Anorthite-reducing glass-crystalline materials synthesized in plasma

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Abstract. The paper presents the experimental results of the glass-ceramic material production using the low-temperature plasma. The dependences are suggested for the main physical-and-mechanical properties (compressive and flexural strengths, density, linear thermal expansion coefficient) of products and the mixture compositions. The centers of secondary recrystallization are identified for the anorthite phase (CaAl₂Si₂O₈). These inclusions chaotically locate on the surface of the synthesis products and resemble dendritic microinclusions up to 90 nm in size. A comparative analysis is given to the properties of glass-ceramic materials produced by the low-temperature plasma and traditional methods.

1. Introduction
Much research on the glass-ceramic material production has shown that both industrial waste and natural raw materials can be used as raw materials [1-4]. Koltsova et al [5, 6] demonstrated a possibility of producing porous and laminated glass ceramics, in which each layer has a bulk weight and mechanical strength. Compressive strength of such glass-ceramic samples was 3.97 and 2.19 MPa, respectively at a load applied along the layers and normal to them. The annealing temperature of those samples was 750°C. Kaz'mina et al [7] studied the microstructure of foamed glass-ceramic materials. They detected the strength of materials, that was higher than that of foam glass fabricated from broken glass. That was associated with the formation of nanostructured inclusions in the vitreous matrix.

This work studies the production of the glass-ceramic material for the purposes of construction industry using thermal plasma processing and presents a novel method of production of anorthite-containing fusion products with the enhanced physical-and-mechanical properties based on melting of sub-standard raw materials.

2. Materials and methods
The production process of glass ceramics includes grinding and thorough mixing of bulk components, melting and molding processes [8]. A series of experiments is carried out to determine the optimum conditions for the glass ceramics production, that are oriented towards the products with the improved physicochemical and mechanical properties. Table 1 summarizes the mixture compositions used in this experiment.

The melting process of these mixture compositions is performed in the electro-plasma system [9, 10]. When plasma jet interacts with the mixture, the latter starts to melt. Melting takes about 10 minutes. The operating parameters of the system include 240 A current, 120 V voltage, thermal...
efficiency not less than 84%, 15 dps heating rate, and 1700-2000°C temperature. These parameters allow a complete melting of the raw materials and removal of gases released. Through a drain, the molten glass is then poured into 50×40 mm cylindrical molds and placed in a muffle furnace for further crystallization and annealing. The initial temperature of 700°C is used for 1-hour exposure followed by a 950°C exposure for 2 hours. After melting and thermal exposure, the weight loss is 15%.

Table 1. Mixture compositions.

| Compositions | Coal ash (wt.%) | Limestone (wt.%) | Silica sand (wt.%) |
|--------------|----------------|-----------------|-------------------|
| A-1          | 100            | -               | -                 |
| A-2          | 60             | 20              | 20                |
| A-3          | 60             | 17              | 23                |
| A-4          | 70             | 20              | 10                |
| A-5          | 75             | 25              | -                 |
| A-6          | 78             | 22              | -                 |
| A-7          | 90             | 10              | -                 |

The photographs of the electro-plasma system, the mold, and the obtained sample are given in figure 1.

![Plasma jet](image1)

![Furnace](image2)

![Exhaust](image3)

**Figure 1.** Photographs of experimental stages: a – electro-plasma system; b – graphite mold; c – glass-ceramic ingot.

A testing machine TP-1-1500 (Russia) was used in this experiment to measure compressive and flexural strengths of the glass-ceramic ingots. The coefficient of linear thermal expansion was measured by a pressure dilatometer DIL 402 C (Netzsch, Germany). We also used a scanning electron microscope (SEM) Quanta 200 (FEI Company, USA) consisting of an integrated energy dispersive X-ray (EDX) system for the analysis of the phase morphology and elemental composition.

### 3. Results and discussion

The most important properties of glass ceramics are density, compressive and flexural strengths, and coefficient of linear thermal expansion. These properties directly depend on the composition of the crystal phase of the material. According to the constitutional diagram of the ternary system CaO–Al₂O₃–SiO₂, the mixture composition localizes at the center of secondary recrystallization of the anorthite phase (CaAl₂Si₂O₈). From the theoretical point of view, the obtained glass-ceramic samples have the low coefficient of linear thermal expansion and the enhanced compressive and flexural strengths.
Figure 2 (a) plots the flexural and compressive strengths depending on the mixture composition. And figure 2 (b) shows the dependences of the density and the coefficient of linear thermal expansion on the mixture composition. As can be seen from figure 2 (a), the mixture composition A-4 comprising 70 wt.% coal ash, 20 wt.% limestone and 10 wt.% silica sand (see table 1), provides the maximum flexural and compressive strengths of the material, namely 110 and 540 MPa, respectively. This is because the homogeneous, fine-grain crystal structure forms during the thermal exposure. This is also proven by curve 1 in figure 2 (b), which demonstrates the maximum density $\rho = 2986 \text{ kg/m}^3$ in the same mixture composition that leads to a decrease in the coefficient of linear thermal expansion (figure 2 (b), curve 2).

The surface morphology of the obtained fusion product with the mixture composition A-4 and EDX results are illustrated in figure 3.

According to figure 3, the surface morphology of the fusion product is homogeneous and consists of chaotically localized dendritic microinclusions. These inclusions are the centers of secondary recrystallization of the anorthite phase.
recrystallization of the anorthite phase \((\text{CaAl}_2\text{Si}_2\text{O}_8)\). The size of these centers achieves 90 nm. The EDX analysis shows the elemental composition of the anorthite phase, namely Ca, Al, Si and O.

Table 2 presents the main properties of the glass-ceramic material obtained by low-temperature plasma. These properties are compared with the glass-ceramic materials obtained by a conventional technique.

Table 2. The main properties of the glass-ceramic materials.

| Glass ceramics                          | Density \(\rho\) (kg/m\(^3\)) | Flexural strength \(R_{\text{fl}}\) (MPa) | Compressive strength \(R_{\text{comp}}\) (MPa) |
|----------------------------------------|---------------------------------|-----------------------------------------|---------------------------------------------|
| Marbled glass                          | 2670 – 2690                     | 60 – 70                                 | 300 – 400                                   |
| Rock glass-ceramics                    | 2880 – 2900                     | 50 – 100                                | 350 – 450                                   |
| Slag glass-ceramics                    | 2730 – 2760                     | 40 – 60                                 | 300 – 400                                   |
| Plasma-assisted process of glass ceramics production | 2900 – 2990                     | 90 – 110                                | 450 – 530                                   |

4. Conclusions
Based on the results, it can be concluded that the optimum mixture composition for the low-temperature plasma production of glass-ceramic materials with the anorthite phase, contained 70 wt.% coal ash, 20 wt.% limestone and 10 wt.% silica sand (see table 1, composition A-4). With that proportion of components and adhering to the thermal processing conditions, the obtained glass-ceramic material possessed the highest physical and mechanical properties, i.e., 530 MPa compressive strength, 110 MPa flexural strength and 2986.2 kg/m\(^3\) density. The centers of secondary recrystallization 90 nm in size were identified for the anorthite phase \((\text{CaAl}_2\text{Si}_2\text{O}_8)\). These inclusions chaotically located on the surface of the fusion products and resembled dendritic microinclusions.

Acknowledgments
The work was financially supported by Grant No. 20-79-10102 from the Russian Science Foundation.

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