SCIENCE FOR GLASS PRODUCTION

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EFFECT OF DIFFERENT VALENCE FORMS OF IRON ON THE PROPERTIES OF GLASSES IN THE SiO$_2$ - Al$_2$O$_3$ - Fe$_x$O$_y$ - CaO - MgO SYSTEM

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The effect of different valence forms of iron on the physicomехanical and crystallization properties of glasses in the SiO$_2$ - Al$_2$O$_3$ - Fe$_x$O$_y$ - CaO - MgO system is described. It is established that the properties of the glasses improve with an increase in the fraction of bivalent iron. A mechanism of crystallization in the glasses is suggested and the effect of the redox synthesis medium on the process of devitrification of iron-containing glasses is substantiated.

A study of the chemical composition of ash slag from many rocks and various waste and tails of industrial production has shown that they can be used for preparing glass in the SiO$_2$ - Al$_2$O$_3$ - Fe$_x$O$_y$ - CaO - MgO system without expensive primary natural resources; the listed components can be mixed with inexpensive available raw materials (like chalk, sand, dolomite). This approach should improve substantially the ecological situation, save a lot of primary natural resources, and increase production efficiency.

At the same time, glasses of this system possess elevated crystallizability, which means that they can be used as a basis for glass ceramic materials (GCM) with a wide spectrum of physicomехanical and chemical properties. The operational characteristics of devitrified glasses and slag devitrified glasses show that they are superior to many commercial materials and in many cases can replace metals and alloys. It should be noted that the quality of devitrified glasses fabricated from nonscarce raw materials can even be higher than that of expensive synthetic materials.

This explains the interest to the effect of various factors on the crystallization process and the properties of glasses of the SiO$_2$ - Al$_2$O$_3$ - Fe$_x$O$_y$ - CaO - MgO system. One such factor is the content of iron and the proportion of its different valence forms in the synthesized glasses. These factors have been studied intensely for the last 30 years. However, the majority of the investigations [1 - 3] were devoted to glasses with a total content of iron oxides exceeding 15 wt.%. Glasses with a lower iron concentration were considered inapplicable for producing GCM without introducing nucleators in the charge, for example, C$_2$O$_3$ or P$_2$O$_5$.

In the present paper we will show that GCM can be prepared from the SiO$_2$ - Al$_2$O$_3$ - Fe$_x$O$_y$ - CaO - MgO system with a content of iron oxides of 12 wt.% without using crystallization catalysts. Different proportions of different valence iron in the synthesized glasses were attained by changing the redox medium in the course of melting. The proportion was controlled by chemical analysis. The FeO / \(\Sigma\)Fe ratio was used as a criterion for evaluating the amounts of different iron phases. Chemical analysis showed that the molar FeO / \(\Sigma\)Fe ratio was 34% in specimen 1, 55% in specimen 2, 75% in specimen 3, 77% in specimen 4, 86% in specimen 5, and 94% in specimen 6.

The investigated glasses had good melting properties, melted completely, and clarified at a relatively low temperature of 1450°C. They did not contain foreign inclusions or bubbles.

The low synthesis temperature seems to be explainable by the fact that some of the iron oxides, more exactly, Fe$_3$O$_4$, perform the function of a lattice former and is present in the structure in the form of [FeO$_4$] tetrahedrons; since the Fe - O bond is less strong than the Si - O one, the processes of glass formation in iron-containing compositions occur at lower temperatures than in iron-free ones. In addition, the larger fraction of iron, especially of bivalent iron, acts as a modifier that dilutes the glass melt, i.e., plays the role of a flux. In order to determine the effect of iron with different valences on the physical and mechanical properties of the synthesized glasses, we investigated the following properties: the den-
Fig. 1. Variation of the properties of the studied glasses as a function of the ratio of different valence forms of iron.

Fig. 2. DTA (°C) of the studied glasses: 1-6) glass compositions.

Fig. 3. Viscosity $\eta$ of the synthesized glasses as a function of the temperature $t$: 1-6) glass compositions.

sity $\rho$, the microhardness $H$, the temperature coefficient of linear expansion (TCLE) $\alpha$, and the temperature of the beginning of deformation $t_{b,d}$. The results are presented in Fig. 1.

It can be seen that as the FeO/ΣFe ratio increases, the density and the TCLE of the studied glasses increase, whereas the microhardness and the temperature of the beginning of deformation decrease. It is obvious that an increase in the amount of Fe$^{2+}$, which is coarser and heavier than the Fe$^{3+}$ ion, exerts a "loosening" action on the structure of the glasses, and their physicomechanical parameters change. The changes can also be caused by the changed degree of bonding in the structure of the synthesized glasses.

A study of the crystallizability of the glasses by the method of mass crystallization showed that the glass with a FeO/ΣFe ratio of 34% has the best crystallization properties. After heat treatment, this specimen had a finely disperse crystal structure uniformly distributed over the entire volume. When the content of FeO in the glass was increased, the crystal structure formed became coarser and the crystallization process started from the surface.

The data on mass crystallization agree completely with the results of differential thermal analysis (Fig. 2). The thermograms of the studied glasses show that their crystallization occurs in a relatively narrow temperature range and at a high rate, which is proved by the quite sharp peak of the exothermic effect and the steep ascent of the dependence of the low-temperature viscosity (Fig. 3).

The exothermic peaks on the thermograms show that the proportion of different valence iron forms substantially affects the crystallizability of the glasses. The maximum peak corresponds to the specimen with FeO/ΣFe = 34%. As the number of Fe$^{2+}$ ions increases, the peaks become less intense. Thus, the specimen with the ratio of different valence forms of iron equal to 34% has the highest crystallizability.

It should be noted that as the proportion of Fe$^{2+}$ increases, the thermograms of the synthesized glasses exhibit a poorly defined inflection at a temperature of about 860°C, which can be associated with segregation of a small amount of a crystalline phase. The inflection becomes better defined, presumably due to the appearance of iron spinelides containing Fe$^{2+}$, which is confirmed by some published data [1, 3]. We could not identify them by x-ray phase analysis, because the peaks of the presumed spinelides correspond to the peaks of the main crystalline phase, i.e., diopside-hedenbergite solid solution.

The crystallization properties of the synthesized glasses as a function of the proportion of different valence forms of iron were also studied with a low-temperature GOI viscometer.

It can be seen from Fig. 3 that all the glasses began to crystallize within 820 – 840°C, which corresponds to the data from DTA and mass crystallization. The minimum value of log $\eta$ in all glasses with FeO/ΣFe = 34% was farther from the empirically determined boundary for slag devitrified glass...