Effect of evaporating additive on sintering and properties of ceramics based on magnesium aluminate spinel

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Annotation: Prospects of appliance of transparent ceramic based on magnesium aluminate spinel are considered. Sintering additive that makes it possible to synthesise transparent ceramic material from spinel was selected. Influence of evaporating additive $\text{B}_2\text{O}_3$ on properties ceramics based on magnesium aluminate spinel is shown.

1. Introduction

In the modern world, a promising development direction of the ceramic industry is the production of transparent ceramics used in the defense industry as visors for helmets and armor window of civil and military transport. Currently, technologies for producing transparent armor based on magnesium aluminate spinel (MAS) are actively used, which has a unique combination of properties, such as chemical inertness to aggressive media, thermal stability, low density, high mechanical performance, as well as excellent optical properties. The stable cubic structure of $\text{MgAl}_2\text{O}_4$ provides light transmission up to 92 % in the visible spectrum and isotropy of optical characteristics [1]. Due to the above properties, as well as the availability of raw materials MAS is one of the most promising materials for the manufacture of transparent ceramics with improved performance.

One of the most important stages of obtaining ceramics from MAS is the synthesis of precursor powder. To obtain materials with a high degree of transparency, it is necessary to achieve perfection of the technological process through the use of special methods of qualitative preparation of the charge, called chemical. The most promising of them should be considered two methods: co-precipitation from aqueous solutions, since it does not require the use of special equipment and high temperatures, and is characterized by a relatively short reaction time; the method of thermal synthesis, which is the easiest to use, does not require special equipment and is reproducible, because its course is not affected by any external parameters, whether the atmospheric pressure or ambient temperature.

It is known that a prerequisite for the creation of transparent ceramics is the complete absence of porosity in it. This is achieved by using expensive and time-consuming methods, such as spark plasma sintering (SPS), hot pressing (HP) and hot isostatic pressing (HIP). Numerous studies conducted over the years [2, 3, 4] have established the effect of evaporating boron oxide additive on the sintering process of spinel ceramics by the method of HIP and SPS at a temperature of 1300 °C. The results of the experiment show that the introduction of $\text{B}_2\text{O}_3$ additive in an amount of 0.15 wt. % significantly reduces porosity and increases the light transmission of the material in the visible spectrum up to 80 % at HIP and up to 70 % at SPS. Further, in [5] the effect of $\text{B}_2\text{O}_3$ additive in the amount of 0-10 wt. % on the properties of ceramics obtained by sintering in a vacuum at 1700 °C. As a result of the experiment, it was revealed that in order to obtain high light transmission and low porosity, it is necessary to introduce no more than 7 wt. % boron oxide.
The aim of this study is to investigate the effect of the concentration of evaporating additives on the sintering process of sample from magnesium aluminate spinel, the precursor of which was obtained by chemical co-precipitation and thermal synthesis.

2. Materials and Methods

The method of reverse chemical co-precipitation from aqueous solutions is carried out by spraying a saturated solution of magnesium and aluminum nitrates taken in a stoichiometric ratio (in terms of oxides: MgO – 28.33 wt. %, Al₂O₃ – 71.67 wt. %, taking into account losses by calcination) in excess of a solution-precipitator as which the aqueous solution of ammonia is used.

The starting materials for thermal synthesis are aluminum hydroxide Al(OH)₃, obtained from aluminum nitrate by precipitation, and the basic magnesium carbonate mMgCO₃·Mg(OH)₂·nH₂O in a ratio of 71.67 and 28.33 wt. %, respectively, in terms of oxides.

Differential scanning calorimetry of the precursors obtained by chemical precipitation was carried out. The results are shown in Figure 1. DSC mixtures of magnesium carbonate and aluminum hydroxide have a similar character.

![Figure 1. Results of DSC of the precursor spinel obtained by chemical precipitation.](image)

On the basis of the results of differential scanning calorimetry, the temperature of the end of the crystallization of spinel equal to 1150 °C. For the purpose of more complete passage of the spinel formation process, a temperature of 1200 °C, was chosen.

To reduce porosity, B₂O₃ was selected as an additive in the concentration range from 5.0 to 6.0 wt. %, which is inserted into spinel powder by wet method. Mixing was carried out for 15 minutes in a planetary mill. Molding of semi-finished products was carried out by semi-dry pressing at a pressing of 100 MPa with paraffin and a solution of carbon tetrachloride as a temporary technological bundle. Removal of bundle was carried out at a temperature of 1100 °C, and firing of samples – at a temperature of 1750 °C in a vacuum with a holding time of 3 hours.

3. Results and discussion

The choice of synthesis method and firing temperature is confirmed by the data of X-ray phase analysis (Figure 2, 3), which show the presence of a single phase of spinel.
Figure 2. Radiograph of spinel synthesized by chemical precipitation.

Figure 3. Radiograph of spinel synthesized by thermal synthesis.

The choice of temperature of removal of bundle is confirmed by results of the x-ray phase analysis of a material (Figure 4, 5) after firing at a temperature of 1100 °C. Radiographs shows the presence of a single spinel phase and the absence of boron compounds, which indicates the complete evaporation of boron oxide as a result of high-temperature treatment.

Figure 4. Radiograph of spinel synthesized by chemical precipitation after removal of bundle.
Figure 5. Radiograph of spinel synthesized by thermal synthesis after removal of bundle.

Photos of spinel microstructure (Figure 5, 6) synthesized both by precipitation and by thermolysis, show that the powder is represented by a polyfractive composition with a predominant content of isometric particles of 5-20 micrometers in size, as well as a small number of agglomerates with an average size up to 50-60 micrometers, which can affect the formation of pores in the material.

Figure 6. Photos of the microstructure of spinel synthesized by chemical precipitation.

Figure 7. Photos of the microstructure of spinel synthesized by thermal synthesis.
It should be noted that this form of crystals allows to obtain the densest ceramics due to the formation of contacts of the type “plane-plane” and “knife-plane”.

The analysis of the obtained data leads to the following indicators of open porosity and the average density of the burned samples (Tables 1, 2).

**Table 1.** Open porosity and the average density of samples obtained by chemical precipitation.

| The concentration of additive, % | Open porosity, % | Average density, g/cm\(^3\) |
|---------------------------------|------------------|-----------------------------|
| 5.0                            | 4.7              | 3.32                        |
| 5.5                            | 4.5              | 3.37                        |
| 6.0                            | 5.3              | 3.25                        |

**Table 2.** Open porosity and the average density of samples obtained by thermal synthesis.

| The concentration of additive, % | Open porosity, % | Average density, g/cm\(^3\) |
|---------------------------------|------------------|-----------------------------|
| 5.0                            | 5.3              | 3.23                        |
| 5.5                            | 9.6              | 3.18                        |
| 6.0                            | 15.0             | 3.01                        |

On the basis of experimental data, it can be concluded that the best properties have samples with a concentration of 5.5 wt. % additive obtained by chemical co-precipitation and samples with an additive concentration of 5.0 wt. % obtained by the method of thermal synthesis. To clarify the more optimal conditions for obtaining ceramics on the basis of MAS, a comparative analysis of the data obtained (Figure 7).

**Figure 8.** Properties of annealed samples.

**4. Conclusion**

As the outcome of the research it is revealed that the ceramics from magnesium aluminate spinel received by chemical co-precipitation with addition of boron oxide in quantity of 5.5 wt. % has the best properties. When included into the powder MAS sintering additives of this concentration, the open porosity becomes quite low – 4.5 %, and the average density – high – 3.37 g/cm\(^3\). This is explained by the fact that the additive acts first by mechanism of liquid-phase sintering at a temperature of 490 °C, which is confirmed by the data of x-ray phase analysis presented in figures 4 and 5. In this case, boron oxide does not affect the composition and properties of the sample. Then sintering passes through a solid-phase mechanism.
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