Dense ceramics based on magnesium aluminate spinel with the addition of gallium oxide

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Abstract. The preparation of dense ceramics based on magnesium aluminate spinel (AMS), a material with unique physicochemical properties, is considered. The work shows methods for producing AMS powders of stoichiometric composition by the method of reverse heterophase co-precipitation, studying the influence of the firing temperature and of the method of introducing of the sintering additive of gallium oxide on the ceramic properties of the obtained samples.

1. Introduction
In the modern world, the production of high-density materials based on ceramics has become quite widespread. This is because such ceramic products are used in the defense industry as armor materials – armored plates, bulletproof vests, and it used to create armor for military equipment also [1,2]. Ceramic armor is quite relevant due to it not only retains its mechanical properties during operation in extreme conditions, but also allows to reduce the weight of armored vehicles, and its use minimizes the possibility of injuries among military soldiers.

To date, the technology for producing armored materials from aluminum oxynitride and aluminum oxide is widely used, but such products are distinguished by high cost due to the high cost of the equipment used and the manufacturing process itself.

Over time, material such as magnesium aluminate spinel is gaining popularity. It has a number of properties that distinguish it from other types of technical ceramics. This material has been an issue of great interest due to the low density (3.58 g/cm³) compared to metals, while having excellent mechanical characteristics, it has an isotropic structure also, and therefore, a high degree of light transmission in the visible region of the spectrum can be achieved under certain conditions. A distinctive feature is the relative simplicity of obtaining the material at relatively low both energy and financial costs [1], compared with the production of products from AION and polycrystalline Al₂O₃, manufactured by growing single crystals [3,4]. However, the production of spinel ceramics is also quite expensive today.

Sintering of magnesium aluminate spinel is known to occur at rather high temperatures up to 1900 °C, but dense ceramics based on it is rather difficult to obtain through the presence of closed porosity, which occurs at the final stage of sintering due to intensive growth crystals. Usually, costly and time-consuming methods are used to remove porosity, for example, hot pressing or spark plasma sintering [2]. Also complete removal of porosity in the material is possible to achieve by introducing sintering additives, which contribute to lowering the sintering temperature and, as a result, achieving the necessary physical, mechanical and optical properties of such ceramics.
Today, gallium oxide, which forms a cubic solid solution with AMS, is a promising additive for creating a transparent magnesium aluminate spinel. Ga₂O₃ contributing to vacancies in the formation of solid solutions in both spinel sublattices. This process contributes to an improvement in sintering, which results in the approximation density of material to theoretical values. Gallium oxide, which belongs to a small group of oxides can form a cubic solid solution with spinel, and which is a relatively inexpensive raw material also, can be successfully used as an additive to obtain ceramics with high operational properties [1].

The following defect formation scheme is possible during the reaction of gallium oxide with magnesium aluminate spinel:

\[
\text{Ga}_2\text{O}_3 \overset{\text{MgO-Al}_2\text{O}_3}{\rightarrow} 2\text{Ga}^{2+}_{\text{Mg}} + 3\text{V}^{\prime \prime}_{\text{Mg}} + 3\text{V}^{\prime \prime \prime}_{\text{Al}} + 3\text{O}^{2-}_0 + 3\text{Mg}^{\text{Mg}} + \text{Mg}^{\text{Mg}}_{\text{Mg}}
\]

The goal of the effort is to obtain a dense ceramic material in the MgAl₂O₄ - Ga₂O₃ system, having high-performance properties and the lowest cost of production compared to foreign analogs, such as AlON and Al₂O₃. The article is described the preparation of samples from magnesium aluminate spinel based on the method of reverse co -precipitation, which is the most advantageous for obtaining a precursor without using specialized equipment and high temperatures, and it has a rather short reaction time also. Also the effects of firing temperature and method introduction of gallium oxide additives on the ceramic properties of the products are considered.

### 2. Materials and Methods

Strict stoichiometry of the components needed to be ensured to obtain the necessary mechanical properties. Calculation it needs to know the loss on ignition (LOI) of the staple. The main components are nitrates of aluminum and magnesium aqueous solution, taken in the proportion of 1:1 mol % in terms of oxides: Al₂O₃ - 71.67 wt. % and MgO - 28.33 wt. %, taking into account the LOI. The precursor of magnesium aluminate spinel was obtained by the method of reverse heterophase co-precipitation from Al(NO₃)₃ and Mg(NO₃)₂ salts aqueous solution, by spraying in an excess of a cooled ammonia solution, the particles crystallize and MgAl₂(OH)₈ is formed. The resulting precipitate was filtered to the pH of 9-11, washed with acetone to prevent particle aggregation and removal of adsorbed water.

The optimum temperature for the synthesis of the precursor powder was selected according to the results of differential scanning calorimetry (DSC).

Gallium nitrate (Ga(NO₃)₃·8H₂O) was the initial component as a modifying additive, which was introduced by the wet method in an amount of 7 mol. % in terms of Ga₂O₃ in one case directly to the precursor, in the other to synthesized spinel. Then the suspension was dried in an oven at a temperature of 80 °C.

The research of shrinkage of composition containing 7 mol. % Ga₂O₃ was determined to the firing mode, the results of which are presented in Figure 1.

![Figure 1. Thermogravimetric and differential thermal curves of a composition containing 7 mol. % Ga₂O₃](image-url)
Based on the survey data, we can assume that in the temperature range of 50 - 1150 °C. There are no significant changes in linear shrinkage, therefore firing in this temperature range can be carried out at high speed. The noticeable change in linear dimensions is observed at temperatures above 1150 °C, therefore, it is advisable to significantly reduce the heat treatment rate.

Forming a green body being carried formed in the P-50 press by semidry single-stage pressing at a pressure of 100 MPa. Paraffin was used as the temporary technological bundle (PTB). It introduced in powder an amount of 5 wt. %.

Two roasting were performed to obtain high-density materials. The first roasting was carried out in air at a temperature of 1100 °C to remove the organic binder from the green body and give it sufficient strength. Firing to complete sintering and achieving transparency by the material was carried out in a high-temperature vacuum furnace at a temperature of 1700 °C and 1750 °C with a three-hour exposure at a maximum temperature for 3 hours.

Scanning electron microscopy (SEM) was performed to analyze the microstructure of powder.

3. Results and discussion
The temperature of synthesis powder of the precursor was determined by differential scanning calorimetry (DSC) data, the results which are shown in figure 2. For the formation of the MgAl₂O₄ phase, this value is 1200 °C.

![Figure 2. DSC results of spinel precursor.](image)

The X-ray phase analysis (XRD) was performed to verify the correctness of the selected synthesis method and firing temperature: the obtained compound has a stoichiometric composition and magnesium aluminate spinel is the only crystalline phase (Fig. 3).

![Figure 3. Diffractogram of MgAl₂O₄.](image)
Scanning electron microscopy was performed to analyze the shape and size of the particles. The results are presented in Figure 4.

![Figure 4. Photos of the microstructure of spinel powder, according to SEM.](image)

Spinel powder has a multifractal composition, particles are represented in various shapes and sizes. As a result of composition material may include pores in the future.

Figure 5 shows photographs of the distribution of gallium oxide in spinel. Additive was introduced to ensure the removal of porosity in the material. You can see aggregated that particles, which consist of particles up to 5 microns in size. The powder is distributed uniformly in volume.

![Figure 5. Pictures of the distribution of gallium oxide in spinel.](image)

The data by X-ray of powder (Fig. 6) confirm the formation of a compound of gallium oxide and magnesium aluminate spinel of variable composition.
Figure 6. Diffraction pattern of solid solutions of Ga$_2$O$_3$ in MgAl$_2$O$_4$.

The introduced dopant does not stand out as an independent phase. As a result it can be assumed that the formation of a substitutional solid solution occurs in the lattice of magnesium aluminate spinel.

The obtained finely dispersed powders have sintering activity, with the result that the particles can be sintered and aggregated at the initial stages of pressing calcining. To prevent this process, it possible, should be carried a synthesis of solid solutions out at lower temperatures.

The properties of the samples were studied with introduced additive into AMS, at a temperature of 1700 and 1750 °C. After analyzing the data obtained, it is worth noting that an increase in the firing temperature leads to a significant increase in the properties of ceramics (table 1).

Table 1. The values of the studied properties of the samples at different firing temperatures.

| Temperature, °C | Average density, $\rho$, g/cm$^3$ | Open porosity, $P_o$, % |
|----------------|----------------------------------|------------------------|
| 1700           | 2.21                             | 11.0                   |
| 1750           | 3.24                             | 3.1                    |

It was decided to check the dependence of the properties of ceramic samples based on alumina-magnesia spinel at a firing temperature of 1750 °C obtained by introducing an additive into a precursor powder in one case, and into a spinel powder in another (table 2).

Table 2. Properties of ceramics obtained at a firing temperature of 1750 °C

| Introduction of additives | Average density, $\rho$, g/cm$^3$ | Open porosity, $P_o$, % |
|--------------------------|----------------------------------|------------------------|
| In the precursor         | 3.20                             | 8.3                    |
| The spinel               | 3.24                             | 3.1                    |

The sample has a porosity of 3.1 %, when an additive is added to AMS powder, and the average density is 91% of theoretical, which may be due to a more complete passage of the defect formation reaction and the formation of a solid solution with a cubic lattice.

Figure 7 shows the XRD of the sample after firing at 1750 °C. According to the X-ray diffractogram, the addition of gallium oxide entered the solid solution of variable composition.
Figure 7. XRD of spinel doped with 7 mol. % gallium oxide.

Figure 8 shows the microstructure of the sample 7 mol. % gallium oxide obtained at a firing temperature of 1750 °C. An increase in the sintering temperature facilitated the preparation of samples with a homogeneous structure, including a small number of intercrystalline and intra-crystalline pores; the crystal sizes vary from 5 to 20 μm.

Figure 8. Microstructure of AMS ceramics with the addition of Ga$_2$O$_3$, $T_f = 1750$ °C.

Figure 9 shows a photograph of a ceramic sample based on magnesium aluminate spinel doped gallium oxide in an amount of 7 mol. %

Figure 9. Photograph of a ceramic sample based on magnesium aluminate spinel doped gallium oxide.

The micro-hardness of the samples sintering additive was introduced into the synthesized spinel with the lowest porosity and optimal density values, and their firing temperature was 1750 °C was measured. The average value is 13.1 ± 0.7 GPa.
4. Conclusion
After the research conducted, the optimal technological parameters were selected for the synthesis of powders of magnesium aluminate spinel using for dense ceramics; the dependence of the average density, open porosity and light transmission of the obtained ceramics on the method of introducing a sintering additive is revealed; the temperature dependence of the properties of ceramics is determined:

1. Highly dispersed, low-aggregate powders were obtained by the method of reverse heterophase co-precipitation.
2. An increase in the firing temperature has a positive effect on the properties of the resulting ceramics. With an increase in the firing temperature from 1700 to 1750 °C, the average density values with the addition of gallium oxide additive to the synthesized spinel increased from 2.21 g/cm³ to 3.24 g/cm³, and the content of open porosity decreased from 11.0 % to 3.1 %.
3. The samples when the additive is added to spinel are higher the ceramic properties, compared with the introduction of gallium oxide into the precursor.
4. The microhardness values of the samples are close to theoretical, which implies that the microstructure of ceramics is close to perfect.

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