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Abstract

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F. K. ALEINIKOV

APPLICATION OF ULTRATHIN SECTIONS FOR DIRECT ELECTRON-MICROSCOPIC INVESTIGATION OF GLASS CRYSTALLIZATION PROCESSES

(Presented by Academician N. N. Semenov on 8 May 1964)

In the process of catalyzed crystallization of glass, a special place is occupied by the so-called precrystallization period, the temperature regime of which has a significant influence on the subsequent stages of crystallization. Elucidating the kinetics of changes in the structure of the material during the precrystallization period is of not only theoretical but also great practical importance. However, at present precisely this stage of the crystallization process is the least studied because of methodological difficulties. For studying the precrystallization period, the X-ray method cannot be used (with the exception of the method of small-angle X-ray scattering), since the crystalline phase is still absent in the material. Electron-microscopic investigation with the use of replicas also is not entirely successful.

For direct electron-microscopic investigation of crystallization processes we have for the first time used ultrathin sections suitable for studying the fine structure of glass and the subsequent stages of crystallization. To prepare thin sections both of the initial glass and of materials at various stages of crystallization, we used an LKB-4800 ultratome with a diamond knife. For electron-microscopic investigation of the thin sections, a JEM-5 microscope was used.

As objects for the present investigation we used a lithium silicate glass, relatively well studied by other authors (^1), of composition 16.67 $Li_2O \cdot 83.33\ SiO_2$ (mol. %); a glass taken from work (^2): 17.4 $MgO \cdot 24.3\ Al_2O_3 \cdot 45.2\ SiO_2 \cdot 13.1\ TiO_2$ (parts by weight), with the conventional designation A; and a glass taken from work (^3), of composition 12 $Li_2O \cdot 20\ MgO \cdot 80\ SiO_2 \cdot 0.01$ Pt (in parts by weight), designated B.

The melted glasses were quenched from a temperature of 1500°C on a metal substrate. After thermographic investigations of these glasses had been carried out, they were subjected to heat treatment at the corresponding crystalliza-

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Figure 1

Figure 1: Figure 1

tion temperatures. It turned out that even the initial quenched lithium silicate glass throughout its entire volume contains numerous particles (regions) of phase separation. When this glass is heated, the number and size of the phase-separation particles both increase, and on contact the particles merge into particles (spherulites) of considerable size, as is seen in the example of glass heated at 560° for 30 min (Fig. 1a). However, after crystals of lithium disilicate of considerable size formed in the glass during crystallization, as a result of which a material was obtained consisting of a silica-rich framework filled throughout its volume with crystals of lithium disilicate, thin sections no longer always give a clear idea of the structure of the glass-crystalline material.

In this case, sections 800-2000 Å thick, treated for 10-30 sec with a 2-4% solution of hydrofluoric acid, give a clearer picture. Here, because lithium disilicate is several tens of times faster

To the article by F. K. Aleinikov

Fig. 1. **a-v**—glass of composition $16.67Li_2O \cdot 83.33SiO_2$ (mol. %): **a**—560°, 30 min; **b**—840°, 2 hr; **v**—560°, 50 hr, treated with a 2-4% HF solution. **g-zh**—glass of composition $45.2SiO_2 \cdot 17.4MgO \cdot 24.3Al_2O_3 \cdot 13.1TiO_2$ (wt. parts): **g**—initial; **d**—additionally heated for 10 min at 680°; **e**—the same +740°, 20 min; **zh**—the same +950°, 30 min. **z-m**—glass of composition $12Li_2O \cdot 20MgO \cdot 80SiO_2 \cdot 0.01Pt$ (wt. parts): **z**—initial; **i**—the same, additionally heated for 5 min at 600°; **k**—the same +640°, 30 min; **l**—the same +680°, 30 min; **m**—the same +750-930°, 40 min.
a-m—50,000× (25,000 × 2).

dissolves in comparison with silicon dioxide, it dissolves completely and a framework remains, consisting of silicon dioxide or else of its crystalline phase. In this case one can observe not only a more contrasty, to some extent three-dimensional picture of the material under study, but also the structure of the framework. If we compare the structure shown for lithium disilicate glass treated for 2 hours at a temperature of 840°, obtained with the use of a thin section (Fig. 1), and the structure of this glass treated at 560° for 50 hours (Fig. 1), obtained by means of sections treated with a hydrofluoric-acid solution, it is not difficult to be convinced of the advantage, in this case, of using thick sections. If in the thin section we see only separate parts of the framework (in the figure this place is circled), then in the thick sections treated with a hydrofluoric-acid solution we clearly see not only the places of dissolved lithium disilicate, but also the structure of the framework of the quartz phase itself (Fig. 1). That this is indeed the quartz phase is confirmed by X-ray analysis, since we carried out not only electron-microscopic but also X-ray studies of these glasses. It is interesting to note that after the crystallization of, for example, lithium disilicate is completed, its individual crystals continue to coarsen; at the same time the framework also undergoes changes, as a result of which a coarser structure of it is formed. Moreover, the process of aggregation of lithium disilicate crystals proceeds faster, and a coarser framework structure is obtained, at higher temperatures of heat treatment.

However, for studying the kinetics of crystallization, crystallization during heating in the electron microscope of ultrathin sections of glasses proved to be the most graphic, since in this case it is possible to observe one and the same place throughout the entire crystallization process. At the same time, we are, of course, aware that the character of crystallization in an ultrathin section may differ to some extent from crystallization occurring in the bulk of the material because of the absence of steric hindrance.

In Fig. 1 — the crystallization of magnesia-aluminosilicate glass A is shown. In the section of the initial glass we see that this glass has indistinct microinhomogeneities (Fig. 1), as do ordinary transparent glasses (~5). After heating this glass at a temperature of 680° for 10 min, the first crystals appear (Fig. 1). However, along with individual chaotically scattered crystals, a whole series of larger microinhomogeneities is formed in the glass in comparison with the microinhomogeneities of the initial glass. With further heat treatment, the size of the microinhomogeneities, or regions of liquid immiscibility, increases. It is interesting to note that here destruction and migration of the previously precipitated individual crystals are observed, and then continuous crystallization of the section begins. It should be noted that primary crystallization in this case proceeds more actively in the region of the primary crystals (Fig. 1). At the beginning of crystallization, individual crystallites have an irregular shape; with further heating, crystals of an increasingly well-defined shape are formed. With further heating, individual crystals, owing to forces of attraction, begin to accumulate into aggregates, from which crystals of comparatively large size subsequently grow. It should be noted that in the process of restructuring of the crystals, as is seen from Fig. 1 , many different defects arise. Apparently, analogous defects, although to a lesser degree, also occur during the crystallization of massive glasses; it is unlikely that the viscous glassy phase would fill all the defects formed in the glass-crystalline material, all the more so because with prolonged crystallization of the amorphous glass mass itself, there probably remains only an insignificant amount of it, or else it is entirely absent. The presence of defects may also explain the fact that, with prolonged crystallization of glass-crystalline materials, as shown in work (~4), their strength decreases considerably.

In order to clarify the possibility of investigating, by the method of ultrathin sections, the role of another, most widely used catalyst in the crystallization process, we carried out an electron-microscopic study of a lithium magnesium silicate glass of composition B, containing platinum (Fig. 1 —). When a section of this glass is examined, even under the action of electron beams—apparently as a result of heating of the section—microinhomogeneities are formed that are

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richer, in comparison with the rest of the glass mass, in metallic platinum (Fig. 1). After heating this glass at 600° for 5 min, the microinhomogeneities that have formed begin to coalesce (join together) into larger inhomogeneities (Fig. 1), and after 30 min of heating at a temperature of 680°, crystals begin to separate out, at first of a less regular form and then of a fairly regular one (Fig. 1). According to X-ray data (^3), lithium disilicate and forsterite crystallize from this glass. After completion of the crystallization of lithium disilicate, upon further heating, along with the outlines of lithium disilicate crystals, stratification is first observed in the section, and then crystallization of magnesium silicates (Fig. 1 ,). With further heating, as in the case of crystallization of magnesium aluminosilicate glass A, individual crystals begin to group into aggregates —at first of several crystals, and then into aggregates of considerable size; in this process, as in the crystallization of the glasses mentioned earlier, numerous defects are formed. At a temperature of 750–930°, fairly perfect magnesium silicate crystals of considerable size grow from numerous individual crystallites. The growth kinetics of these crystals are approximately as follows: after the formation of numerous randomly arranged crystallites, upon further heating of the section they begin gradually to group, to join together, and gradually to create clear outlines of the future crystal (Fig. 1). It should be noted that if at first the outlines of individual crystallites are still visible on the crystals formed in this way, then with further heating they disappear completely, and the crystal attracts other, smaller crystals and continues its further growth.

Thus, we see that the ultrathin sections first applied by us for the direct electron-microscopic study of materials at various stages of their crystallization are chiefly most suitable for studying their structure at the initial stages of crystallization; while for studying the subsequent stages of crystallization, comparatively thick sections treated, in the case of the Li_2O-SiO_2 system, with a solution of hydrofluoric acid are more suitable. For a direct and visual study of the kinetics of the process of glass crystallization, the most suitable approach is the use of ultrathin sections with their subsequent heating. Especially promising is the direct electron-microscopic study of thin sections, begun by us, with the application of the microdiffraction method (after complete processing of these data, the results will be published in a separate article). In this case, along with the electron-microscopic study of the kinetics of the crystallization process, more complete data will be obtained on the appearance or disappearance of crystalline phases.

Although in the present work we did not set ourselves the task of systematically studying crystallization processes and the role of catalysts in the crystallization process of glass-crystalline materials, nevertheless, from the data presented it is already possible to draw certain conclusions about the crystallization process and the role of the catalyst. Thus, at the first stages in lithium silicate glasses, individual particles (spherulites), formed as a result of liquation, unite into aggregates of large size, from which the corresponding crystals subsequently crystallize. Analogous processes also occur when catalysts are used; only in this case crystals crystallize out from particles of comparatively smaller size.

The action of catalysts, in particular, can be explained by the fact that catalysts form primary crystals (when TiO_2 is used) or micro-inhomogeneities (in the case of Pt), and, in the process of diffusion of the catalysts in the glass mass, defects are created (ruptures, sites with weakened energy bonds, etc.), as a result of which the glass mass becomes more reactive. Apparently, during liquation without catalysts the glass mass also becomes more defective and thereby more reactive.

It should be noted that after, according to X-ray diffraction analysis, some phase has completely crystallized out, the crystallization process does not cease; rather, further aggregation of individual crystals and of the remaining mass of material takes place, as a result of which numerous defects appear in the glass-ceramic material which, along with other factors, reduce the strength of these materials.

Institute of Chemistry and Chemical Technology
Academy of Sciences of the Lithuanian SSR

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