UDC 666.266.6
DOI https://doi.org/10.15589/znp2022.2(489).5

INVESTIGATION OF THE PHASE FORMATION MECHANISM IN MAGNESIUM ALUMOSILICATE GLASSES DURING THERMAL TREATMENT

ДОСЛІДЖЕННЯ МЕХАНІЗМУ ФАЗОУТВОРЕННЯ В МАГНІЙАЛЮМОСИЛІКАТНИХ СТЕКЛАХ ПРИ ТЕРМІЧНІЙ ОБРОБЦІ

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Abstract. The aim of this work is to study the structure of magnesium aluminosilicate glasses under heat treatment. The type and amount of the crystalline phase were determined using XRD (DRON-3M) and petrographic (NU-2E polarizing microscope) methods. The glass microstructure was studied using an «EMV 100 AK» electron microscope. The glass viscosity was determined by the method of stretching the thread.

According to the results of investigations, the mechanism of structure and phase formation of magnesium aluminosilicate glass-ceramic materials has been established. The initial glasses are characterized by the ratio $MgO:Al_2O_3:SiO_2$ = 1.0:2.5:5.0, the content of modifying oxides $\Sigma(CaO, K_2O, B_2O_3)$ = 12.5 wt. %, and the nucleation catalyst TiO_2 = 2.5 wt. %.

The scientific novelty consists in establishing a three-stage mechanism for the structure formation of magnesium aluminosilicate glass-ceramic materials under conditions of low-temperature two-stage heat treatment. At the first stage in the glass secondary drop-shaped inhomogeneities 0.01÷0.05 μm in size are formed due to the phase separation. Their presence and increased viscosity of glass at a temperature of 800 ºC leads to agglomeration of spherulites with a size of 0.5÷0.8 μm and the appearance of granular aggregates of crystallization nuclei (second stage). It was found that providing an increased viscosity ($\eta = 10^{8.6}$ Pa·s) of experimental glass causes the formation of a developed two-frame drop structure in a short time. This makes it possible to lower the temperature of formation of the crystalline phase nuclei. At the next stage, at a temperature of 990 ºC, the formation of a sitallized submicron high-strength structure of the material is observed. It is characterized by the presence of nano-inhomogeneities, α-cordierite crystals in the form of isometric prisms, and octahedral spinel crystals. These crystalline phases at a temperature of 1050 ºC form a fine-crystalline structure of a glass-ceramic material with a crystal size of 0.5÷1.0 μm.

The practical significance of the work lies in the development of compositions of high-strength glass-ceramic materials and technological parameters for their production.These materials can be used as a basis for the development of composite protective elements of machinery and equipment.
Key words: magnesium aluminosilicate glasses, glass-ceramic materials, phase formation, structure, viscosity.

Анотація. Метою даної роботи є дослідження структури магнійалюмосилікатних стекол в умовах термічної обробки. Вид та кількість кристалічної фази визначали за допомогою рентгенофазового (дифрактометр ДРОН-3М) та петрографічного (мікроскоп NU-2E) методів аналізу. В'язкість скла визначали за методом розтягнення нитки. Мікроструктуру стекол досліджували з використанням електронного мікроскопа «ЕМВ 100 АК».
За результатами проведених досліджених встановлено механізм структуро- та фазоутворення магнійалюмосилікатних склокерамічних матеріалів зі співвідношенням $MgO:Al_2O_3:SiO_2$= 1,0:2,5:5,0 та вмістом модифікуючих оксидів (CaO, K_2O, B_2O_3) 12,5 мас. % та каталізатору кристалізації (TiO_2) 2,5 мас.%. Наукова новизна полягає у встановленні тристадійного механізму формування структури магнійалюмосилікатних склокерамічних матеріалів в умовах низькотемпературної двостадійної термічної обробки. На першому етапі утворення вторинних краплевидних неоднорідностей розміром 0,01÷0,05 мкм при температурі 800 ºС в умовах підвищеної в'язкості приводить до агломерації сферолітів розміром 0,5÷0,8 мкм та появи зернистих агрегатів зародків кристалізації на другому етапі. Встановлено, що забезпечення високої в'язкості ($\eta = 10^{8,6}$ Па·с) дослідного скла обумовлює формування розвиненої крапельної двокаркасної структури за короткий термін, що дозволяє знизити температуру формування зародків кристалічної фази. На четвертому етапі спостерігається формування ситалізованої субмікронної високоміцної структури, яка характеризується наявністю нанонеоднорідностей, кристалів α-кордієриту у вигляді ізометричний призм та октаедричних кристалів шпінелі при температурі 990 ºС, які при температурі кристалізації 1050 ºС формують тонкокристалічну структури з розміром кристалів 0,5÷1,0 мкм.
Практична значимість роботи полягає у розробці складів високоміцних склокристалічних матеріалів та технологічних параметрів їх одержання. Вони можуть бутивикористані як основа при розробці композиційних захисних елементів техніки та обладнання.
Ключові слова: магнійалюмосилікатні стекла, склокристалічні матеріали, фазоутворення, структура, в'язкість.

TASK STATEMENT

Glass-ceramic technology bases on obtaining materials from glasses by directed nucleation and crystal growth. Glass-ceramic materials can have high strength and toughness, unique electrical, electronic or magnetic properties, exceptional optical or unusual thermal or chemical properties [1]. One of the most promising areas in this field is the production of materials with a heterogeneous crystalline phase. Activation of both heterogeneous surface and heterogeneous volume nucleation processes of sintered glass-ceramics is currently gaining importance for armor applications [2]. Magnesium aluminosilicate glass-ceramic is one of the most promising materials for producing high-strength armor elements. However, obtaining high-strength materials in this system is complicated by the complexity of crystallization as a process of formation of solid solutions and their transformations, which are not well understood. That is why the study of the patterns of structure and phase formation of magnesium aluminosilicate glasses under heat treatment conditions is an urgent task.

ANALYSIS OF RECENT RESEARCHES AND PUBLICATIONS

The greatest number of scientific articles is devoted to developments concerning the study of the mechanisms of nucleation and growth of crystals and phase separation. This topic also includes works related to: evaluation of various theories of nucleation, growth and phase separation in glassy systems; description of advanced microscopic and spectroscopic analytical tools for studying the structure of glass-ceramics [3]. The production of heterogeneous materials containing phases of different nature and morphology is of greatest interest in the field of glass-ceramics.

It has been shown in many glass-forming systems that the mechanism of formation of separated phases differs according to the initial glass composition. A description of the Gibbs free energy variation during the phase separation process can distinguish between two regions where phase separation occurs by different processes [4].

Depending on the composition of the initial glass, liquation can proceed by nucleation or spinodal mechanisms. In the first case, the energy barrier is overcome during the formation of nuclei of crystals of a critical size. In the second case, the energy of formation of crystal nuclei approaches zero, and the appearance of even slight composition fluctuations leads to phase separation with a decrease in the free energy of the system (without the formation of nuclei in the unstable area).

If there is a metastable liquation in the glass melt and the glass composition approaches the stoichiometric one, it is possible to envisage a sitallized structure of the material, which is a prerequisite for obtaining glass-ceramic materials. However, obtaining a high-strength nanostructure is more achievable by implementing the spinodal mechanism of phase separation.

The problem of the influence of liquid-phase separation (LPS) on the nucleation of crystals is still an urgent problem in materials science and causes active scientific discussions. The authors [5] carried out a broad review of the latest studies of the project on the kinetic analysis of LPS and simultaneous crystallization of glasses in the $BaO–SiO_2$ and $Li_2O–SiO_2$ systems. The LPS of high-silicon glass-ceramics ($7.6Na_2O·4K_2O·8.4CaO·70SiO_2·8.9CaF_2·1.0Al_2O_3$) based on canasite during heat treatment has also been extensively studied [6].

It is known [7], that the fluctuation structure is of a kinetic nature and, therefore, is able to develop most strongly in systems with low energy barriers to structural-chemical transformations with a short relaxation time, in particular, in systems with low viscosity. However, the high viscosity of glass makes an important contribution in the kinetics of the process: in the foreseeable time, the glass cannot separate into two layers, and the glassy phase that separates forms finely dispersed droplets. This leads to the formation of a developed drop two-frame glass structure in a short time by the spinodal mechanism. Magnesium aluminosilicate glasses are characterized by high viscosity and the possibility of implementing the nucleation by the spinodal phase separation mechanism. This will ensure the formation of a high-strength structure of materials, with high physical, mechanical and operational properties, capable of withstanding high dynamic loads.

SELECTING PREVIOUSLY UNSOLVED PARTS OF THE GENERAL PROBLEM

The study of the mechanism of phase separation and nucleation in aluminosilicate systems, which are widely used in the development of multifunctional glass-ceramic materials, is of considerable interest. However, most studies refer to lithium aluminosilicate systems [5, 7], while magnesium aluminosilicate systems, which are characterized by the complexity of the mechanism for the formation of solid solutions during crystallization, have not been fully studied.

Analyzing the above data, it should be noted that the study of the mechanism of complex interdependence between viscosity and the mechanism of nucleation under heat treatment conditions is an important step in the development of high-strength magnesium aluminosilicate glass-ceramic materials, which determines the relevance of this scientific work. The study of phase transformations in magnesium aluminosilicate glasses under heat treatment conditions will make it possible to establish the possibility of obtaining cordierite glass-ceramic spinels on their basis with an adjustable level of light transmission for armor protection elements.

The aim of this work is to study the structure of magnesium aluminosilicate glasses under heat treatment.

METHODS, OBJECT AND SUBJECT OF INVESTIGATION

The type and amount of the crystalline phase were determined using XRD (DRON-3M) and petrographic (NU-2E polarizing microscope) methods. The glass microstructure was studied using an «EMV 100 AK» electron microscope. The glass viscosity was determined by the method of stretching the thread.

The object of investigation was the previously synthesized CGC-1 magnesium aluminosilicate glass of the following composition, wt. %: MgO – 10; Al_2O_3 – 25, SiO_2 – 50, Σ(CaO, K_2O, B_2O_3) – 12.5, TiO_2 – 2.5. The initial CGC-1 glass was obtained by melting the glass batch at a temperature of 1550 ºC in a corundum crucible in electric furnace with subsequent gradual cooling in it for 12 hours. The subject of the study is the processes of structure and phase formation of a glass-ceramic material during heat treatment and their relationship with the viscosity of glass.

The glass-ceramic material based on this glass was obtained by two-stage heat treatment (stage I – T = 780 °C, τ = 5 h.; stage II – T = 1050 °C, τ = 5 h.). After heat treatment, the glass-ceramic material was characterized by the content of crystalline phases, in vol. %: α-cordierite – 20, mullite – 10 and spinel – 25.

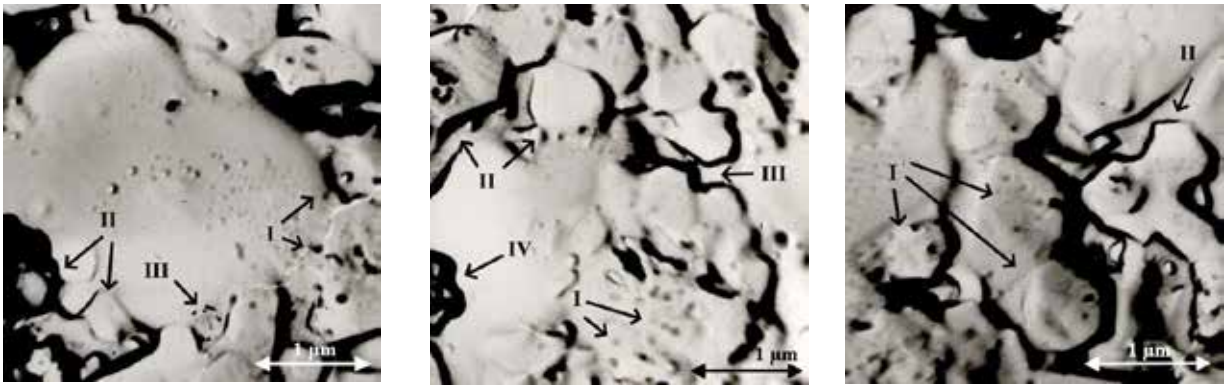
BASIC MATERIAL

In order to study the formation of crystallization nuclei and their growth for CGC-1 glass, characteristic temperatures were chosen according to the data of differential thermal and gradient thermal methods of analysis [8] at which phase formation processes are observed.

In accordance with the results of transmission electron microscopy, the CGC-1 glass material after heat treatment at 800 ºC is a multiphase system. The system is formed from mother glass, accumulations of spherulites (fig. 1a, I) 0.5÷0.8 μm in size, granular aggregates (fig. 1a, II) and secondary drop-shaped inhomogeneities (fig. 1a, III) 0.01÷0.05 μm in size, which may indicate the occurrence of phase separation.

When the sample is processed at a temperature of 990 °C, along with the presence of nanoinhomogeneities (fig. 1b, I), α-cordierite crystals are observed in the form of isometric prisms. These inhomogeneities were formed due to the occurrence of metastable liquation as a phase transition below the liquidus temperature. The indicated prisms of α-cordierite have the form of a hexagon with the base plane of the unit cell with the index «001» (fig. 1b, II).

Crystals of high-temperature α-cordierite (idialite) are short-prismatic in habit. They belong to the rhombic



a *b* *c*

Fig. 1. The structure of CGC-1 glass-ceramic material after heat treatment at temperatures: a – 800 ºC; b – 990 ºC; c – 1050 ºC

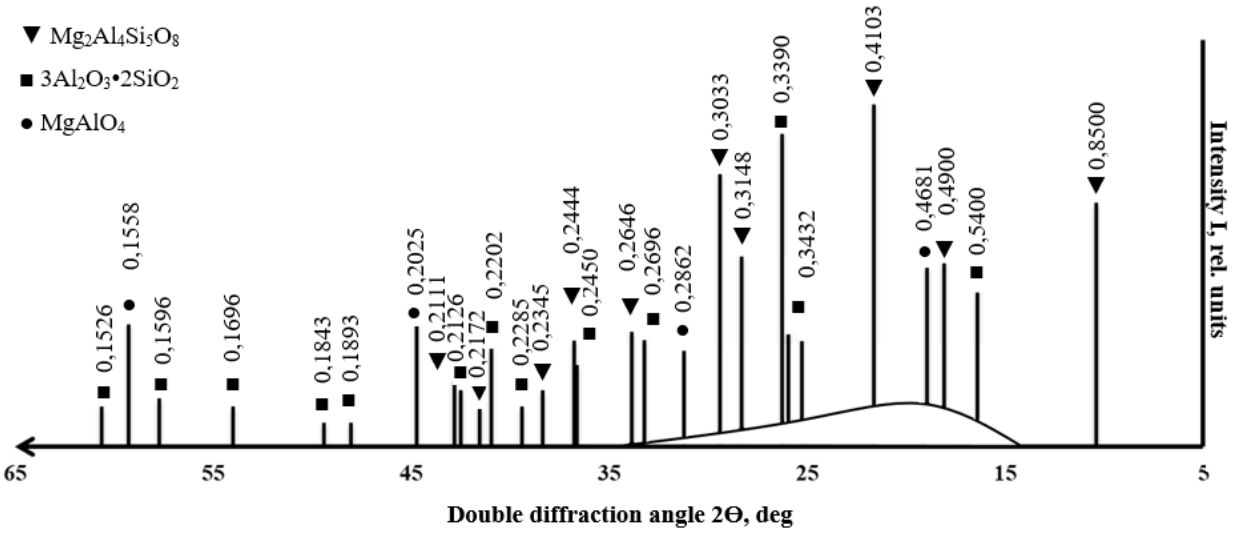


Fig. 2. Line-diffractogram of CGC-1glass-ceramic material

system and are sometimes twinned in such a way that they appear to be hexagonal.

Spinel occurs predominantly in the form of octahedral crystals. In this case, spinel twins with fusion along the plane with the index «111» (fig. 1b, III) acquire a characteristic triangular-lamellar shape with bifurcated corners. Isometric grains and granular aggregates (fig. 1b, IV) are found separately. Crystals of μ-cordierite in the form of ellipsoids of revolution or hexagonal stars, which are formed in the temperature range of 935÷938 ºC, and X-phase in the form of rhombuses or rectangles, are not observed in the structure of the material.

Heat treatment at a temperature of 1050 ºC leads to melting of the glass phase of the material and the formation of a fine-grained structure with a crystal size of 0.5÷1.0 μm. Crystals of α-cordierite (fig. 1c, I) along the plane with index «100» and octahedral crystals of spinel (fig. 1c, II) along the plane with index «111» of the twin type are clearly observed. Mullite crystals, which are fixed on the diffractogram (fig. 2) with insignificant intensity, are difficult to identify. Acicular crystals and sheaf-like aggregates characteristic of mullite are not observed, and thin hexagonal prisms look like α-cordierite (along the «001» plane).

According to the results of the study of viscosity (fig. 3), it was established that a feature of the experimental glass is an anomalous increase in viscosity in the glass transition interval T_g–T_f, which is associated with the formation of fluctuations. As the temperature rises in the transition region, there comes a moment when the rate of temperature increase begins to outpace the increase in viscosity, which leads to a dip in the viscosity curve. This state is quickly eliminated, since under new temperature conditions there is a more intense increase in the crystal-

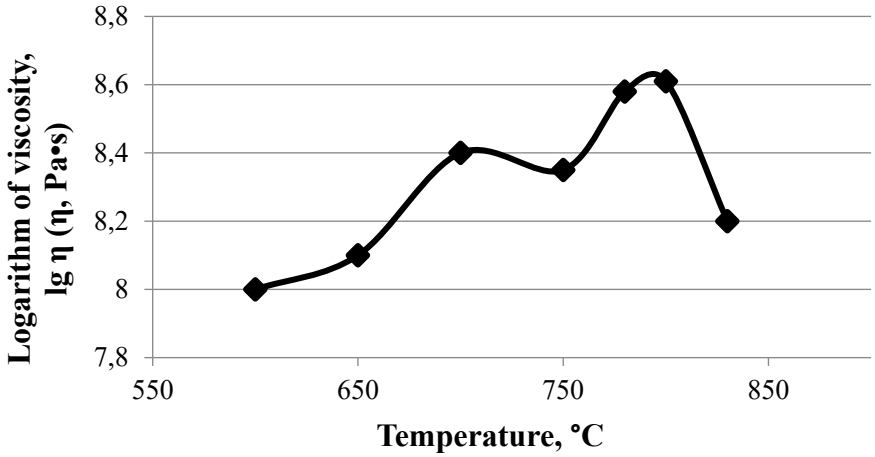


Fig. 3. Change in the viscosity of CGC-1 glass material during heat treatment

line phase due to a decrease in the amount of the glassy phase. This determines the re-increase in viscosity before the end of heat treatment. The increase in viscosity ($\eta = 10^{8.6}$ Pa·s) in the temperature of about 800 °C indicates both the intensive formation of nucleators and the growth of crystals (fig. 3).

It is the high viscosity of the experimental glass that determines the important contribution in the kinetics of the process: for a certain time, the glass cannot separate into two layers. However, the glassy phase forms finely dispersed droplets, which leads to the formation of a developed two-frame droplet structure in a short time.

It is the provision of phase separation via the spinodal mechanism that makes it possible, during further heat treatment, to create conditions for intensive nucleation and the formation of a nano- and microheterogeneous structure of a glass-ceramic material with a crystal size of up to 0.4 μm. This, along with the presence of cubic spinel crystals in an amount of up to 50 vol. %, is an important factor in the formation of a nanosized sitallized structure with light transmission up to 70 % and high strength properties. Therefore, the developed material can be used as a basis for the development of high-strength transparent glass-ceramic materials for armor protection.

CONCLUSIONS

According to the results of investigations, the mechanism of structure and phase formation of magnesium aluminosilicate glass-ceramic materials has been established. The initial glasses are characterized by the ratio $MgO:Al_2O_3:SiO_2$ = 1.0:2.5:5.0, the content of modifying oxides Σ(CaO, K_2O, B_2O_3) = 12.5 wt. %, and the nucleation catalyst TiO_2 = 2.5 wt. %.

At the first stage in the glass secondary drop-shaped inhomogeneities 0.01÷0.05 μm in size are formed due to the phase separation. Their presence and increased viscosity of glass at a temperature of 800 ºC leads to agglomeration of spherulites with a size of 0.5÷0.8 μm and the appearance of granular aggregates of crystallization nuclei (second stage). At the next stage, at a temperature of 990 ºC, the formation of a sitallized submicron high-strength structure of the material is observed. It is characterized by the presence of nano-inhomogeneities, α-cordierite crystals in the form of isometric prisms, and octahedral spinel crystals. These crystalline phases at a temperature of 1050 ºC form a fine-crystalline structure of a glass-ceramic material with a crystal size of 0.5÷1.0 μm.

Ensuring the sitallized structure of magnesium aluminosilicate glass-ceramic material allows it to be used as a basis for the further development of transparent armored materials for glazing military equipment.

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Дата надходження статті до редакції: 29.07.2022
Дата затвердження статті до друку: 28.07.2022