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*S.G. Polozhaj, O.V. Zaichuk, A.G. Polozhaj***FUSIBLE GLASS-CRYSTALLINE BINDER IN THE SPODUMENE–MANGANESE CORDIERITE SYSTEM****Ukrainian State University of Science and Technologies, Dnipro, Ukraine**

Low-melting glass-crystalline materials with a low temperature coefficient of linear expansion (TCLE) are widely used in various engineering fields. These materials are utilized for joints, protective coatings, additives in sintering of ceramic materials, including as matrices for high-strength dispersion-reinforced materials based on oxygen-free silicon compounds. This paper presents the results of a study on glass-crystalline materials in the pseudo-binary spodumene–manganese cordierite system. Based on experimental data, a fusibility diagram was constructed. Crystalline phases formed during the cooling of the glass melts were identified using X-ray phase analysis and their crystallization tendency was evaluated. It was found that the crystallization ability of the glasses decreases with an increasing content of manganese cordierite. The most promising, low-melting glass composition was identified, with a $\text{LiAlSi}_2\text{O}_6:\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ratio of 30:70 wt.%. The glass formation temperature for this composition lies in the range of 1200–1250°C, and the practical melting temperature is 1450°C. The synthesized glass exhibits softening and intensive crystallization onset temperatures of 760°C and 960°C, respectively. The TCLE of the glass is $34.9 \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$. The primary crystalline phase, β -spodumene, forms bundles of needle-like crystals 10–15 μm in length within the residual glass phase, reducing the material's TCLE to $20.9 \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$. The developed material shows potential as a glass-crystalline binder for producing high-strength ceramic materials (wear-resistant and impact-resistant) based on SiC and Si_3N_4 with reduced sintering temperatures.

Keywords: glass-crystalline binder, spodumene, manganese cordierite, melting diagram, crystallization, phase composition, microstructure.

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Introduction

The continuous development of various industries dictates the demand for fusible glass and glass-crystalline materials with low temperature coefficient of linear expansion (TCLE). These materials are widely used for solders, protective coatings, additives in sintering of ceramic materials, including as a matrix for high-strength (wear-resistant and impact-resistant) dispersion-hardened materials based on oxygen-free silicon compounds.

Experience shows that the mechanical properties of dispersion-hardened composite materials are largely determined by the properties of the binder, its content and phase composition [1–3]. The strength of

dispersion-hardened composite materials on glass-crystalline binders is significantly higher compared to glass binders. Values of bending strength can reach 800 MPa and more when oxygen-free silicon compounds (SiC, Si_3N_4) are used as dispersed fillers [4]. For such composite materials operating under conditions of high thermomechanical loads, an important condition is the need to match the TCLE of all its components (dispersed filler, crystalline phase and residual glassy phase of the binder) [5,6].

Given the relatively low TCLE of oxygen-free silicon compounds, the choice of glass-forming systems for the synthesis of crystallizable bonds is usually limited to alkali-free aluminosilicate systems, in

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particular, the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system [3,7–9]. However, the high refractoriness of the components makes it difficult to synthesize glass binders in these systems and subsequent sintering of glass-ceramic composites [10–12]. In our opinion, an approach is interesting, in which the search for the most fusible compositions is carried out in pseudo-binary systems of crystalline compounds, which are supposed to be used as base phases in crystallizing glass-bonds. This approach is also promising in that it is very likely to produce binders with a high degree of crystallinity and to reduce the probability of formation of associated crystalline phases.

Considering the desire to minimize the temperature of synthesis of glass-crystalline binders for dispersion-strengthened composite materials, the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{MnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ silicate systems were chosen as base systems. The first system contains such stable crystalline compounds with low thermal expansion as spodumene ($\text{LiAlSi}_2\text{O}_6$) and eucryptite (LiAlSiO_4). Among lithium aluminosilicates, spodumene exhibits a greater tendency to crystallization and chemical stability [13]. In the $\text{MnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, the formation of manganese cordierite ($\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) was observed. In addition to low TCLE, its peculiarity is the incongruent character of melting with release of liquid phase at the temperature of about 1200°C , which can facilitate the process of glass pulping [14]. Therefore, the $\text{LiAlSi}_2\text{O}_6-\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ pseudo-binary system was chosen for the study.

Taking into account the above stated, the purpose of this research was to search for compositions of the most easily fusible glasses by constructing fusibility diagram in the pseudo-binary $\text{LiAlSi}_2\text{O}_6-\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ system. In addition, properties of promising glass binders for oxygen-free ceramic materials, both in the glassy and crystallized states, their microstructure and phase composition were investigated.

Materials and methods

To obtain prototypes, lithium carbonate (chemically pure grade), SiO_2 in the form of marshalite, Al_2O_3 in the form of technical alumina (G-0 grade) and MnO (chemically pure grade) were used as raw materials. Raw mixtures, corresponding to the chemical compositions of $\text{LiAlSi}_2\text{O}_6$ and $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, were prepared by joint grinding of components in porcelain drum mills to the residue on the mesh No. 0063 not more than 1%. According to the experiment design, the raw material mixtures were studied in the range of $\text{LiAlSi}_2\text{O}_6:\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ratios of 10:90 to 90:10 with a step of 10 wt.%. The final mixing of the components of raw material mixtures was carried out by grinding in a planetary

mill until passing through mesh No. 0045. Chalcedony drums were used. Coding of experimental raw mixes was made in accordance with the conditional content in raw mixture $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ divided by 10. Thus, the composition of charge No. 1 corresponded to the mixture of 90 wt.% spodumene and 10 wt.% $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, and the composition of No. 9 corresponded to the mixture of 10 wt.% spodumene and 90 wt.% $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$.

The heat treatment of experimental raw material mixtures was carried out in an electric resistance furnace with silicon carbide heaters in the temperature range of $1200-1400^\circ\text{C}$ in air. Experimental charges were placed in corundum crucibles of 5 cm^3 capacity, heated to the maximum temperature and kept for 2 h. The conclusion about melting of the raw material mixture was made based on visual observation. Cooling of heat-treated samples was carried out together with the furnace. The rate of cooling to the temperature of 700°C was $50-60^\circ\text{C}/\text{h}$ and allowed qualitatively assessing the ability of experimental melts to crystallization.

The glass was melted in an electric resistance furnace with silicon carbide heaters in air at $1440-1450^\circ\text{C}$. The holding time for homogenization of glass melt was 1 h. Corundum crucibles of 400 cm^3 capacity were used for melting.

The experimental studies were carried out using generally accepted methods for determining the properties of glasses and glass-crystalline materials. TCLE in the range of $20-400^\circ\text{C}$ was measured on a quartz vertical dilatometer at the heating rate of $4-5^\circ\text{C}/\text{min}$. Thermal effects related to the glass softening onset temperature and crystallization were determined by differential thermal analysis on a Q-1500D derivatograph in the temperature range of $20-1000^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$. The mineralogical composition of crystallized samples was determined by X-ray phase analysis on a Philips APD-15 diffractometer in $\text{Co-K}\alpha$ radiation. Electron microscopic studies (SEM) of the samples on the fracture were carried out using a scanning electron microscope TESCAN Mira 3 LMU.

Results and discussion

At the first stage, the propensity of materials in the $\text{LiAlSi}_2\text{O}_6-\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ pseudo-binary system to melt formation at different temperatures was investigated. The study was carried out in the region of compositions with the ratio $\text{LiAlSi}_2\text{O}_6:\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ of 10:90 to 90:10 (wt.%). The temperature range was $1200-1400^\circ\text{C}$. Visual and X-ray analysis revealed four main groups of samples. The first one is melts represented by dense and/or low-porous molten mass that forms a meniscus with a characteristic glassy

luster in the crucible. These melts are more or less prone to crystallization. The second group includes dense, strong, and sintered to porous state samples that have not lost their original shape due to melting, but have undergone significant shrinkage during heat treatment. The third group includes weakly sintered and friable specimens, which have undergone virtually no shrinkage during firing. Finally, the group includes foamed but not fully melted specimens with matte texture both on the surface and in the chipping. The formation of such samples is observed for compositions No. 8 and No. 9 which is probably related to incongruent melting of manganese cordierite. Graphically, the obtained results are presented in the form of a melting diagram (Fig. 1).

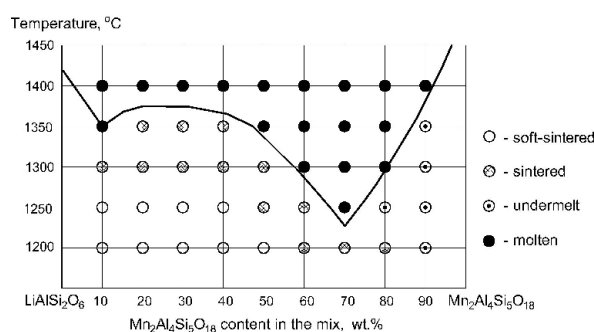


Fig. 1. Melting diagram in the $\text{LiAlSi}_2\text{O}_6$ – $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ pseudo-binary system

Two minima can be noted on the conditional curve showing the temperature of melt formation in studied pseudo-binary system. The first minimum is at the ratio $\text{LiAlSi}_2\text{O}_6:\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}=90:10$ (melt formation temperature is approximately 1350°C) and the second minimum is at the ratio $\text{LiAlSi}_2\text{O}_6:\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}=30:70$ (melt formation temperature is in the range of 1200 – 1250°C). In the investigated range of compositions, however, melts were obtained at 1400°C . All of them are prone to crystallization. To evaluate the degree of crystallization of cooled melts, X-ray phase analysis of the samples was carried out, results of which are shown in Fig. 2.

Analysis of the obtained XRD patterns shows that in accordance with change in the composition of experimental melts, there are changes both in propensity to crystallization and in the composition of precipitating crystalline phases. In the series of samples (compositions No. 1–8), β -spodumene is the only crystalline phase. The β -spodumene phase is isolated in significant amounts, which is evident from the intensity of the peaks in the diffractograms. The crystalline phase of β -spodumene is not fixed only in composition No. 9, in which its content is minimal and amounts to 10 wt.%. At the same time,

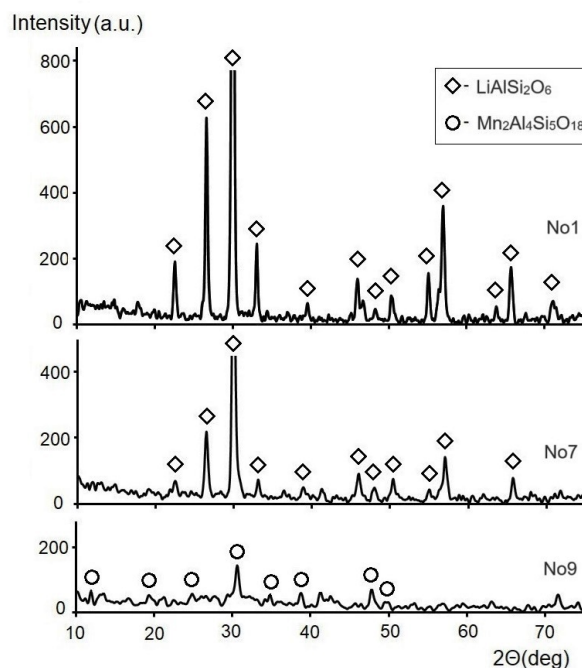


Fig. 2. XRD patterns of samples of experimental glass-crystalline materials in the $\text{LiAlSi}_2\text{O}_6$ – $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ pseudo-binary system synthesized at 1400°C

crystallization of manganese cordierite was observed in composition No. 9.

Based on the assumption that the temperature of practical melting of glasses of a given composition is related to the temperature of its melting (liquidus temperature), the composition No. 7 was chosen for further studies. The temperature of glass melting was 1440 – 1450°C with holding time for homogenization of 2 h. The study of samples of the obtained glass allowed determining its basic properties. According to the data of differential thermal analysis, the softening onset temperature and crystallization intensity maximum for glass No. 7 are observed at 760°C and 950°C , respectively. TKLE of the experimental glass is equal to $34.9 \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$.

In accordance with the obtained results of differential thermal analysis, additional thermal treatment of glass samples of composition No. 7 was carried out at the temperature of intensive crystallization ($950 \pm 3^\circ\text{C}$) for 2 h. TCLE of crystallized glass samples is equal to $20.9 \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$. The XRD pattern of specially crystallized glass (Fig. 3a) differs from that of the molten glass cooled in the furnace (Fig. 2) only by the higher intensity of peaks. Thus, the X-ray phase analysis did not reveal crystallization of other crystalline phases except β -spodumene (Fig. 3a). This fact is also confirmed by the results of scanning electron microscopy (Fig. 3b). The SEM

ЛЕГКОПЛАВКЕ СКЛОКРИСТАЛІЧНЕ В'ЯЖУЧЕ В СИСТЕМІ СПОДУМЕН–МАРГАНЦЕВИЙ КОРДІЄРИТ

С.Г. Положай, А.В. Зайчук, К.М. Сухий, А.Г. Положай

Легкоплавкі склокристалічні матеріали з низько-температурним коефіцієнтом лінійного розширення (ТКЛР) широко використовуються в багатьох галузях техніки. Такі матеріали використовують для з'єднань, захисних покриттів, добавок при спіканні керамічних матеріалів, у тому числі як матрицю для високоміцних дисперсно-зміцнених матеріалів на основі безкисневих сполук кремнію. У даній роботі наведено результати досліджень склокристалічних матеріалів у псевдобінарній системі сподумен–марганцевий кордієрит. На основі експериментальних даних побудовано діаграму плавкості. Методом рентгенофазового аналізу визначено кристалічні фази, що утворюються при охолодженні отриманих склорозплавів, та оцінено їх схильність до кристалізації. Встановлено, що кристалізаційна здатність стекел зменшується зі збільшенням вмісту марганцевого кордієриту. Визначено перспективний, найбільш легкоплавкий склад скла, що має співвідношення $\text{LiAlSi}_2\text{O}_6:\text{Mg}_0\text{Al}_4\text{Si}_3\text{O}_{18}=30:70$ мас. Температура скловаріння для нього лежить в інтервалі 1200–1250°C, а температура практичного варіння – 1450°C. Синтезоване скло характеризується температурами початку розм'якшення та інтенсивної кристалізації 760°C та 960°C, відповідно. ТКЛР скла становить $34,9 \cdot 10^{-7} \cdot \text{C}^{-1}$. Основна кристалічна фаза – β -сподумен, що утворює в залишковій скляній фазі пакети голчастих кристалів довжиною 10–15 мкм, – сприяє зниженню ТКЛР матеріалу до $20,9 \cdot 10^{-7} \cdot \text{C}^{-1}$. Розроблений матеріал може бути використаний як перспективне склокристалічне зв'язуюче для одержання високоміцних керамічних матеріалів (зносостійких та ударостійких) на основі SiC та Si_3N_4 зі зниженими температурами спікання.

Ключові слова: склокристалічне в'язуче, сподумен, марганцевий кордієрит, діаграма плавкості, кристалізація, фазовий склад, мікроструктура.

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Keywords: glass-crystalline binder; spodumene; manganese cordierite; melting diagram; crystallization; phase composition; microstructure.

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