Sol-Gel synthesis of high-temperature aluminosilicate glass-ceramics and composite materials on its basis

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Abstract. Powders of strontium aluminosilicate glass-ceramics were synthesized by a sol-gel method. Composite materials based on them with the addition of industrial powders α-Si₃N₄, β-Si₃N₄, Y₂O₃, ZrO₂ and HfO₂ were obtained by the method of spark plasma sintering. It was found that reinforcement with silicon nitride leads to an increase in K_{IC} of glass-ceramics by more than 2 times. The temperature of sintering and the properties of composite materials (CM) are complexly dependent on the nature of the refractory oxide. Maximum strength is typical for CM containing Y₂O₃ additive, and maximum microhardness is for material with HfO₂ additive. Modification by refractory oxides leads to an improvement in oxidation resistance of composite materials.

1. Introduction

One of the most important problems of modern materials science is the development of new materials that can be operated under the influence of high temperatures and various aggressive media. From this point of view, a great deal of attention is being devoted to glass-ceramics in the system SrO-Al₂O₃-SiO₂. A review of scientific-technical data and patents [1–10] shows that strontium aluminosilicate glass-ceramics are promising to use as matrices of high temperature composites for application in aerospace technology. This is because strontium aluminosilicate glasses have high softening temperatures T_s (700–800 °C) while the principal phase crystallizing in this system (monoclinic strontium anorthite SrAl₂Si₂O₈) possesses a high melting point of 1650 °C, good mechanical properties (E = 100 GPa, σ_{bend} = 100–120 MPa), low thermal coefficient of linear expansion (26–48 × 10⁻⁷ °C⁻¹) and phase stability up to the melting point [11, 12].

Strontium aluminosilicate glass-ceramics of stoichiometric composition (Sr₂O-Al₃O₃·2SiO₂) is shows excellent service characteristics due to minimum content of residual glass phase in it. But it is necessary to use high temperatures for production of such glass-ceramics using conventional glass methods and developing ceramic (powder) technologies. Thus the preparation of strontium aluminosilicate glass-ceramics of stoichiometric composition by a sol-gel method is promising. The main advantage of the sol-gel method is the possibility of obtaining materials with a nanocrystalline structure at low temperatures.

Increases of fracture toughness and bending strength are the main goals of development of high temperature composites by reinforcement of strontium aluminosilicate glass-ceramics with various fillers. The most promising fillers are particles and whiskers of Si₃N₄ [13–17]. Recently, research in the field of synthesis of composites with barium aluminosilicate glass-ceramic matrices and dispersed
fillers based on Si₃N₄ has been actively carried out in China. For example, the authors of [16] demonstrated that the critical stress intensity factor (Kᵥ) of the barium aluminosilicate glass-ceramics increases to 8.9 MPa m⁻¹/² upon introduction of silicon nitride grains in an amount of 70 wt %. This value of Kᵥ is maximally attained to the present moment when the glass-ceramic matrix is reinforced with a dispersed filler. In [17], use of 60 wt % Si₃N₄ led to an increase in the Kᵥ of the barium aluminosilicate glass-ceramics to 7.4 MPa m⁻¹/², which exceeds by 270% that of the glass-ceramic matrix.

The sintering temperature of these materials is very high (~1800°C), while its operating temperature is low due to the high propensity of silicon nitride to oxidation when exposed to elevated temperatures. To lower the sintering temperature and reduce the sintering time, so far the relatively effective sintering method is spark plasma sintering (SPS). To increase the operating temperature modification of glass-ceramics by refractory oxides, such as Y₂O₃, ZrO₂ and HfO₂ is of great interest [14–16].

The goal of our study was sol-gel synthesis of high-temperature aluminosilicate glass-ceramics and synthesis of composite materials on its basis via introduction of finely dispersed powders of α-Si₃N₄ and β-Si₃N₄, Y₂O₃, ZrO₂ and HfO₂ using of spark plasma sintering and to examine the influence of the nature of refractory oxides on the sintering, phase composition, structure and properties of the materials obtained.

2. Experimental

The stoichiometric composition of strontium anorthite (SrO·Al₂O₃·2SiO₂, SA2S) was used to prepare sol-gel solutions. Solutions were prepared by sequentially adding components. The composite materials were obtained by the method of spark plasma sintering (SPS) using equipment from FCT (Germany). As the main methods of study were used laser granulometry (Analysette 22 MicroTec, Fritsch), differential scanning calorimetry (STA 449 C Jupiter, Netzsch), X-ray phase analysis (XPA) (D2 Phaser, Bruker), and dilatometric method for determining the shrinkage during heating in argon (DIL 402 PC dilatometer, Netzsch). Four-point bending strength and Vickers microhardness were determined using a T1-FR010THW A50 testing machine (Zwick Germany) and an HV-1000 microhardness tester (TIME Group, China), respectively. The analysis of the microstructure of materials was carried out on a JSM-6490LV scanning electron microscope (Jeol, Japan). Apparent density was measured by using the Archimedes principle.

3. Results and discussion

After completion of the hydrolysis and polycondensation processes, the gels were dried. The study of dried gels by the DSC/TG method showed that in the temperature range of 100–900 °C, crystalline water and solvent are removed from them, as well as the decomposition of inorganic residues of salts of the starting elements. The ongoing physical and chemical transformations are accompanied by significant mass losses of more than 50%, which stabilize only in the temperature range of 900 °C. In the temperature range of 900–1400 °C, gels crystallize with the formation of monoclinic strontium anorthite by successive transformations of strontium silicates and hexagonal strontium anorthite. According to the results of DSC data analysis, the dried gels were subjected to high-temperature treatment until the formation of the monoclinic strontium anorthite phase was completed.

Industrial powders α-Si₃N₄, β-Si₃N₄, Y₂O₃, ZrO₂ and HfO₂ were used as fillers of composite materials. Intergrinding in a planetary mill of fillers and glass-ceramic powders, obtained after high-temperature treatment was carried out. The dominant particle size in the mixtures was 4 μm (Fig. 1).

The study of linear shrinkage curves obtained by dilatometric method showed that the introduction of silicon nitride in glass-ceramics leads to a shift in temperature range of composites sintering to higher temperatures (Fig. 2). The presence of refractory oxides in composites intensifies their sintering. The consolidation of composites is occurs by the viscous-flow mechanism and accompanied by a shrinkage of 8–15% in the temperature range from 1200 °C to >1800 °C. At a temperature of ~1600 °C, sintering slows down due to the phase transition of α-Si₃N₄ to β-Si₃N₄.
Figure 1. Results of laser granulometry of powder mixtures of composite materials

The study of linear shrinkage curves during the SPS process showed that the initial temperature of sintering of CM was in the temperature range of 1100–1350 °C. The introduction of refractory oxides into glass-ceramics leads to decrease of initial temperature of sintering in the series: (SA2S+Si₃N₄) → (SA2S+Si₃N₄+HfO₂) → (SA2S+Si₃N₄+ZrO₂) → (SA2S+Si₃N₄+Y₂O₃) (Fig. 3). The dependence of the relative density of the synthesized composites on the nature of the oxides is of a similar nature. However, the shorter sintering range (Fig. 3) during isothermal holding at the sintering temperature of the composite with the addition of ZrO₂ led to its density being lower than the density of the sample with HfO₂ addition (table 1).

Figure 2. Curves of linear shrinkage dL/L₀ of the materials in their heating in argon
Figure 3. The dependence of the initial temperature of sintering (columns) and the sintering range during isothermal holding at the sintering temperature (symbol) on the nature of the refractory oxide

Figure 4 shows scanning electron micrograph of the fractured surface of synthesized composites. It was found that all composite materials are characterized by a fine-grained structure. The samples (SA2S+Si₃N₄) and (SA2S+Si₃N₄+HfO₂) contain intergranular pores with a size of about 1–2 μm. In CM, containing Y₂O₃ and ZrO₂, intergranular pores with a size of about tenths of a micrometer are found. The content of pores in the samples with refractory oxides is significantly lower compared with composite (SA2S+Si₃N₄).

Figure 4. Scanning electron micrograph of the fractured surface of the composites
The results of the study of the mechanical properties of the synthesized composites are presented in table 1. It was found that samples containing Y$_2$O$_3$ are characterized by maximum strength. This may be due to their highest density. However, it should be noted that despite the higher density of samples containing additives of HfO$_2$ or ZrO$_2$ than CM without additives, their bending strength is lower than for the sample (SA2S+Si$_3$N$_4$).

| Composition of composites | $\rho_{\text{apparent}}$ (kg/m$^3$) | $\rho_{\text{relative}}$ (%) | $\sigma_{\text{bend}}$ (MPa) | $H_v$ (GPa) | K$_{IC}$ (MPa·m$^{1/2}$) |
|---------------------------|--------------------------------------|-----------------------------|----------------------------|------------|------------------------|
| SA2S+Si$_3$N$_4$          | 2730                                 | 87 $\pm$ 0.5               | 174 $\pm$ 10              | 14 $\pm$ 1 | 5.3 $\pm$ 0.1          |
| SA2S+Si$_3$N$_4$+Y$_2$O$_3$ | 3140                                 | 99 $\pm$ 0.5               | 186 $\pm$ 10              | 17 $\pm$ 1 | 5.3 $\pm$ 0.1          |
| SA2S+Si$_3$N$_4$+HfO$_2$  | 3080                                 | 97 $\pm$ 0.5               | 128 $\pm$ 10              | 19 $\pm$ 1 | 5.3 $\pm$ 0.1          |
| SA2S+Si$_3$N$_4$+ZrO$_2$  | 3000                                 | 95 $\pm$ 0.5               | 155 $\pm$ 10              | 17 $\pm$ 1 | 5.3 $\pm$ 0.1          |

The modification with refractory oxides did not affect the fracture toughness of composite materials. Regardless of the nature of the modifying oxide, the critical stress intensity factor for all samples were (5.3 $\pm$ 0.1) MPa·m$^{1/2}$, which is more than twice the K$_{IC}$ value of strontium aluminosilicate glass-ceramics (2.9 MPa·m$^{1/2}$). This demonstrates the effectiveness of the use of selected fillers for the reinforcement of glass-ceramics.

The study of the thermal properties of samples showed that the modification by all refractory oxides leads to an improvement in oxidation resistance of composite materials.

4. Conclusions

Thus, as a result of the research, it has been established that the temperature range of sintering and properties of composite materials based on synthesized by a sol-gel method strontium aluminosilicate glass-ceramics with the addition of industrial powders $\alpha$-Si$_3$N$_4$, $\beta$-Si$_3$N$_4$, Y$_2$O$_3$, ZrO$_2$ and HfO$_2$ obtained by the SPS are in complex dependence on the nature of the refractory oxide. The initial temperature of sintering during SPS is decreases in the series: (SA2S+Si$_3$N$_4$) → (SA2S+Si$_3$N$_4$+HfO$_2$) → (SA2S+Si$_3$N$_4$+ZrO$_2$) → (SA2S+Si$_3$N$_4$+Y$_2$O$_3$). Maximum strength is typical for CM containing Y2O3 additive, and maximum microhardness is for material with HfO$_2$ additive. The modification with refractory oxides did not affect the fracture toughness of composite materials. Regardless of the nature of the refractory oxides reinforcement with silicon nitride leads to an increase in K$_{IC}$ of glass-ceramics by more than 2 times. The modification by refractory oxides leads to an improvement in oxidation resistance of composite materials.

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