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Abstract

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CHANGE IN THE STRUCTURE OF CERTAIN GLASSES DURING THE PROCESS OF GLASS-CERAMIC FORMATION

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Physical chemistry

The physicochemical properties of glass-crystalline materials obtained by the method of controlled bulk crystallization of glass—glass-ceramics ([1–15])—are determined to a considerable extent by the heat-treatment regime of the initial glasses containing crystal nuclei. Establishing the regularities in the change of the structure and physical properties of glass during the process of glass-ceramic formation has not only theoretical but also great practical importance for obtaining new materials with specified properties.

The present article gives the results of electron-microscopic studies of structural changes in glasses in the system Li_2O—Al_2O_3—SiO_2 with various crystallizing additions (catalysts)—at 710° with TiO_2 (glass No. 1) and at 775° with ZrO_2 (glass No. 2)—and also establishes the correspondence between structural changes and changes in physical properties.

Earlier ([15]), one of the authors established the regularities in the change of the physical properties of these glasses during heat treatment, confirmed by X-ray structural analysis. It turned out that the process of glass-ceramic formation in the temperature interval studied consists of three periods (Fig. 1). The initial period, which may be defined as precrystallization, is characterized by the absence of substantial changes in the main physical properties—density ρ, refractive index n_D, and coefficient of thermal expansion α. The difference in the shapes of the curves of deformation under one-sided compression at this stage of crystallization, obtained in a quartz dilatometer ([15,16]), for different glasses is determined by the character of the changes in the viscous flow of the specimens. The abrupt change in all physical properties observed in the second, principal stage of crystallization at a given temperature is associated with the most intense separation of the crystalline phase. The steepness of the deformation curve suddenly increases as a result of the sharp rise in density. During the concluding (third) period of crystallization the physical properties change slowly, and the absolute values of ρ, n_D, and α may not only increase slightly but also decrease as a result of recrystallization. In accordance with the changes in density, the course of the deformation curve also changes; at the final stage of crystallization, under the adopted load, it depends mainly on the change in density.

Figure 1

Figure 1: Figure 1

In order to connect the previously established regularities in the change of the physical properties of glasses during glass-ceramic formation at constant temperature with changes in structure, an electron-microscopic study was carried out. The investigations were performed on a Tesla BS-242A electron microscope at direct magnifications of 3000-4000× with subsequent photographic enlargement. A replica technique was used, the replicas being obtained by simultaneous oblique deposition of platinum and carbon onto the specimen.

The initial glass No. 1 reveals small inhomogeneities 20-50 mμ in size (Fig. 2a), which are evidently the basis for the separation and growth, during subsequent heat treatment, of particles of a new phase. When this glass is held for one hour at a temperature of 710°, separate droplet-like particles 0.3-0.4 μ in size appear in it, with small

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Fig. 2. Electron-microscopic photographs of the structure of glass No. 1 as a function of holding time at 710°: *a*–initial glass; *b*–1 hour; *v*–1 hour 15 min.; *g*–1 hour 45 min.; *d*–2 hours 10 min.; *e*–2 hours 30 min.; *zh*–3 hours 30 min.; *z*–15 hours 25 min.

Fig. 3. Electron-microscopic photographs of the structure of glass No. 2 as a function of holding time at 775°. *a*–initial glass; *b*–1 hour; *v*–2 hours 30 min.; *g*–3 hours; *d*–3 hours 20 min.; *e*–3 hours 55 min.; *zh*–5 hours 30 min.

deviations from the average dimensions, the number and size of which increase as the duration of holding increases. Holding at a constant temperature for more than an hour leads to the formation of groups of two or three such particles, and the characteristic necks between them indicate that the groups may have been formed by coalescence of the initially formed droplets. With increasing holding time, the number of such aggregates and the number of particles in each of them increase until they fill the entire volume of the specimen. Beginning from this moment, the structure stabilizes and acquires an entirely different character; particles with average dimensions of 0.6μ acquire faceting,

Fig. 1. Changes in the physical properties and uniaxial compression deformation of glass No. 1 (catalyst TiO_2) as a function of holding time at 710°: **1** – compressive deformation $\left(\frac{\Delta l}{l_0}\right)$, pressure on the specimen 2.6 g/mm^2; **2** –average coefficient of thermal expansion in the temperature interval 20-300° (α); **3** – density (ρ); **4** –refractive index (n_D); **5** –coefficient of total light transmittance (τ).

and their number and dimensions subsequently do not change even when the holding time is increased to tens of hours. The changes in structure observed in

this series of specimens are unambiguously correlated with the curves of property change obtained for the same glasses: in the pattern of structural change, two breaks are found, corresponding to the inflection points of the curves (Figs. 2 and 2).

Similar structural changes can readily be traced for the series of specimens of glass No. 2 (Fig. 3). The series is also constructed according to the principle of increasing holding time at a constant temperature. The droplet-like microinhomogeneities observed in the initial glass, upon heating, give well-faceted crystalline particles, whose dimensions grow with holding. Subsequently these particles serve as the basis for the growth upon them of a secondary crystalline phase in the form of droplet-like particles.

The content of these particles in the specimen increases until they occupy the entire volume of the specimen. Thus, for this series of specimens as well, the two inflection points on the curve of the material properties are readily explained by sharp changes in structure associated with the onset of growth of a new phase (Fig. 3)

and with the completion of its growth at its maximum content (Fig. 3d). For both compositions studied, X-ray structural analysis showed that the round particles, which by their shape could easily be taken for droplets, are crystals. On some particles of this type, rays emanating from the center are visible, characteristic of spherulites.

From the illustrations presented it follows that the nature of the final structure is the same for both compositions; however, owing to the higher temperature of heat treatment, the particle sizes in the second glass are considerably larger.

Thus, the electron-microscopic study has established an unambiguous correspondence between the curves of the change in properties and the structural changes occurring in the glasses studied with increasing holding time at a constant temperature. A difference has been shown in the initial stages of the growth process of particles of the principal crystalline phase for glasses whose compositions differ only in the content of crystallizing additives: replacement of titanium oxide by zirconium oxide leads to a different initial structure of the specimen, while the overall pattern of crystallization and the crystalline phases are the same.

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REFERENCES

1. I. I. Kitaigorodskii, *Glass and Glassmaking*, Moscow, 1950.

2. I. D. Tykachinskii, I. O. Tomashevich et al., *Bulletin of the State Scientific-Research Institute of Glass*, **5**, 33 (1959).

3. I. D. Tykachinskii, *Proceedings of the Seminar on the Application of Glass and Glass Materials in Mechanical Engineering, Instrument Making, and Radio Electronics*, Collection No. 1, 1960.

4. S. M. Brekhovskikh, *Materials for the Conference of Workers of the Glass Industry in Vladimir in October 1958*, Moscow, 1958.

5. A. I. Berezhnoi, *Photosensitive Glasses and Glass-Crystalline Materials of the "Pyroceram" Type*, Moscow, 1960.

6. St. N. Lungu, D. Popescu-Has, *Industria Usoara Usoara*, No. 2, 63 (1958).

7. R. D. Maurer, *J. Appl. Phys.*, **29**, 1 (1958).

8. S. D. Stookey, *Glastechn. Ber. Sonderband. V Intern. Glaskongress*, **32**, Munich, 1959, S. I.

9. R. D. Maurer, *J. Chem. Phys.*, **31**, 444 (1959).

10. H. R. Lillie, *Class Technology*, **1**, No. 3, 115 (1960).

11. N. V. Solomin, V. I. Shelyubskii, N. M. Vaisfeld, *DAN*, **140**, No. 5, 1087 (1961).

12. R. D. Maurer, *J. Appl. Phys.*, **33**, No. 6, 2132 (1962).

13. S. I. Silvestrovich, E. M. Rabinovich, *Proceedings of the Moscow Chemical-Technological Institute named after D. I. Mendeleev*, issue 37 (1962).

14. K. T. Bondarev, V. A. Minakov, *Optical-Mechanical Industry*, No. 9, 26 (1962).

15. E. S. Sorokin, *Optical-Mechanical Industry*, No. 10, 33 (1962).

16. E. S. Sorkin, *Glass and Ceramics*, No. 10, 40 (1958).

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