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Abstract

Full Text

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Electron-Microscopic Study of the Catalyzed Crystallization of Glasses of the System

$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$

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In the present work an electron-microscopic study was carried out of the catalyzed crystallization of a glass close in composition to spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$). Titanium dioxide, introduced into the glass in an amount of 1-10 wt.%, was used as the crystallization catalyst. Heat treatment of glasses with a weight content of TiO_2 differing by 1% was carried out in a gradient furnace in the temperature range 500-1400° for 24 hours.

The structure of the glasses was studied by the replica method, the replicas being obtained from the surface of a fresh fracture of the specimen. In a number of cases the surface of the specimens was polished. To reveal the glass structure, etching was carried out for 5-15 sec in 10% hydrofluoric acid. Both carbon replicas with preliminary shadowing of the surface with a Pt (80%)-Pd (20%) alloy^(1,2) and replicas obtained by simultaneous evaporation of carbon and platinum were used. Shadowing was performed at angles of 15-30°. The replicas were separated from the specimens by means of a thick gelatin film, which was subsequently dissolved in hot water.

In the work, certain results of an electron-microscopic study of the influence of TiO_2 additions on the process of catalyzed crystallization of lithium aluminosilicate glass are compared. According to the results of the study, the glasses are divided, depending on the TiO_2 content, into two groups with sharply different crystallization processes. The first includes glasses with additions not exceeding 3%; the second group includes all the remaining glasses, with TiO_2 contents from 4 to 10%.

Visual inspection of boats with glasses that had undergone heat treatment in a gradient furnace shows that the changes occurring in the glasses of the first group during heat treatment do not differ from the processes taking place during treatment of the initial glass without TiO_2 addition. Glasses in the temperature region 500-800° remain as homogeneous and transparent as the initial glass; electron-microscopic examination confirms that no noticeable structural changes are observed in this case. Visible crystallization of the glasses of this group occurs at temperatures of about 850°. Electron-microscopic examination makes it possible to observe large blocks 5-7 μ in size; with further increase of the

temperature to 1350°, the block sizes increase continuously, reaching 60 μ (Fig. 1, see insert, p. 729). The block sizes decrease when the amount is increased to 3%.

Visual inspection of boats with glasses of the second group (4–10% TiO₂), which had undergone heat treatment in the temperature interval 500–1400°, makes it possible to divide the entire crystallization process into several stages as the temperature is raised.

1. At the first stage no visible changes occur in the glass.
2. With further increase in temperature, a sharp darkening of the glass is observed.
3. The glass again becomes lighter and slightly opalescent.
4. With further increase in temperature, the opalescence disappears.
5. Finally, strong opalescence appears again, and then the glass crystallizes completely with the formation of an opaque, dense material.

According to the results of the electron-microscopic investigation of glass with 6% TiO₂ during the first stage, covering the temperature range 500–650°, no structural changes are observed in the glass samples; the crystalline phase is absent (Fig. 3a, see inset, p. 729).

Other methods of investigation during this period show changes in a number of glass properties, such as optical properties, chemical durability, and density. Apparently, at this stage a hidden preparation of the glass for the subsequent crystallization process takes place.

The most important, from the standpoint of obtaining a glass-ceramic material, are stages 2, 3, and 4, covering the temperature range 650–850°. In this temperature range, small (0.05–0.1 μ) rounded crystalline formations appear in the samples, the number of which increases continuously with increasing treatment temperature (Fig. 3b). If at first the crystalline formations are isolated and far apart from one another, subsequently they already fill the entire space, being separated from one another only by a thin interlayer of the glass phase.

The next stage (850° and above) is characterized by the fact that, along with the fine-crystalline phase, a coarse-crystalline phase separates in the glass. In cross section the crystals have a shape close to hexagonal. With increasing temperature the crystal sizes increase successively (Fig. 3c, d).

In photographs of opaque, crystallized samples (1000° and above), groups of small (up to 0.1 μ) rounded crystalline formations are always observed, similar to those seen in photographs of transparent or opalescent samples treated at lower temperatures (650–820°). The fine-crystalline phase is concentrated mainly at the centers of large blocks (Fig. 3d, e, f), and its amount decreases with further

increase in the heat-treatment temperature.

Heat treatment of glasses containing more than 5% TiO_2 at temperatures above 1000° leads to the appearance, along with the main crystalline phase, of crystals having the form of sharply elongated prisms, sometimes knee-shaped twinned crystals (Fig. 2). It may be assumed that these are crystals of rutile or aluminum titanate.

The investigation showed that the crystallization process of a glass close in composition to spodumene changes depending on the amount of titanium dioxide introduced. Volume crystallization occurs only for glasses containing 4% TiO_2 and more. This is apparently connected with the fact that titanium dioxide promotes the formation in the glass of extremely fine regions of phase separation, which are centers of crystallization of the main phase. In glass of the given composition, a titanium dioxide content below 4% proves insufficient for the formation of phase-separation regions; therefore the course of crystallization of these glasses practically does not differ from that for glass without titanium. The transition from glass to a completely crystallized material takes place very rapidly—at a temperature of about 900° , bypassing the stage of formation of small crystallites (Fig. 1).

By the crystal-optical method it was established that up to approximately 900° the main crystalline phase in glasses containing 0–3% TiO_2 is β -eucryptite, and above 900° it is β -spodumene.

With a content of 4% TiO_2 and more in the glass, the transition from transparent glass to opaque glass occurs over a broad temperature interval. For glass with 6% TiO_2 this transition occurs in the interval from 650 to 850° . The maximum number of crystalline particles, with their small sizes, is observed for this glass at a treatment temperature of about 840° .

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Note: Figure translations are in progress. See original paper for figures.

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