion
Spinel-based pigments can be divided into two groups. Pigments consisting of coloured spinels obtained from oxides that are chromophores (CoO, NiO, FeO, CoO₂, Co₂O₄, Fe₂O₃, FeO, Cr₂O₃, etc.) are referred to the first group. These pigments have always bright colour and high purity of color.

Another group includes spinel-based pigments synthesized from oxides that are not chromophores, for example Al₂O₃, ZnO, MgO, SnO₂, etc. In this case, the colouring cations are added to the reaction mixture as salts or oxides of transition metals. Embedded in the crystal lattice of white spinel, the chromophores form coloured solid substitutional solutions with low purity of colour.

The introduction of cobalt cations into tetrahedral voids provides bright blue spinels, and the substitution of Al³⁺ for Cr³⁺ cation in octahedral voids provides pink spinels. Depending on the number of Co³⁺ and Cr³⁺ cations embedded in the isomorphous crystal lattice of MgAl₂O₄ magnesium-aluminate, the bright blue and pink pigments of different shades were obtained.

The synthesis of pigments is carried out in the mode of layered combustion. During the exothermic oxidation of aluminum and boron, a large amount of heat is released, the initial components are heated up to temperatures above 1000°C, at which spinels are formed with the release of heat. Figure 1 shows the temperature-time profile during the SHS process of pink pigment. As can be seen the ignition occurred at the temperature of ~330°C and reached a maximum temperature of ~1400°C.

The obtained pigments were studied by X-ray phase diffraction that confirmed the formation of spinels. Figure 2 demonstrates X-ray diffraction patterns of white magnesium-aluminate spinel (curve I), blue Mg₀.₉₂Co₀.₀₇Al₂O₄ (curve II) and pink MgAl₁.₉₄Cr₀.₀₄ (curve III) magnesium-aluminate-based pigments synthesized from magnesium and aluminum oxides and magnesium nitrate taken in the amount to obtain MgAl₂O₄ with a stoichiometric composition containing 2wt.% boron with the ratio (B:Al=1:3.6). Magnesium-aluminate spinel contains MgAl₂O₄ as the main phase, as well as a
phase of rhombohedral α-Al₂O₃. Blue pigment contains the CoAl₂O₄ phase. When Co²⁺ cation is added to the MgAl₂O₄ spinel, solid solutions are formed between the blue aluminum-cobalt and blue magnesium-aluminate spinels (figure 2, curve II).

Figure 1. Temperature-time profile during the synthesis of MgO-Cr₂O₃-Al₂O₃ pink pigment.

Figure 2. X-ray diffraction patterns of magnesium-aluminate-based pigments based: (I) white pigment (MgO-Al₂O₃); (II) blue (MgO-CoO-Al₂O₃); (III) pink (MgO-Cr₂O₃-Al₂O₃), where (1) magnesium-aluminate spinel, (2) Al₂O₃ (Rhombohedral), (3) CoAl₂O₄.

This fact is confirmed by the shift of diffraction maxima toward smaller angles (figure 3). The parameter of the elementary cell \(a\) for the cubic syngony of the crystal lattice of MgO-CoO-Al₂O₃ spinel, calculated using the Maud program, slightly increases and is equal to 8.0614 Å (for MgAl₂O₄ \(a=8.0567\) Å) (table 1). The coordination number of Cr³⁺ is equal to six for spinel and corundum, and the structure of complexes is octahedral [CrO₆]. The addition of Cr³⁺ cation to the MgO-Cr₂O₃-Al₂O₃ structure leads to the considerable broadening and shifting the diffraction peaks towards smaller angles, and the lattice parameter increases and is equal to 8.0900 Å (figure 2, curve III). The use of
Cr\textsuperscript{3+} cation during the synthesis of MgAl\textsubscript{2}O\textsubscript{4} accelerates solid-phase reactions to form spinels, which is associated with greater mobility of Cr\textsuperscript{3+} ions compared to Al\textsuperscript{3+} those.

Figure 3. Shift of diffraction maxima of magnesium-aluminate spinel: (1) MgAl\textsubscript{2}O\textsubscript{4}, (2) partial replacement of Mg\textsuperscript{2+}→Co\textsuperscript{2+}, (3) partial replacement of Al\textsuperscript{3+}→Cr\textsuperscript{3+}.

Table 1. Parameter (\(a\)) of the elementary cell for cubic syngony of the crystal lattice of spinel as a function of the cation of transition metal in the composition of spinel.

| System cation & colour | Radius of cation, Å | \(a\), Å | Spinel phase | note |
|----------------------|---------------------|--------|-------------|-------|
| MgO-Al\textsubscript{2}O\textsubscript{3} | Mg\textsuperscript{2+} white | 0,65 | 8.0567 | MgAl\textsubscript{2}O\textsubscript{4} | - |
| MgO-Al\textsubscript{2}O\textsubscript{3} | Al\textsuperscript{3+} white | 0,50 | | | |
| MgO-CoO-Al\textsubscript{2}O\textsubscript{3} | Co\textsuperscript{2+} blue | 0,72 | 8.0614 | Co\textsubscript{x}Mg\textsubscript{1-x}Al\textsubscript{2}O\textsubscript{4} | x=0.07 |
| MgO-Cr\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} | Cr\textsuperscript{3+} pink | 0,64 | 8.0900 | MgCr\textsubscript{y}Al\textsubscript{2-y}O\textsubscript{4} | y=0.10 |

Morphology of the surface of the MgAl\textsubscript{2}O\textsubscript{4} synthesized product and MgAl\textsubscript{2}O\textsubscript{4}-based pigments obtained using 2wt.% additive of boron was studied by scanning electron microscopy (PhilipsSEM 515) (figure 4). The sizes of the spinel crystals are from 1 to 10 μm.
During the SHS of pigments the skeletal spinel crystals are formed (figure 4) with the participation of liquid phase formed due to the addition of boron to the reaction mixture. Boron plays a dual role. Firstly, during the oxidation of boron, a significant amount of heat is released, which makes it possible to synthesize pigments without preheating the reaction mixture. Secondly, $\text{B}_2\text{O}_3$ being an oxidation product accelerates the formation of magnesium-aluminate spinel. The melting point of $\text{B}_2\text{O}_3$ is 450°C. Furthermore, the liquid phase occurs during high-temperature synthesis due to the formation of low melting eutectics and borates, for an example in the systems such as $\text{MgO} - \text{B}_2\text{O}_3$ ($T_{\text{melt}} = 1180^\circ\text{C}$), $\text{B}_2\text{O}_3 - 2\text{CoO} - \text{B}_2\text{O}_3$ ($T_{\text{melt}} = 900^\circ\text{C}$), $2\text{CoO} - \text{B}_2\text{O}_3 - 3\text{CoO} - \text{B}_2\text{O}_3$ ($T_{\text{melt}} = 1080^\circ\text{C}$) и $3\text{CoO} - \text{B}_2\text{O}_3 - \text{CoO}$ ($T_{\text{melt}} = 1200^\circ\text{C}$), etc. Increased volatility of $\text{B}_2\text{O}_3$ at high temperatures leads to its evaporation, which also contributes to the formation of skeletal crystals.

4. Conclusion
The use of mixed aluminum and boron as fuel intensifies the combustion process in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{Al-B}$ system to obtain magnesium-aluminate spinel and magnesium-aluminate-based pigments. A small amount of boron, low-melting boron oxide formed during combustion, borates of aluminum, magnesium and cobalt, as well as low-melting eutectics result in the appearance of liquid phase that contributes to the formation of skeletal crystals with a size of 1÷10 $\mu\text{m}$ during the high-speed SHS process.

The partial replacement of $\text{Mg}^{2+}$ for $\text{Co}^{2+}$ and of $\text{Al}^{3+}$ for $\text{Cr}^{3+}$ provides bright blue and pink spinels and leads to the shift of diffraction maxima towards smaller angles, while the parameter of the elementary cell $a$ for cubic syngony of the crystal lattice of spinel increases, which indicates the formation of solid substitution solutions.

References
[1] Horoshavin L B 2009 Spinel refractory materials (Ekaterinburg: UrB RAS) p 600
[2] Ramana Rao M V 2006 Magnesia-alumina spinels in action Industrial Minerals (No.1) 50
[3] Senina M O and Lemeshev D O 2017 Obtaining of powder magnesium-aluminate spinel by the method of co-precipitation Journal Adhvances in Chemistry and Chemical Technology 31 75
[4] Maslennikova G N and Pishch I V 2009 Ceramic pigments (Moscow: RIF "Stroimaterialy") p 224
[5] Li H, Wei H-Y, Cui Y, Sang R-L, Bu J-L, Wei Y-N, Lin J and J-H Zhao 2017 Journal of the Ceramic Society of Japan 125 100
[6] Eliziario S A, Andrade J M, Lima S J G, Paskocimas C A, Soledade L E B, Hammer P, Longo E, Souza A G and Santos I M G 2011 Materials Chemistru and Physics 129 619
[7] Ahmed I S, Dessouki H A and Ali A A 2011 Polyhedron 30 584
[8] Tong Y, Zhang H, Wang S, Chen Z and Bian B 2016 Journal of Nanomaterials 7
[9] Patent RF No. 2580343 Radishevskaia N I, Kasatsky N G, Nazarova A Yu, Lvov O V and Maksimov Yu M Method for the obtaining of ceramic pigments based on magnesium-aluminate spinel. (10.04.2016) 6 p