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## **Influence of the Nano- and Submicron Structure of Magnesium–Aluminosilicate Glasses on the Crack Resistance of High-Strength Glass-Ceramics**

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The main directions of the development of glass-ceramic materials for technical purposes, which are distinguished by a complex of high physico-chemical, technological and operational properties, reduced cost and can be obtained using energy-saving and resource-saving technologies, are analysed. A detailed analysis of the state of development of cordierite glass-ceramic materials and the principles of their design made it possible to establish the possibility of developing high-strength materials on their base characterized by the formation of a dissipative nanostructure in the process of directed crystallization. The composition of magnesium–aluminosilicate glass is optimized by introducing a combined crystallization catalyst ( $ZrO_2$ ,  $TiO_2$ ,  $Sb_2O_5$ ,  $ZnO$ ,  $CeO_2$ ,  $P_2O_5$ ) to ensure the nucleation process and the formation of crystalline phases in the low-temperature range as well as the formation of a sitalized structure of a glass-ceramic material by the phase separation mechanism. As found, ensuring phase separation (800–850°C) by the spinodal mechanism for experimental magnesium–aluminosilicate glass in the pre-crystallization period is an important stage in the formation of solid solutions with a high-temperature quartz structure in the low-temperature region (850–900°C), spinel crystallization (900–1000°C),  $\alpha$ -cordierite (980–1050°C) and recrystallization of  $\alpha$ -cordierite to mullite at 1050–1100°C. The main conditions for the formation of a self-organized sitalized nano- and submicron structure of glass-ceramic materials based on mullite are determined as follow: the content of phase-forming oxides  $\Sigma(MgO, Al_2O_3, SiO_2)$  is of 87.0 wt.%; type and content of crystallization catalysts  $\Sigma(TiO_2, ZrO_2, CeO_2, P_2O_5)$  is of 8.0 wt.% and content of modifying additives  $\Sigma(SrO, CaO, B_2O_3)$  is of 5.0

wt.%; low-temperature synthesis and three-stage heat treatment (melting at 1550°C, 6 h; I stage at 800°C, 2 h; II stage at 900°C, 2 h; III stage at 1100°C, 1 h). As established, ensuring a high index of crack resistance ( $K_{1c} = 6.5 \text{ MPa}\cdot\text{m}^{1/2}$ ), Young's modulus of elasticity ( $E = 350 \text{ GPa}$ ) and low weight ( $\rho = 2800 \text{ kg/m}^3$ ) simplifies the technology by reducing the temperature and allows it to compete successfully with cost-effective ceramic counterparts.

Проаналізовано основні напрями розробки склокерамічних матеріалів технічного призначення, які відрізняються комплексом високих фізико-хімічних, технологічних та експлуатаційних властивостей, пониженою вартістю та можуть бути одержані із застосуванням енерго- та ресурсоощадних технологій. Проведено детальну аналізу стану розробок кордієритових склокерамічних матеріалів і принципів проектування їх для змоги встановити можливість розробки на їхній основі високоміцних матеріалів, які характеризуються формуванням дисипативної наноструктури в процесі направленої кристалізації. Оптимізовано склад магнійалюмосилікатного скла шляхом введення комбінованого каталізатора кристалізації ( $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{ZnO}$ ,  $\text{CeO}_2$ ,  $\text{P}_2\text{O}_5$ ) для забезпечення перебігу нуклеації й утворення кристалічних фаз в області нижчих температур і формування ситалізованої структури склокерамічних матеріалів за механізмом фазового розподілу. Встановлено, що забезпечення фазового розділення (800–850°C) за спинодальним механізмом для дослідного магнійалюмосилікатного скла у передкристалізаційному періоді є важливим етапом формування твердих розчинів зі структурою високотемпературного кварцу у низькотемпературній області (850–900°C) за в'язкості у  $10^{8.8} \text{ Па}\cdot\text{с}$ , кристалізації шпінелі (900–1000°C),  $\alpha$ -кордієриту (980–1050°C) та перекристалізації  $\alpha$ -кордієриту до муліту за 1050–1100°C. Визначено основні умови формування самоорганізованої ситалізованої нано- та субмікронної структури склокристалічних матеріалів на основі муліту: вміст фазоутворювальних оксидів —  $\Sigma(\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2)$  — 87,0 мас.%; тип і вміст каталізаторів кристалізації  $\Sigma(\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{P}_2\text{O}_5)$  — 8,0 мас.%, а модифікувальних добавок  $\Sigma(\text{SrO}$ ,  $\text{CaO}$ ,  $\text{B}_2\text{O}_3)$  — 5,0 мас.%; низькотемпературна синтеза та тристадійне термічне оброблення (вариво — 1550°C, 6 год.; I стадія — 800°C, 2 год.; II стадія — 900°C, 2 год.; III стадія — 1100°C, 1 год.). Встановлено, що забезпечення високого показника тріщиностійкості ( $K_{1c} = 6,5 \text{ МПа}\cdot\text{м}^{1/2}$ ), модуля Юнга ( $E = 350 \text{ ГПа}$ ) і низької ваги ( $\rho = 2800 \text{ кг/м}^3$ ), спрощення технології за рахунок пониження температури та тривалості синтезу дають змогу йому успішно конкурувати з дорогими керамічними аналогами.

**Key words:** glass-ceramic materials, magnesium–aluminosilicate glasses, phase separation, cordierite, mullite.

**Ключові слова:** склокерамічні матеріали, магнійалюмосилікатні стекла, фазове розділення, кордієрит, муліт.

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## 1. INTRODUCTION

The transition to high technologies requires the creation of fundamentally new structural materials, the functional parameters of which are determined by the properties of nano-regions formed in a given way, as well as by the processes taking place in nanovolumes. The need to create high-strength materials to protect structures and devices from high-speed dynamic and thermal loading has contributed to the widespread use of glass-ceramic materials, which are distinguished by high performance properties and are worthy competitors to ceramic materials due to the simplification of the production technology and the reduction in the cost of products [1].

Most technical glass-ceramics are synthesized on the basis of glasses of aluminosilicate systems  $Me_2O$  ( $MeO$ )– $Al_2O_3$ – $SiO_2$ , into which other components can be added in order to modify the composition and control phase transformations, to obtain a glass-ceramic with a defined structure and properties. Industrial production in different countries of the world demonstrates the wide possibilities of manufacturing various types of products based on glass-ceramics. So world famous companies: Corning Inc. (U.S.A.) [2], Schott (Germany) [3], Ohara Inc., Hoya, Nippon Electric Glass Co. Ltd. (Japan) [4] produce products from glass-ceramic materials for the industries of mechanical engineering and instrument making, the chemical industry and the military-industrial complex.

Today, special attention is paid to glass-ceramic materials, which are distinguished by a complex of high physicochemical, technological and operational properties, reduced cost and can be obtained using energy- and resource saving technologies. The leading place among these materials is occupied by glass-ceramics based on the  $MgO$ – $Al_2O_3$ – $SiO_2$  (MAS) system due to its high operational properties: bending strength  $\sigma_{\text{bend}} = 120$ – $350$  MPa, Young's modulus of elasticity  $E = 100$ – $120$  GPa, microhardness  $H = 6.1$ – $11.0$  GPa, coefficient of thermal expansion (CTE)  $\alpha = (11$ – $57) \cdot 10^{-7}$  K<sup>-1</sup>, deformation temperature not lower than  $1300^\circ\text{C}$ , heat resistance at  $800$ – $1000^\circ\text{C}$ , dielectric constant  $\varepsilon = 6$ – $7$  (at a frequency of  $10$  MHz), the tangent of the dielectric loss angle  $\text{tg}\delta = (4$ – $10) \cdot 10^{-4}$  and a relatively low melting point ( $T \leq 1600^\circ\text{C}$ ), which is determined by the peculiarities of their chemical composition and structure [5].

An important stage in the development of glass-crystalline materials of the MAS system is the design of their fine-crystalline structure with the content of crystalline phases:  $\alpha$ -cordierite, mullite, spinel, clinoenstatite, forsterite, which will determine their high electrical insulation characteristics and high mechanical strength [6]. Especially valuable in establishing the mechanism of glass crystallization is the determination of the effect of various nucleating

agents on crystallization processes, microstructure and properties of glass-ceramics.

A detailed analysis of the state of development of cordierite glass-ceramics carried out by the authors [7, 8] made it possible to establish that titanium and zirconium oxides are the most common crystallization catalyst for glass-ceramic materials of the MAS system. The catalytic role of titanium oxide is the phase separation of glass and the precipitation of a crystalline phase enriched with a crystallization catalyst, and the precipitation of this phase can precede or occur simultaneously with the precipitation of a quartz-like solid solution, which, with an increase in the heat treatment temperature, transforms into a stable phase of  $\alpha$ -cordierite, which has an ordered orthorhombic structure. When titanium oxide is used as a nucleating phase for glasses of the MAS system, the formation of a pseudo-brookite solid solution is observed, the composition of which is in the range of  $\text{Al}_2\text{TiO}_5$ – $\text{MgTi}_2\text{O}_5$ . In general, the role of  $\text{TiO}_2$  as a catalysing agent is determined by the initial composition of the glass. In this case, the main point is the creation of conditions leading to the formation of a glass phase enriched in  $\text{SiO}_2$ . This can occur for some glass compositions (with a low MgO content) due to the traditional phase distribution, for others due to the primary precipitation of mullite and aluminium titanate, due to which the residual glass phase becomes similar in composition to quartz-like solid solutions. The mechanism of the catalytic action of  $\text{ZrO}_2$  in the MAS system is more complex. At the initial stage, nucleation and growth of  $\text{ZrO}_2$  nanocrystals occurs, which appear at a temperature several degrees above the glass transition temperature. In the same system,  $\text{ZrO}_2$  promotes the phase distribution of amorphous glass with the formation of regions (with a radius of about 4.5 nm) enriched in zirconium oxide.

The authors of [9] found that the use of a composite nucleating agent ( $\text{TiO}_2 + \text{ZrO}_2$ ) made it possible to increase the content of  $\alpha$ -cordierite, change the stability and kinetics of glass crystallization in the direction of the formation of a fine-crystalline structure. Due to the uniform distribution of elements without agglomeration in the crystal phase and the compact structure, the Vickers hardness ( $HV$ ) and the bending strength ( $\sigma_{\text{bend}}$ ) can reach 9.70 GPa and 312 MPa, respectively. The authors of [8] investigated the effect of  $\text{Y}_2\text{O}_3$  on the microstructure, crystallization, and properties of glass ceramics of the MAS system. It was found that the addition of  $\text{Y}_2\text{O}_3$  to MAS glass-ceramics increases the amount of the crystalline phase and promotes the formation of indialite. Studies of the kinetics of sintering and crystallization have shown that alloying of glass with  $\text{Y}_2\text{O}_3$  reduces the activation energy of sintering, intensifies crystallization and increases the compaction of the structure during sintering and

the formation of the crystalline phase, which significantly improves the mechanical properties. MAS glass-ceramics with a content of 1 wt.%  $Y_2O_3$  is characterized by high mechanical properties:  $E = 89$  GPa,  $\sigma_{\text{bend}} = 211$  MPa,  $\alpha = 46.8 \cdot 10^{-7} \text{ K}^{-1}$ . The introduction of an  $Y_2O_3$  crystallization catalyst into glass containing  $ZrO_2$  of the chemical composition (mol.%):  $SiO_2 = 51.9$ ,  $MgO = 21.2$ ,  $Al_2O_3 = 21.2$ ,  $ZrO_2 = 5.7$ , which crystallized at different stages of firing ( $T$ : st. I— $950^\circ\text{C}$ , st. II— $1060^\circ\text{C}$ ) leads to the formation of glass-ceramics with a solid solution of  $\alpha$ -quartz as the main crystalline phase and  $ZrO_2$  and  $MgAl_2O_4$  crystals as secondary crystalline phases [9]. When 2,5 mol.%  $Y_2O_3$  is added to the glass composition during heat treatment, the appearance of dendritic crystals of  $ZrO_2$  as the main crystalline phase and  $MgAl_2O_4$  as the secondary crystalline phase is observed at both stages. For such glasses, the formation of a solid solution of  $\alpha$ -quartz does not occur, since  $Y_2O_3$  enters the residual glass matrix and stabilizes it. It was found that the presence of  $\alpha$ -quartz is not a prerequisite for changing the mechanical properties of glass-ceramic materials based on the MAS system.

The effect of a combining crystallization catalyst (oxides —  $SnO_2 + CeO_2$  and ions —  $[SO_4]^{2-} + Cl^-$ ) on obtaining transparent glass ceramics with the composition (wt.%):  $SiO_2 = 35-60$ ,  $B_2O_3 = 4-10$ ,  $P_2O_5 = 0-10$ ,  $Al_2O_3 = 16.5-40$ ,  $TiO_2 = 1-10$ ,  $Ta_2O_5 = 0-8$ ,  $Y_2O_3 = 0-6$ ,  $ZrO_2 = 1-10$ ,  $MgO = 6-20$ ,  $CaO = 0-10$ ,  $SrO = 0-4$ ,  $BaO = 0-8$  and  $ZnO = 0-4$  [10]. It was found that to ensure fine crystallization, the content of crystallization catalysts  $\Sigma(P_2O_5, TiO_2, ZrO_2, SnO_2, Ta_2O_5)$  should be of 5–12 wt.%. In this case, the  $TiO_2$  content should not exceed 7 wt.%, otherwise there is a risk of separation of the crystalline phase of rutile during the sintering process. On the other hand, the  $TiO_2$  content should not be lower than 1 wt.%; otherwise, the number of nuclei will not be insufficient to achieve a uniform, compact-granular structure with a crystallite size of about 300 nm, which is necessary to ensure transparency. The efficiency of using  $Ta_2O_5$  is explained by the possibility of catalysing the crystallization process and forming a transparent structure even when combined with other elements (for example, Fe and Zn). The use of crystallization catalysts  $SnO_2$  and  $CeO_2$  is effective in the preparation of transparent glass-ceramics by the float method. Likewise, the use of mixed sulphate/chloride to provide illumination of the molten glass. In general, to obtain high-quality transparent substrates characterized by a density of  $\rho = 2693 \text{ kg/m}^3$ , Young's modulus  $E = 98-120$  GPa, CTE  $\alpha_{(30-300)} = 40 \cdot 10^{-7} \text{ K}^{-1}$ , in the production of displays and solar cells, the content of crystallization catalysts  $\Sigma(SnO_2 + CeO_2 + [SO_4]^{2-} + Cl^-)$  should be from 0.01 to 4 wt.%.

Complex action of crystallization catalysts for the composition of magnesium–aluminosilicate glass (wt.%):  $SiO_2 = 43.8-52.5$ ,

$\text{Al}_2\text{O}_3 = 24.6\text{--}30.2$ ,  $\text{MgO} = 9.3\text{--}11.9$ ,  $\text{TiO}_2 = 8.8\text{--}12.9$ ,  $\text{As}_2\text{O}_3 = 0.1\text{--}1.9$ ,  $\text{ZnO} = 0\text{--}1.5$  and  $\text{CeO}_2 = 0\text{--}2.5$  [7] can be traced in the formation of the structure of glass ceramics with a content of  $\alpha$ -cordierite, obtained by a two-stage heat treatment with a temperature crystallization  $1270\text{--}1320^\circ\text{C}$  and is characterized by the following properties:  $\alpha = (18\text{--}20) \cdot 10^{-6} \text{ K}^{-1}$  and  $\text{tg}\delta = (5\text{--}9) \cdot 10^{-4}$  and  $\varepsilon = 6.3\text{--}6.9$  ( $f = 1010 \text{ Hz}$ ,  $T = 20^\circ\text{C}$ ). It has been established that the combination of components in the specified quantitative ratio makes it possible to obtain glass-ceramic materials with thermal stabilization of the dielectric constant up to  $1200^\circ\text{C}$  and to reduce the cooking temperature to  $1540\text{--}1560^\circ\text{C}$ .

Despite significant advances in the development of MAS glass-ceramic materials, an urgent direction in the development of these materials is the implementation of their application as nanomaterials characterized by the formation of a dissipative nanostructure in the process of directional crystallization.

It is the provision of a homogeneous nanodispersed structure of a glass-crystalline material due to a high volume concentration of uniformly distributed crystalline nuclei, namely,  $10^{12}\text{--}10^{15}$  pieces/cm<sup>3</sup> in the pre-crystallization period, which will make it possible to form a structure at the nano- and submicron level to ensure high performance characteristics.

## 2. EXPERIMENTAL

### 2.1. Aim Setting and Research Methodology

The aim of this work is to study the effect of phase separation of magnesium aluminosilicate glasses during nucleation on the formation of the structure and properties of magnesium aluminosilicate glass-ceramics.

The study of phase transformations in glasses and the setting of the temperatures of their heat treatment were carried out using gradient thermal analysis in a gradient furnace with holding for 6 hours and polarizing microscope NU-2E. The nature of the formation of the structure of glasses at the initial stages of nucleation was investigated using a scanning electron microscope SEM Tesla 3 LMU with a resolution of 1 nm. Crack resistance of materials was measured using PMT-3 and TMV-1000 devices.

### 2.2 Optimization of Magnesium–Aluminosilicate Glass Composition

Preliminary results of studies on the development and characteristics of crystallization of magnesium–aluminosilicate materials in

the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system [11] made it possible to establish that the provision of high performance characteristics (Vickers hardness of 10.4 GPa, fire resistance 1350°C) and reduced cost due to two stages of processing at temperatures of 850°C and 1150°C is realized due to a certain content and ratio of modifying, glass-forming and phase-forming components and the introduction of a combined crystallization catalyst  $\Sigma(\text{TiO}_2, \text{ZrO}_2, \text{CeO}_2, \text{P}_2\text{O}_5)$  in order to form a sitalized structure based on solid solutions of mullite. However, taking into account the insufficient fracture toughness of the developed glass-ceramic material CGC-10  $K_{1c} = 3.5 \text{ Mpa}\cdot\text{m}^{1/2}$  and the duration (10 hours) of the heat treatment mode, its composition was optimized (CGC-10.1) in terms of the content of components and the heat treatment mode (Table).

Optimization of the composition was realized by ensuring a certain ratio and content of components, which will have a decisive influence on the nature of the formation of the structure at the initial stages of nucleation.

To implement the nucleation process by the phase distribution mechanism, it is necessary to stabilize the glass-forming state, including due to the presence of four-coordinated titanium Ti<sup>4+</sup>. This is facilitated by the simultaneous introduction of oxides SrO, CaO, MgO, ZnO into the glass composition by increasing its basicity. At the same time, the presence of SrO, CaO, MgO, ZnO in a total amount of 12.5 wt.% is an important factor in increasing the hardness of glass. Partial (0.5 wt.%) replacement of ZrO<sub>2</sub> with an appropriate amount of TiO<sub>2</sub> will reduce the temperature of the onset of crystallization and reduce the temperature interval between the onset of crystallization and the glass transition temperature. This will make it possible to obtain defect-free products with an increase in the amount of the crystalline phase. To ensure the occurrence of nucleation and the formation of crystalline phases in the region of lower temperatures, ZnO was additionally introduced, which, along with CeO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>, will contribute to the phase separation of glass and the formation of a nanodispersed structure of glass during its heat treatment. The predisposition to phase separation is determined by the absence of alkaline components, the presence of B<sub>2</sub>O<sub>3</sub>, a significant content of CaO and MgO, and the presence of refractory compounds Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.

An important condition for ensuring high strength properties is the presence of an optimal content of CeO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, and B<sub>2</sub>O<sub>3</sub>, which play an exceptional role for the crystallization kinetics of  $\mu$ -cordierite and  $\alpha$ -cordierite. In general, an increase in the content of CeO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> leads to an increase in the content of  $\alpha$ -cordierite. To increase the content of  $\mu$ -cordierite, *i.e.*,  $\alpha$ -quartz-like solid solution of MgO·Al<sub>2</sub>O<sub>3</sub> in SiO<sub>2</sub>, it is necessary to increase the content of P<sub>2</sub>O<sub>5</sub>.

TABLE. Chemical composition of experimental materials and their synthesis temperature.

Marking samples	Chemical composition of model glasses, wt. %										Synthesis temperature, °C
	Phase-forming components			Crystallization catalysts		Modifying additives		Glass-forming additive			
	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	type	quantity	type	quantity	type	quantity	quantity	
CGC-10	9	29	51	TiO <sub>2</sub> , ZrO <sub>2</sub> , CeO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub>	6.0	SrO	3.0	B <sub>2</sub> O <sub>3</sub>	2.0		1550
CGC-10.1	9	28	50	TiO <sub>2</sub> , ZrO <sub>2</sub> , CeO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> , Sb <sub>2</sub> O <sub>5</sub> , ZnO	8.0	CaO, SrO	3.0	B <sub>2</sub> O <sub>3</sub>	2.0		1500



It is known [12] that the heterogeneous nucleation of  $\mu$ -cordierite, which has the character of a spherulite-dendritic structure, occurs in impurities on the surface of the source glass. The  $B_2O_3$  additive forms a dendritic branch and an interdendritic interface between the residual glass and  $\mu$ -cordierite. The addition of  $P_2O_5$  accelerates the growth of  $\mu$ -cordierite and the transition from controlled diffusion to controlled phase separation, inhibits the formation of the dendritic nature of  $\mu$ -cordierite and helps transform it into a hexagonal crystal structure.

There are two types of phase transformations of  $\alpha$ -cordierite in the glass structure. In the first case, the nucleation of  $\alpha$ -cordierite occurs between the interdendrite residual glass and the boundary of the  $\mu$ -cordierite branches. In this case, the growth of  $\alpha$ -cordierite occurs due to the glass matrix and interdendritic residual glass. The growth rate of  $\alpha$ -cordierite increases with an increase in the interface area between the residual glass and  $\mu$ -cordierite. In the second case, the formation of  $\alpha$ -cordierite occurs by transformation of the formed  $\mu$ -cordierite. The transformation rate increases with decreasing thickness of  $\mu$ -cordierite crystal branches.

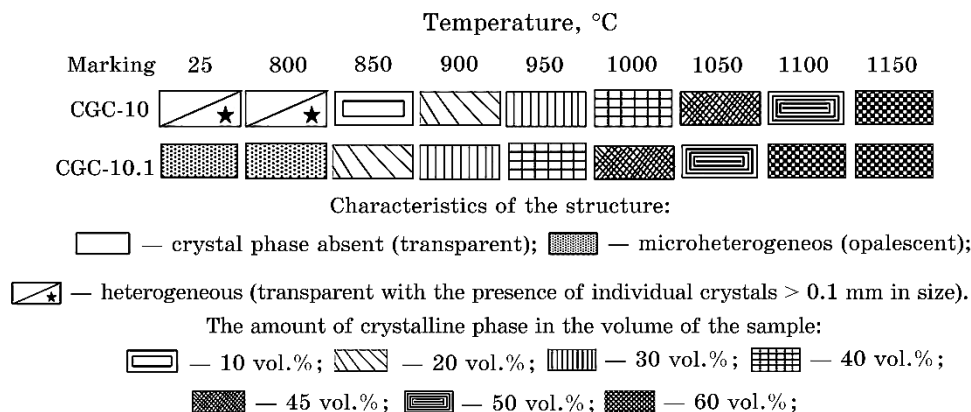
Thus, the introduction of  $P_2O_5$  promotes the formation of  $\mu$ -cordierite, while  $B_2O_3$  increases or enhances the release of  $\alpha$ -cordierite. The temperature effect of  $P_2O_5$  in the composition of glasses is less than that of  $B_2O_3$ , since the growth rate of  $\mu$ -cordierite is lower than that of  $\alpha$ -cordierite with increasing temperature.

Calcium and strontium oxide are used along with  $B_2O_3$  to reduce the viscosity at high temperatures and melting points, and to increase the tensile strength in compression and bending. The introduction of antimony oxide also helps to reduce the viscosity of the melt, improve the lighting conditions of the molten glass, and create additional crystallization centres.

Optimization of the composition of CGC-10.1 made it possible to reduce its cooking temperature to  $1500^\circ\text{C}$ , which is an essential aspect of the implementation of energy-saving technology in the development of high-strength materials.

### **2.3 Investigation of Changes in the Phase Composition of Glass-Ceramic Material as a Result of Heat Treatment**

Gradient thermal analysis of CGC-10.1 glass (Fig. 1) made it possible to establish that after melting its structure is heterogeneous: transparent with the presence of mullite crystals about 0.1 mm in size, due to which the residual glass phase becomes close in composition to quartz-like solid solutions. When the temperature rises to  $800^\circ\text{C}$ , its opalescence is observed, which may indicate the progress of



**Fig. 1.** Scheme of phase transformations and features of crystallization in materials of the CGC series during heat treatment.

the phase separation of glass, and, as a result, a gradual increase in the volume of the crystalline phase from 20 to 60 vol.% in the temperature range 850–1100°C when compared with CGC-10 glass, which is characterized by delayed formation of the crystalline phase at low temperatures. This may indicate the intensification of the crystallization of  $\mu$ -cordierite due to phase separation. Due to the simultaneous introduction of  $\text{CeO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{ZnO}$  into the composition of CGC-10.1 glass, a shift in the appearance of the first crystalline phase to the region of lower temperatures is observed, which will make it possible to obtain a hardened crystal structure, which is closer to the composition of the original glass.

An increase in temperature to 1150°C affects the growth of crystals in the CGC-10.1 structure, which is a negative factor in the formation of a high-strength fine-dispersed structure. This is due to the fact that the developed glass-ceramic material is a metastable system. The transition to a stable, equilibrium state with prolonged high-temperature holdings leads to a deterioration in the properties of the material due to recrystallization and destruction of contacts between crystals, an increase in surface tension and loss of bond between the glass and the crystal.

#### 2.4. Investigation of Changes in the Structure of Glass-Ceramic Material as a Result of Heat Treatment and Its Effect on Its Crack Resistance

To study the mechanism of phase distribution, nucleation, and structure formation in the CGC-10.1 glass material, the following characteristic temperatures were selected: temperature in the phase

separation region  $t_1$ ; temperature in the area of the embryo  $t_2$ ; temperature of appearance of the first crystalline phase  $t_3$ ; final crystallization temperature  $t_4$ . To identify the structure of the glass material at the initial stages of the nucleus, areas free from crystallization were selected. The holding time of the prototypes at each stage was 2 hours.

According to the results of electron microscopy, the sample at  $t_1 = 800^\circ\text{C}$  represents a multiphase system formed of densely packed spherical inhomogeneities with a size of  $0.1\text{--}1.0\ \mu\text{m}$  (Fig. 2, *a*, I), which are formed by smaller spherulites with a size of about  $0.01\ \mu\text{m}$  (Fig. 2, *a*, II). All these inhomogeneities during rapid cooling will significantly affect the nature of crystallization: the sequence of separation of crystalline phases, their appearance and size.

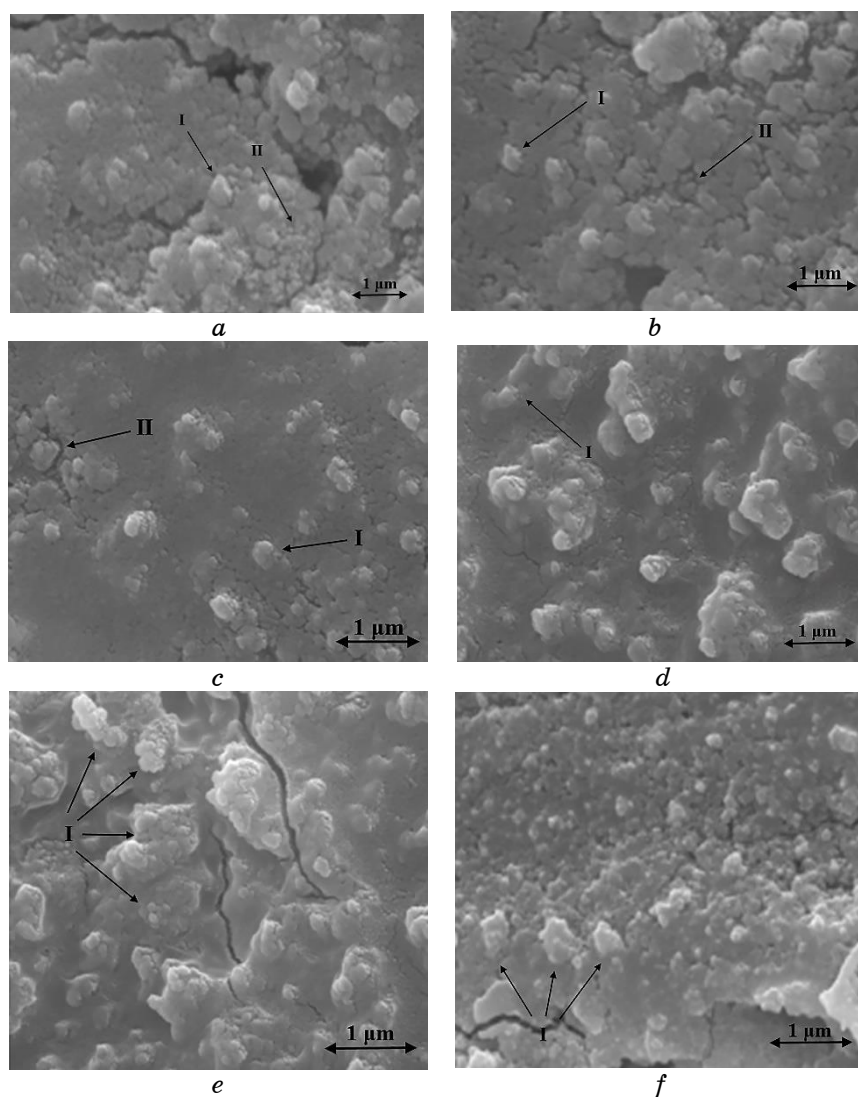
Continuous growth of spherical inhomogeneities in the glass structure at  $t_2 = 850^\circ\text{C}$  is a characteristic feature of the occurrence of metastable liquation as a phase transition. Along with spherical inhomogeneities, clear inhomogeneities are observed in the form of ellipsoids of revolution (Fig. 2, *b*), which is evidence of the aggregation of identical structural elements of  $\mu$ -cordierite even in the glass melt. Such self-organization of the structure is characteristic of segregation by the spinodal mechanism and manifests itself in the form of spheres of nanoinhomogeneities of the order of  $100\ \text{nm}$  in separate interpenetrating phases  $0.5\text{--}1.0\ \mu\text{m}$  in size (Fig. 2, *b*, II), which merge and become larger (Fig. 2, *b*, III).

Spinodal segregation is realized without the formation of nuclei in the unstable region, when the energy of their formation approaches zero and the appearance of even insignificant fluctuations of the composition leads to phase separation with a decrease in the free energy of the system [13].

An increase in temperature to  $900^\circ\text{C}$  leads to intensification of the process of formation of solid solutions with the structure of high-temperature quartz; along with crystals in the form of ellipsoids (Fig. 2, *c*, I), prismatic crystals of  $\mu$ -cordierite are observed (Fig. 2, *c*, II), decomposing at a temperature of  $980^\circ\text{C}$  into spinel crystals of an octahedral shape with an elongated crystal habit (Fig. 2, *d*, I).

The appearance of clusters of nano- and submicron nuclei of  $\alpha$ -cordierite crystals coated with a glass phase (Fig. 2, *e*, I) is observed already at a temperature of  $1050^\circ\text{C}$ , and with an increase in temperature to  $1110^\circ\text{C}$ , crystals of a short-columnar structure are observed against the general background of nanoinhomogeneities (Fig. 2, *f*, I).

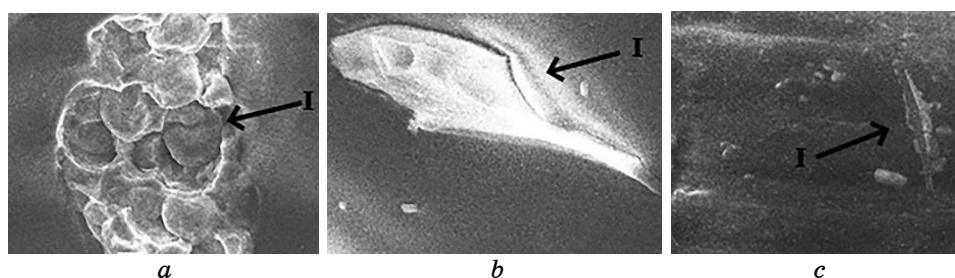
Due to the difficulty in identifying nano- and submicron crystals coated with a glass phase, the holding time of the samples at temperatures of  $850^\circ\text{C}$ ,  $1050^\circ\text{C}$ , and  $1110^\circ\text{C}$  was doubled. This made it



**Fig. 2.** The structure of the glass-ceramic material CGC-10.1 after exposure to temperature: *a*—800°C; *b*—850°C; *c*—980°C; *d*—1050°C; *e*—1100°C.

possible to enlarge and isolate crystals of ellipsoidal  $\mu$ -cordierite (Fig. 3, *a*, I), hexagonal  $\alpha$ -cordierite (Fig. 3, *b*, I) and mullite (Fig. 3, *c*, I).

The formation of the nano- and submicron structure of glass-ceramic materials is extremely important to ensure a high speed of wave propagation in the material. The finer the grains in the struc-



**Fig. 3.** The structure of glass-ceramic material CGC-10.1 after exposure for 4 hours at temperatures: *a*—850°C; *b*—1050°C; *c*—1100°C.

ture of the material, the more often barriers are encountered at the grain boundary on the path of gliding dislocations, and therefore higher stresses are required for plastic deformation of the material already at its initial stages [14]. Nanocrystalline materials have high damping properties, since, due to the differences in the elastic moduli of the grains themselves and the boundary layers, elastic vibrations propagate inhomogeneously and significantly dissipate. The greater the difference in the speed of propagation of a sound wave in the projectile material and in the armour material, the more the projectile will be destroyed. This explains the efficiency of using nanostructured glass materials under conditions of high-speed damaging factors.

According to the research results, the heat treatment mode for CGC-10.1 glass was selected: stage I— $T = 800^{\circ}\text{C}$ ,  $\tau = 2$  hours; stage II— $T = 980^{\circ}\text{C}$ ,  $\tau = 2$  hours; stage III— $T = 1100^{\circ}\text{C}$ ,  $\tau = 1$  hour.

The study of the fracture toughness of the developed material CGC-10.1 made it possible to establish that an increase in the fracture toughness index  $K_{1C}$  to  $6.5 \text{ MPa}\cdot\text{m}^{1/2}$  and Young's modulus  $E = 350 \text{ GPa}$  at a relatively low cost (due to a decrease in temperature and duration of heat treatment stages) and weight ( $\rho = 2800 \text{ kg/m}^3$ ) is a determining factor in their successful application as high-strength materials for the protection of machinery and equipment. The competitiveness of the developed material is determined by its technological advantages over ceramic materials ( $\text{Al}_2\text{O}_3$ , SiC,  $\text{B}_4\text{C}$ ), which have high synthesis temperatures ( $2000^{\circ}\text{C}$ ), are characterized by the complexity of production, high cost of raw materials and have an insufficiently high fracture toughness index  $K_{1C} = 4\text{--}5 \text{ MPa}\cdot\text{m}^{1/2}$ .

### 3. CONCLUSIONS

For the developed magnesium–aluminosilicate glass, ensuring the

phase distribution according to the spinodal mechanism and nucleation of  $\mu$ -cordierite at low temperatures (750–850°C) is realized due to:

— providing the content of phase-forming oxides  $\Sigma(\text{MgO}, \text{Al}_2\text{O}_3, \text{SiO}_2) = 87.0$  wt.%, crystallization catalysts  $\Sigma(\text{ZnO}, \text{Sb}_2\text{O}_5, \text{TiO}_2, \text{ZrO}_2, \text{CeO}_2, \text{P}_2\text{O}_5) = 8.0$  wt.% and modifying components  $\Sigma(\text{CaO}, \text{SrO}) = 3$  wt.%;

— their ratio 1.0 MgO:1.31 Al<sub>2</sub>O<sub>3</sub>:5.5 SiO<sub>2</sub>.

It has been established that the intensive formation of spherical inhomogeneities with a size of 0.01–0.1  $\mu\text{m}$  in the pre-crystallization period for the developed magnesium aluminosilicate glass is an important stage in the sequential crystallization of solid solutions based on: ellipsoids of  $\mu$ -cordierite (850°C), prismatic crystals of  $\mu$ -cordierite (900°C), octahedral spinel crystals (980°C), hexagonal crystals of  $\alpha$ -cordierite (1050°C) and prismatic crystals of mullite (1100°C).

Formation of the nano- and submicron structure of the developed glass-ceramic material with a content of 80 vol.% mullite according to the low-temperature regime (stage I— $T = 800^\circ\text{C}$ ,  $\tau = 2$  hours; stage II— $T = 980^\circ\text{C}$ ,  $\tau = 2$  hours; stage III— $T = 1100^\circ\text{C}$ ,  $\tau = 1$  hour) allows to ensure high mechanical properties  $K_{1C} = 6.5$  MPa·m<sup>1/2</sup> and  $E = 350$  GPa.

Providing high crack resistance and elasticity at a relatively low weight ( $\rho = 2800$  kg/m<sup>3</sup>) and processability of the developed glass-ceramic material is a determining factor in its successful use as a high-strength material for protecting equipment and technology.

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