Dense ceramics based on solid solutions

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Abstract. The work compiled the main results of research devoted to the production of high-density nonporous ceramics, namely ceramics based on aluminum-magnesium spinel (AMS). The article discusses questions about the role of reducing the sintering temperature, increasing the performance of the material. A promising solution to these issues is the introduction of modifying additives. Various additives and their mechanism are considered. Particular attention is paid to solid solution-forming agents. The basic laws of the interaction of sintering additives that do not react with the basic compound are described. Possible schemes for the formation of a solid solution for yttrium and gallium oxides are presented. The economic component of the raw materials used is also considered. It was determined that the most advantageous is the use of gallium oxide as an additive, and the diagrams of state of gallium oxide are also given. It has been revealed that the method of introducing the additive on the example of introducing gallium oxide plays an important role in improving the properties of ceramics based on aluminum-magnesium spinel.

1. Introduction
The production of high-density nonporous ceramics is a topical issue in material science. It is practically impossible to synthesize such ceramics without the use of special sealing additives, the mechanism of action of which can be different.

In addition, in modern technology, the issue of reducing the sintering temperature comes to the fore when creating high-temperature functional materials. This is especially true for materials, during sintering of which a solid-phase mechanism of mass transfer is realized when the formation of a liquid phase during high-temperature processing is undesirable.

In order to carry out the process more efficient and reduce temperatures, special sintering additives are used that do not form a liquid phase and enter with the main compound in the defect formation reaction, during which various types of vacancies are formed in the crystal lattice, contributing to a more intense mass transfer.

A significant number of works have been devoted to the problems of defect formation in ceramics; there are a large number of schemes of the process. Despite this, the problem of the formation of solid solutions is not fully understood now.

It remains relevant to study the regularities of the effect on the formation of defects in crystal lattices of the nature of the modifier, the technological mode in which the additive is introduced into the batch, the mode of heat treatment, which ensures the completeness of the passage of defect formation.

In particular, ceramics made of magnesium aluminate spinel are of interest, the selection of sealing, effective and inexpensive additives to which is an urgent task.
Modifying additives forming solid solutions are the most promising for controlling the solid-phase sintering process, namely, the final sintering stage, at which the ceramic microstructure is formed. This is due to the regulation of the concentration of vacancies in the crystal lattice of the compound upon the introduction of modifying additives with a charge of the cation different from the main one, as a result of which cationic or anionic vacancies arise [1].

It is known that in heteroionic materials, including spinel, the sintering rate is controlled by the diffusion of either a cation or an ion of oxygen. The sintering additive increases the concentration of precisely those defects that are responsible for limiting the sintering rate. But, unfortunately, it is almost impossible to establish the specific type of defect responsible for this stage.

By adding soluble additives, it is possible to achieve the formation of solid solutions of introduction or replacement. This is possible in the case when the lattice parameters of the main compound and the additive have rather close values, that is, the difference in the ionic radii of the cations is not more than 15%, and the charges of the cations of oxide in the solid solution may coincide. The formation of interstitial solutions is possible when the size of the cation of the additive is less than the basic one [2].

In works [3, 4], it was experimentally confirmed that the use of additives that form solid solutions significantly accelerates sintering, while the removal of pores occurs before the growth of crystals begins, which makes it possible to obtain a material that is nonporous and transparent. Based on the foregoing, it can be concluded that, when sintering oxide materials, the processes of pore removal and crystal growth are separated. The sintering of the powder is carried out at the final stage by adjusting the boundaries during deformation of the particles due to rather intense volumetric diffusion, due to the action of the additive, which forms a solid solution. In the billet, there is practically no growth of crystal before the complete sintering of the particles, due to the flow of vacancies towards the surface of the particles from the pores, which prevents the transition of atoms from the surface of the crystals from one to another. The described mechanism is the effect of the additive as a crystal growth restrictor during the removal of porosity. Only later does the intensive growth of crystals begin.

However, the formation of a solid solution suggests that the sintering rate is significantly increased in comparison with the rate of crystal growth, due to the sharp increase in the diffusion coefficient of the dissolved additive. Here, the decisive role is played not so much by the limitation of crystal growth as by the rather intense process of removing pores at the final stage of sintering, while the particles, still deformed by diffusion, adjust to each other, while the growth of crystals does not occur due to the flow of vacancies over the surface of the particles from the pores filled with them. Thus, additives that dissolve in the crystal lattice are responsible for the high diffusion mobility of particles, thereby contributing to an increase in the concentration of vacancies by several orders of magnitude in comparison with the equilibrium one, and, as a consequence, the highest density and transparency of materials is observed, while preserving monophase is maintained.

The effect of the additives is significantly increasing by the introduction into the matrix of compounds that form solid solutions of isovalent and heterovalent substitution. The only limitation, in this case, is that the additives should not react with each other to form the compound.

For compounds are represented by a cubic crystal lattice, it was found that the degree of crystal growth in ceramic materials depends on the sign of the change in the crystal lattice parameter of the basic oxide. If the lattice parameter decreases with the addition of an additive, then the crystal sizes, in comparison with pure oxide, also decrease, and vice versa, with an increase in the lattice parameter of the solid solution, significant growth of the crystal is observed. This dependence is valid for all oxides and their compounds having a cubic crystal lattice [5].

All, with some exceptions, additives are introduced into the MgO - Al₂O₃ system to ensure the removal of almost all porosity, among them there are those that form solid solutions in one of the sublattices of spinel. Relatively recently, it became possible to create such conditions for introducing additives into the resulting material so that they dissolve in the sublattice of the oxide with which the additive forms a solid solution. If the addition of the additive is carried out over 100%, then its dissolution in any sublattice will promote the formation of vacancies in the anion or cation in another

\[ \text{Equation} \]
Additives have a favorable effect on the process of reducing or completely removing porosity, the introduction of which significantly increases the concentration of vacancies in the $\text{Al}_2\text{O}_3$ sublattice due to their dissolution in the MgO sublattice [6].

So, to achieve a high density of ceramics $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$ are introduced; $\text{CaO}$, $\text{MgO}$, $\text{Sc}_2\text{O}_3$, $\text{SrO}$, oxides of rare earth. Yttrium oxide has some solubility in MgO, $\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, $\text{CaO}$ in MgO, MgO in $\text{Al}_2\text{O}_3$, $\text{Sc}_2\text{O}_3$ dissolves in both oxides that make up the compound, $\text{SrO}$ should dissolve in MgO, oxides of some rare earth are also used, for example, $\text{Nd}_2\text{O}_3$ [7], $\text{Eu}_2\text{O}_3$ [8], $\text{Sm}_2\text{O}_3$ [9]. So, with the introduction of $\text{Y}_2\text{O}_3$ into $\text{MgO} \cdot \text{Al}_2\text{O}_3$, the formation of a solid solution is possible according to the scheme:

$$\text{Y}_2\text{O}_3 \rightarrow 2\text{Y}^{+}_{\text{Mg}} - 2\text{V}^{0}_{\text{Mg}} + 2\text{V}^{00}_\text{Al} + 3\text{V}^{00}_\gamma + \text{Mg}^{\gamma}_\text{Mg} + 3\text{O}^{0}_\gamma$$

In this case, cationic and anionic vacancies are formed in the sublattice of magnesium. Usually, yttrium oxide is introduced in an amount of 0.1 to 0.2 wt. %, which is sufficient to ensure a high concentration of defects in the crystal lattice, and, consequently, to increase the degree of sintering. In magnesium aluminate spinel, cations of aluminum diffuse much more slowly than magnesium cations; therefore, it is advisable to introduce additives increasing the concentration of a slowly diffusing ion, leading to an increase in the sintering rate [10].

Thus, it can be concluded that it is necessary to choose the material of the modifying additive so that it becomes part of the solid solution. In the case of the formation of heterovalent solid solutions, the required amount of additives can vary from 0.1 to 5 mol. %; isovalent - from 15 to 30 mol. %.

With isovalent substitution, you can use oxides of elements that are located in one subgroup of the Periodic table or oxides (for those having a +3 cation charge), oxides of rare earth. For heterovalent, oxides of elements of neighboring subgroups, or rare earth, are used. Of particular interest is the visible noticeable effect when using oxides, whose cations have rather large differences in ionic radii, which ensures the appearance of significant stresses in the lattice of the basic oxide and favorably affects the diffusion processes [11].

The additives that dissolve in the sublattice of magnesium and therefore create a high concentration of vacancies in the sublattice of aluminum act especially favorably in the process of removing porosity [5]. Such additives can be scandium or gallium oxides.

The additives listed above play an important role in the formation of solid solutions in both sublattices of spinel with the appearance of vacancies, which will ensure a density close to the theoretical one at the sintering stage, which makes it possible to obtain ceramics with a high level of light transmission. The light yield of ceramics from spinel can reach up to 85% in visible wavelengths [12].

Despite the high efficiency of the additives of rare earth, they are extremely disadvantageous economically, since they are inaccessible due to their high cost, so for some elements, the price can reach several thousand dollars per gram. Therefore, the development of cheaper analogs that will act on a par with oxides of rare earth is urgent.

Based on a comprehensive analysis of the properties of magnesium aluminate spinel, oxide of magnesium, and oxides of various metals, which are often used as additives, it is possible to justify the expediency of using as an activator of the sintering process to further obtain dense ceramics, additives of gallium oxide. When choosing an additive, first of all, it is worth referring to the state diagrams. The state diagram of the three-component system MgO - $\text{Al}_2\text{O}_3$ - Ga$_2$O$_3$ is shown in figure 1 [13].
Figure 1. State diagram of the three-component system MgO - Al₂O₃ - Ga₂O₃ [13].

The authors of [13] studied the MgAl₂O₄ – Ga₂O₃ system (Fig. 2) and phase equilibria in it. The concentration dependences of the lattice parameters, unit cell volume, and pycnometric density are linear practically over the entire range from 0 to 100 mol. % MgGa₂O₄, which indicates the formation of a continuous solid solution. The melting point of MgAl₂O₄ was 2135 ± 20 °C, which is quite close to theoretical values.

Figure 2. Phase diagram of the MgAl₂O₄ – Ga₂O₃ system [13].

Since magnesium aluminate spinel contains cations of different valences, the addition of Ga₂O₃ will carry out both heterovalent (with magnesium) and isovalent (with aluminum) substitution. According to [14], the ionic radii of cations are: Al³⁺ - 0.062 nm; Mg²⁺ - 0.086 nm; Ga³⁺ - 0.076 nm. Thus, the ionic radius of gallium is less than the radius of magnesium, which can lead to the creation
of interstitial defects in the crystal lattice of magnesium aluminate spinel. The defects created in the crystal lattice contribute to the vacancy removal of pores from the material.

The scheme of defect formation during the reaction of gallium oxide with a magnesium aluminate spinel can be represented as follows:

\[
\text{Ga}_2\text{O}_3^{MgO\cdot\text{Al}_2\text{O}_3} \rightarrow \frac{2\text{Ga}^{Mg} + V_{\text{Mg}}'' + 3V_{\text{Al}}'' + 3V_{\text{O}}' + 3O_{\text{O}}' + Mg^{Mg}_M}{\text{Gallium oxide}}
\]

Gallium oxide also has disadvantages as an additive. It is rather unstable at low temperatures; during firing in a vacuum, the valence of the cation can change with a sharp decrease in the melting temperature, and sintering is rather difficult in an air atmosphere. However, it is still of interest as a modifying additive.

The technology of using gallium oxide as a sealing additive for ceramics made of magnesium aluminate spinel has a great influence. So, in this article, 2 methods of introducing an additive into spinel were considered: in one case, directly into the synthesized spinel powder, in the other, into the precursor of spinel powder. When the additive was added to the powder of AMS, the average density of the sample turned out to be higher than when it added to the precursor and amounted to 91% of the theoretical, which may be associated with a more complete passage of the defect formation reaction and the formation of a solid solution with a cubic lattice.

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