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Abstract

Full Text

CHEMISTRY

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ON THE QUESTION OF THE FORMATION OF GLASS-MICROCRYSTALLINE STRUCTURES

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Recently, great importance has been attached to questions of the crystallization of glasses. The starting material is a melt consisting for the most part of silicates. In some cases, substances are introduced into the melt to form nuclei of crystalline phases in it—platinum, gold, and silver. Articles formed from the melt are subjected to heat treatment, the purpose of which is to bring about the formation in the article of crystalline phases in the form of small crystals, whose dimensions are measured in fractions of a micron. Acceleration of the process of formation of a microcrystalline structure for a number of materials of this group is achieved by ultraviolet and shorter-wavelength irradiation.

A substantial improvement in the properties of the crystallizing material, in comparison with the initial glasslike semi-finished product, can be achieved only with a sufficiently uniform structure in the size and concentration of crystalline formations. Therefore it is necessary to take into account the regularities in the separation of new phases in melts, noted earlier in works in which a special role was assigned to the process of redistribution of the sizes of newly formed particles, namely the growth of larger islands of the new phase with a simultaneous decrease in the sizes of small newly formed particles ([1],[2]).

Fig. 1. Electron-microscopic photographs of the structure of samples of crystallized glass held at the highest crystallization temperature of 1050°: *a* –1 hour, *b* –4 hours

In subsequent works, in which certain questions of the theory of formation of glass-microcrystalline structures were considered ([3]-[6]), attention was not

Fig. 2. Electron-microscope photographs of the structure of samples of the same glass crystallized under another regime at 1050° with holding: a –0 h, b –2 h, v –4 h, g –5 h.

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paid to the above-mentioned regularity; meanwhile, it is confirmed by direct experiment, as will be seen from the further exposition.

In accordance with the second law of thermodynamics, the indicated redistribution process is regular, because in this process the total area of the phase-boundary surface decreases and the entropy of the system increases.

The change in the area of the phase-boundary surface by an amount Δs and the change in the isobaric-isothermal potential ΔZ can be related by the following equation:

$$I\Delta s = \Delta Z,$$

where I is the factor of intensity of the surface energy.

As is known, the change in entropy is

$$\Delta S = -\left(\frac{\partial \Delta Z}{\partial T}\right)_p;$$

therefore, in the case of interest to us,

$$\Delta S = -\Delta s \left(\frac{\partial I}{\partial T}\right)_p,$$

and the change in enthalpy is

$$\Delta H = \Delta s \left[I - T\left(\frac{\partial I}{\partial T}\right)_p\right].$$

Fig. 2. Electron-microscope photographs of the structure of samples of the same glass, crystallized under another regime at 1050° with holding:
a –0 h, *b* –2 h, *v* –4 h, *g* –5 h.

For an experimental study of the process of redistribution of the sizes of newly formed particles during crystallization of glass whose composition included SiO_2, Al_2O_3, and TiO_2, the following experiments were carried out.

Fig. 3. Change in the sizes (R) and concentration (n) of crystals in samples of series II as a function of the duration of heat treatment at 1050°. 1 –sizes (length) of rutile crystals, 2 –sizes of disthene crystals, 3 –number of crystals of both phases in 1 cm^3

Figure 3: Fig. 3. Change in the sizes (R) and concentration (n) of crystals in samples of series II as a function of the duration of heat treatment at 1050°. 1 –sizes (length) of rutile crystals, 2 –sizes of disthene crystals, 3 –number of crystals of both phases in 1 cm^3

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Samples of the initial glass were subjected to crystallization under two different temperature regimes. At the final stage of the crystallization regimes, samples of both series were thermostated at 1050°. The samples in each of the series differed in the duration of holding at this temperature. The crystallized samples were examined on an EM-100 electron microscope by the method of carbon replicas (7) at a magnification of 14000×. Fresh fractures of the samples were studied. To reveal the fracture relief, the fractures were etched in 12% HF for 5-20 sec.

During crystallization of the glass studied, two crystalline phases are mainly separated in it; by X-ray structural analysis they were identified as disthene and rutile.

Disthene crystals have the form of short prisms with dimensions almost identical in all directions; rutile crystals are strongly elongated prisms with smaller faces beveled in the form of pyramids.

The change in structure as a function of the duration of heat treatment for samples of the first series is shown in Fig. 1, and for the second–in Fig. 2.

Table 1 and Fig. 3 present typical results of measurements of the concentration of particles and their sizes, obtained by electron-microscopic–

···microscopic photographs. It is necessary to note the comparatively small scatter in the sizes of the crystallites of each of the phases under a given heat treatment.

Electron-microscopic study of the crystallization kinetics showed that, with increasing duration of heat treatment at constant temperature, coarsening of the crystals occurs and their number decreases without a change in the phase composition; this can be explained by the diffusional absorption of smaller crystals by larger ones.

Table 1

Duration of heat treatment, h	Size of diopside crystals, μ	Size of rutile crystals (length), μ	Total number of crystals in 1 cm^3
1	0.11	0.38	$18 \cdot 10^{13}$
4	0.33	0.56	$2.2 \cdot 10^{13}$

The foregoing shows that the process of redistribution of the sizes of microcrystalline formations during heat treatment is very substantial.

Since the presence of compositional inhomogeneities in the initial semi-finished product contributes to broadening of the size-distribution band of newly formed particles in the initial and, consequently, in the final stage, in order to achieve the greatest homogeneity of the glass-microcrystalline structure it is necessary to ensure maximum homogeneity of the glassy semi-finished product in chemical composition.

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