Production of dense ceramics based on magnesium aluminate spinel with an evaporating additive

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Abstract. The influence of the evaporating additive on the properties of ceramics based on magnesium aluminate spinel obtained by high-temperature sintering in vacuum was investigated. The spinel precursor was obtained by chemical reverse co-precipitation, which after that was calcined at a temperature of 1200 °C. As an additive, boron oxide B₂O₃ was used in the concentration range of 5.0-7.0 wt.% Sintering of the samples was carried out at temperatures of 1700 and 1750 °C. Identified trends allowing to obtain the densest samples with minimal porosity.

1. Introduction

Currently, an important direction of chemical technology is the material creation with several functional properties. Polycrystalline ceramic materials occupy a leading position in modern materials science.

In particular, one of the most promising directions for the development of the ceramic industry is the production of transparent ceramics. Interest in this way arises due to the creation of devices capable of working under conditions of elevated temperatures and pressures, aggressive environments, etc. The use of glass for these purposes limits the capabilities of these devices.

The basic direction of research in the field of creating transparent ceramics is the development of unique compositions of materials and the improvement of methods for preparing a mixture with uniformly distributed additives to obtain products that can provide light transmission not only in the infrared range, but also in the visible part of the spectrum.

A promising material in the above applications is ceramic made of magnesium aluminate spinel.

The technology of producing transparent ceramics from magnesium aluminate spinel (MAS) includes the use of sintering additives of various mechanisms of action. The advantage of using such additives is the possibility of obtaining a dense transparent material, they also reduce the processing temperature.

Magnesium aluminate spinel MgAl₂O₄ is recognized for its valuable properties, including the availability of raw materials, chemical inertness to aggressive media, thermal stability, low density, excellent optical properties, and high melting point [1]. The main advantage of MAS-based ceramics is, first of all, the isotropy of the structure, which makes it possible to exclude light scattering. Also, spinel gives an advantage in the spectrum and availability of raw materials over the main competitive material - AlON.

To obtain transparent ceramic products, it is necessary to use finely dispersed powders that are sintering active [2]. One of the promising methods for producing finely dispersed powders is reverse
heterophase co-precipitation from aqueous solutions. The use of reverse co-precipitation allows the joint crystallization of several components with the formation of a solid phase.

The method of co-precipitation in the aqueous solutions is relatively simple, since it does not require special conditions and equipment. These advantages allow the deposition to be applied in industry by significantly reducing production costs.

It is known that a prerequisite for creating transparent ceramics is the complete absence of porosity. This is achieved using expensive and time-consuming methods such as spark plasma sintering (SPS), hot pressing (HP), and hot isostatic pressing (HIP). As a result of numerous investigations, it was found that the introduction of various additives, called sealing, favorably affects the production of materials with a high degree of transparency [3].

Recently, additives have been actively used that give a liquid phase as a result of firing, which helps to remove porosity. Such additives form a eutectic melt, in the presence of which the density increases. It is important to select the additive so that as a result of high-temperature processing, foreign compounds are not formed that can disrupt the monophase of the system.

One of these additives is B₂O₃, which forms a melt at a temperature of 470 °C, initiating liquid-phase sintering, and subsequently evaporates without forming new compounds. Major research in this area was conducted by the Japanese scientist K. Tsukuma in [4]. It was experimentally established that ceramics with the addition of 0.15 wt. % sealing additive obtained by HIP at a temperature of 1300 °C has almost zero porosity and light transmission in the visible part of the spectrum exceeds 80%.

Identical results were obtained by scientists from Turkey [5], who obtained a light transmission of ceramics above 70% in the visible spectrum, with the addition of 0.15 wt. % B₂O₃ by SPS at a temperature of 1300 °C.

Later, in [6] it was found that the introduction of 5 wt. % boron oxide by subsequent sintering in a vacuum at a temperature of 1650 °C significantly reduces the porosity of ceramics, proving the indispensable contribution of sealing additives to the technology of transparent ceramics based on MAS.

2. Materials and Methods
An important task of obtaining MAS is to preserve its stoichiometry, therefore, the process of synthesis of spinel powder must be carried out with maximum compliance with the conditions. The stoichiometric composition of spinel in terms of oxides is represented by the following ratio: MgO -50 mol.%, Al₂O₃ -50 mol. %.

To obtain the precursor spinel used the method of reverse chemical co-precipitation from aqueous solutions by spraying a saturated solution of magnesium and aluminum nitrates, taken in a stoichiometric ratio (including loss on ignition), the excess solution precipitator, which is used as the aqueous solution of ammonia.

After obtaining the precursor powder of magnesium aluminate spinel, differential scanning calorimetry (DSC) was performed using a high-temperature synchronous thermal analyzer Netzsch STA 449 F3 Jupiter to select the optimal synthesis temperature for obtaining the stoichiometric spinel phase.

After the synthesis of magnesium aluminate spinel, an X-ray phase analysis was performed to identify the phases in the material. The analysis was carried out on the DRON-3M device, the results were processed using the program Crystallographica, as well as using the program" Match! " Crystal Impact V. 3.8.1.143 with an optional calculation module FullProf Suite.

Microstructure studies were carried out by scanning electron microscopy (SEM) using a scanning electron microscope Tescan Mira XMU III.

Boron oxide additive in the concentration range of 5.0-7.0 wt. % introduced into spinel powder by wet method. The blanks were formed by the method of uniaxial double-sided semi-dry pressing on a hydraulic press P-50 in a metal form at a pressing pressure of 100 MPa. The resulting samples were labeled and air-dried.

The dried blanks were subjected to removal of a temporary technological bundle in air in a furnace with lanthanum chromite heaters at a temperature of 1100 °C. Firing of samples after removal of the
A temporary technological bundle was carried out in a vacuum furnace at temperatures of 1700 °C and 1750 °C.

The properties of the fired products were determined by saturating the ceramic body with water and then hydrostatic weighing.

3. Results and discussion

According to the DSC data (fig. 1), active crystallization of MAS begins at a temperature of about 890 °C, and the end of spinel crystallization occurs at 1100 °C. To complete the spinel formation process and improve the structure, the synthesis temperature of 1200 °C was chosen.

The results of X-ray phase analysis (fig. 2) show that at a synthesis temperature to 1200 °C, a single phase of MAS is formed and other compounds are absent.

Figure 1. DSC of the MAS precursor.

The results of X-ray phase analysis (fig. 2) show that at a synthesis temperature to 1200 °C, a single phase of MAS is formed and other compounds are absent.

Figure 2. Radiograph of synthesized MAS.
Based on the results of microscopic analysis (fig. 3), it can be noted that the powder is represented by a polyfractional composition with a predominant content of isometric particles with sizes of 5-20 µm and a small amount of agglomerates with an average size of 50-70 µm, which can affect the formation of pores in the material.

After firing at a temperature of 1700 °C the values of open porosity and an average density of samples with concentrations of boron oxide additive from 5.5 to 7.0 wt. % were determined. The data are presented in table 1.

| The concentration of additive, % | Open porosity, % | Average density, g/cm³ |
|---------------------------------|-----------------|------------------------|
| 5.5                             | 9.6             | 2.78                   |
| 6.0                             | 9.9             | 2.78                   |
| 6.5                             | 12.5            | 2.64                   |
| 7.0                             | 13.2            | 2.56                   |

As a result of dependency analysis, one can identify the best indicators of sample properties with the addition of 5.5 wt. % boron oxide. Increase in the concentration of the B₂O₃ additive over 6.0 wt. % leads to a significant deterioration in the properties of ceramics obtained at a firing temperature of 1700 °C, so the next study was the effect of increasing the firing temperature to 1750 °C on the properties of ceramics obtained from MAS with boron oxide additives in the concentration range of 5.0-6.0 wt.%. Boron oxide additive with a concentration of 5.0 wt. % is selected to perform a comparative analysis of the dependence obtained in the previous stage.

After firing at a temperature of 1750 °C the values of open porosity and an average density of samples with the additive concentration in the range of 5.0-6.0 wt % were determined. The results are presented in table 2.

| The concentration of additive, % | Open porosity, % | Average density, g/cm³ |
|---------------------------------|-----------------|------------------------|
| 5.0                             | 4.7             | 3.32                   |
| 5.5                             | 4.5             | 3.37                   |
| 6.0                             | 5.3             | 3.25                   |
As a result of the analysis of the obtained dependencies, one can distinguish the best indicators of average density and open porosity with the addition of 5.5 wt. % boron oxide. With a further increase in the concentration of the additive, these properties of products burned at a temperature of 1750 °C deteriorate.

Such regularities can be explained by the fact that at concentrations of sintering additive less than 5.5 wt. % of the amount of melt formed is not enough to form a dense structure. At concentrations above 5.5 wt. % is formed much larger the liquid phase, however, later when the boron oxide evaporates, this leads to the formation of voids, which does not allow obtaining a high-density material.

The most optimal properties of products at a concentration of boron oxide additives of 5.5 wt. % confirmed with increasing firing temperature. Combined results of studies conducted at firing temperatures of 1700 and 1750 °C are presented in table 3.

| Firing temperature, °C | The concentration of additive, % | Open porosity, % | Average density, g/cm³ |
|------------------------|----------------------------------|------------------|-----------------------|
| 1700                   | 5.5                              | 9.6              | 2.78                  |
|                        | 6.0                              | 9.9              | 2.78                  |
| 1750                   | 5.5                              | 4.5              | 3.37                  |
|                        | 6.0                              | 5.3              | 3.25                  |

The presence of pores in the material is confirmed by photos of the microstructure of samples with an additive concentration of 5.5 wt.%, firing at temperatures of 1700 °C and 1750 °C. The results of microscopy are shown in figure 4.

**Figure 4.** Photos of the microstructure of samples from MAS with boron oxide added, firing at a temperature of: a) 1700 °C; b) 1750 °C

The microstructure of ceramics after firing in the case of a) is heterogeneous and is represented by irregular-shaped crystals up to 20 µm in size. It is also noted that there are open intercrystalline pores up to 10 µm in size and intracrystalline pores up to 1 µm in size, which does not allow obtaining high-density indicators. In the case of b), you can see a structure with a uniform distribution of 10-15 µm in...
size, in contrast to the structure observed during firing at 1700 °C. There are also open intercrystalline and intracrystalline pores are observed in the structure, which can lower the density of the ceramic.

4. Conclusion
The resulting powder magnesium aluminate spinel of stoichiometric composition. According to the results of the X-ray phase analysis, spinel is the only phase in the resulting powder.

Experimental samples were obtained, in which the open porosity and average density were determined. It was found that samples with an additive concentration of 5.5 wt. % have the most optimal properties not only at the firing temperature of 1700 °C, but also at the temperature of 1750 °C. Further increase in the concentration of the additive leads to an increase in the open porosity and average density of products. Increasing the firing temperature of samples with a concentration of boron oxide additive of 5.5 wt. % at 50 °C leads to a decrease in open porosity from 9.6 to 4.5 % and an increase in average density from 2.78 to 3.37 g / cm³. Based on these conclusions, it can be concluded that the introduction of boron oxide additives with a concentration of 5.5 wt. % and increasing the firing temperature has a positive effect on the denser samples of magnesium aluminate spinel.

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