I. I. Kitaigorodskii, R. Ya. Khodakovskaya, M. V. Artamonova

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I. I. Kitaigorodskii, R. Ya. Khodakovskaya, M. V. Artamonova

Phase Transformations in the Process of Catalytic Crystallization of Glass in the System SiO_2 –Al_2O_3–MgO

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The creation of materials with specified properties raises the problem of deliberately controlling their phase composition. As was shown by previous studies ([1,2]), the phase composition of a material is one of the principal factors determining its properties. In this connection, the crystalline phases of the system SiO_2–Al_2O_3–MgO—forsterite, clinoenstatite, cordierite—are of particular interest, possessing properties that are extremely important for modern technology. These compounds already now form the basis of many ceramic, glass-ceramic, and glass-crystalline materials.

The aim of the present investigation was to study the process of crystallization of glass of cordierite composition, containing, as a catalytic additive, 10 mol.% TiO_2.

The glass was melted in corundum crucibles in a disilicide-molybdenum furnace at a temperature of 1550° with a holding time of 4 hours. Crystallization of the glass was carried out in gradient and muffle furnaces, whose temperature regime was automatically regulated and recorded by an EPD-12 electronic potentiometer. The following heat-treatment regime was adopted: gradual heating of the glass to the crystallization temperature (in the range 800–1200°), holding for 2 hours, and then rapid cooling in air.

Table 1

Crystallization temp., °C	Composition of crystalline phases in the material
850	Solid solutions—anosovite and based on high-temperature quartz (of the silica O type)
900	Quartz, spinel, and magnesium aluminotitanates
950	Quartz, spinel, rutile
1000	Quartz, sapphirine, rutile
1050	Quartz, sapphirine, rutile

Crystallization temp., °C	Composition of crystalline phases in the material
1100	Quartz, sapphirine, cordierite, rutile
1200	Cordierite, rutile

According to the data of X-ray phase and differential thermal analyses, the lower limit of crystallization of the glass lies in the region of 850°. In this case, the first main crystalline phase to form is a compound successfully identified as a solid solution based on high-temperature quartz. A broad series of such solid solutions was described by R. Roy for the system $SiO_2-Al_2O_3-Li_2O$ under the names silica O, silica K, etc. (3). Taking into account the closeness of the ionic radii of Mg and Li (4) and the analogy in their position in the glass structure, it may be supposed that similar solid solutions may also occur in the system $SiO_2-Al_2O_3-MgO$ (5).

Raising the crystallization temperature leads to a fundamental change in the composition of the crystalline phases (Table 1). For each crystalline phase, at a given duration of heat treatment, a definite temperature of formation and a temperature interval of stability are characteristic.

for quartz 900-1000°, spinel 900-950°, sapphirine 1000-1100°. Finally, at 1200° the crystallization process is completed by the formation of the final product—cordierite.

In parallel with the formation of silicates, crystalline phases of the catalyst are separated out—magnesium aluminotitanates, which are anosovite solid solutions of aluminum titanate and magnesium dititanate (6) (850-900°) and rutile (950-1200°).

The data presented show that the formation of cordierite during glass crystallization occurs not directly from the glass, but through a series of intermediate compounds that separate out successively during its heat treatment. In this process, crystallization proceeds from solid solutions and simple mono- and binary compounds to more complex, ternary ones.

The sequence of formation of the individual crystalline phases and their interrelation are especially clearly manifested when comparing the data of relative quantitative X-ray phase analysis (Fig. 1) and differential thermal analysis (Fig. 2). As can be seen from Fig. 1, the amount of quartz, spinel, and sapphirine formed increases with increasing temperature, reaches a maximum, and then falls again, up to the complete disappearance of the corresponding phase. At a temperature of 900-950° the primary solid solutions of the silica O type and anosovite (curve 1

Fig. 1. Relative change in the quantitative content of crystalline phases during glass crystallization (according to X-ray phase analysis).

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

1—solid solutions: anosovite and based on high-temperature quartz; 2—quartz; 3—spinel; 4—sapphirine; 5—cordierite; 6—rutile

Fig. 2. Thermogram of the glass

completely decompose with the formation of quartz, spinel, and rutile (curves 2, 3, 6). At 1000° spinel transforms into sapphirine—the curve of the latter, as it were, continues the spinel line. The parallel increase in the quartz content makes it possible to assume that this transition occurs not at the expense of the previously formed crystalline SiO_2, but at the expense of silicon dioxide from the glassy phase. Finally, in the temperature interval above 1050°

decomposition and recrystallization of the crystalline phases (quartz and sapphirine) take place, with the formation of cordierite (1100°), which is manifested in a sharp decrease in the content of the first two (curves 2, 4).

Similar results are given by differential thermal analysis of the glass. As can be seen from Fig. 2, its thermogram contains three exothermic effects (at 870, 920-950, and 1085°) accompanying the formation of definite crystalline phases. Their identification by X-ray phase analysis of powders quenched immediately after the end of the corresponding effects showed that the first of them is associated with the precipitation of the above-mentioned solid solutions; the second, double, effect is cumulative and is associated with the formation of quartz, sapphirine, and rutile; the third is associated with the formation of cordierite. The latter is in complete agreement with the results of Karkhanavala and Hummel (^7) and disagrees with Sorrell' s data (^8) on the endothermic character of the cordierite synthesis process. The considerable endothermic effect actually present on the thermogram in the temperature range from 1000 to 1040° is apparently due to recrystallization and decomposition processes of the phases that had separated earlier and only precedes the formation of cordierite, since X-ray phase analysis does not detect cordierite in the powder quenched from 1040°.

It is characteristic that although the first exothermic effect on the glass thermogram is associated with the formation of solid solutions, nevertheless in the material heat-treated in the course of DTA up to 1000° (after the second effect), only quartz, sapphirine, and rutile are present. This direct experiment directly indicates decomposition of the first crystalline phases occurring during the crystallization of the glass.

The similarity between the DTA curves (Fig. 2) and the temperature dependence of the relative content of the corresponding crystalline phases (Fig. 1) is noteworthy. This analogy makes it possible to assume that the first of the maxima of the second exothermic effect (920°) corresponds to the precipitation of spinel (curve 3, Fig. 1), and the second, in the region of higher temperatures (945°), to the formation of sapphirine. A certain discrepancy between the temperatures of the maxima of the corresponding crystalline phases in Figs. 1 and 2 is apparently due to differences in the methods used in the two cases (different specimens, heat-treatment regimes, etc.). Nevertheless, the results obtained in crystallizing the glass by different methods—during stepwise heating of massive specimens with the use of a special holding period at a specified temperature and during continuous heating of glass powder in the DTA process—coincide completely.

Thus, on the basis of the results of the investigation, the entire process of glass crystallization up to the formation of the final crystalline phase—α-cordierite—may be represented as proceeding in several principal stages, namely:

1 —precipitation of the first crystalline phases—solid solutions of the anosovite and silica O types; 2 —decomposition of the solid solutions with the formation of quartz, spinel, and rutile; 3 —transformation of spinel into sapphirine; 4 —interaction of sapphirine with quartz with formation of cordierite.

Such a stepwise character of the process is typical of solid-state reactions (⁀9). In this case the course of the reaction, described by a number of investigators in the synthesis of cordierite from a mixture of crystalline oxides, is analogous to that obtained by us in glass crystallization. A. S. Berezhnoi and L. I. Karjakin (⁀10) showed that the primary product of the reaction in the system SiO_2 $-Al_2O_3-MgO$, at any ratios of the oxides, is spinel, whose interaction with quartz leads to the formation of sapphirine or cordierite, depending on the composition of the initial mixture. W. Eitel (⁀11) notes a close relationship of sapphirine with spinel and cordierite; in particular, during incongruent melting of sapphirine, spinel separates as a solid phase. According to Friedman (⁀12), natural sapphirine and cordierite are formed as a result of a secondary reaction from spinel.

It is interesting to note that in our studies of the crystallization process of glass of cordierite composition with the addition of TiO_2, no separation of the low-temperature form of cordierite—μ-cordierite—was observed (7). The reason for this may have been the considerable amounts of extraneous impurities (in this case TiO_2). In connection with this, μ-cordierite was synthesized by the method proposed by Karkhanavala and Hummel (7). The melted glass of pure cordierite composition was cast, ground until it passed through a sieve with 10,000 openings/cm^2, and then crystallized at a temperature of 850°. X-ray phase analysis of the material showed that, as the first phase after 70 h of heat treatment, in this case as well, a compound is formed whose X-ray pattern is identical to that of solid solutions based on high-temperature quartz ($d =$ 4.41; 3.39; 2.23; 1.85). Only increasing the duration of heat treatment to 150 h led to the formation of a crystalline phase whose interplanar spacings correspond to those for μ-cordierite according to (7) ($d = 4.49$; 3.45; 2.27; 1.88).

However, this dependence of the interplanar spacings of the resulting crystalline phase on the conditions of its synthesis—namely, a gradual increase in the interplanar spacings (for example, for the 100% maximum, from 3.39 to 3.45)—makes it possible to conclude that this phase is not a compound of constant composition, but rather a solid solution. In this connection, it appears most probable that the phase obtained by a number of investigators as an independent low-temperature modification of cordierite ([7],[13]) is in fact one of the members in the series of solid solutions based on high-temperature quartz.

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