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Figure 1

Figure 1: Figure 1

Abstract

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ELASTIC PROPERTIES AND CRYSTAL FORMATION IN GLASSES

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Scientific research and experimental work in recent years in the field of the synthesis and study of the properties of photosensitive glasses has led to the discovery of a method for obtaining glass-crystalline materials of a new type, possessing high mechanical strength, thermal stability, and other valuable properties.

Fig. 1. *1*—curve of the dependence of deformation on temperature for the initial glass; *2*—thermogram of the initial glass

The combination of interesting technological and technical features of these materials immediately attracted broad attention from researchers.

We have investigated the mechanical properties of the initial glasses and glass-crystalline materials of two systems: 1) alumino-potassium-lithium-silicate (AKLS), 2) alumino-magnesium-titanium-silicate (AMTS).

In principle, the behavior of the materials of these systems proved to be identical; therefore, in what follows the results of their study are generalized.

The deformation-temperature dependence of the initial glasses under a constantly acting load and heating (Fig. 1, curve *1*) shows that in the temperature interval 20°—T_g the magnitude of their deformation does not change. At temperatures above T_g a deformation jump is observed; the point T_k is revealed quite clearly, above which, in contrast to ordinary glasses (point T_3 (1)), the curve goes with a noticeable downward slope (temperature interval T_k—T_{k1}). Then, with a further increase in temperature, a secondary increase in deformation is observed (interval T_{k1}—T_{k2}). Above the point T_{k2} the deformation curve runs parallel to the abscissa axis up to the point T_f^*.

The thermogram of the glasses, plotted in the same figure (curve *2*), shows that the increase in deformation at temperatures above T_g corresponds to an endothermic effect; the slope of the deformation curve above T_k is associated with an exothermic effect and, finally, the changes at the points T_k and T_{k2} correspond to the second endothermic and exothermic effects.

In addition to the deformations developing in the interval during the process of continuous– during heating under a continuously acting load, we investigated the deformation values corresponding to each temperature point separately. It turned out that the greatest deformations during heating of the initial glass develop in the interval T_g—T_k, and the smallest occur on the plateau in the interval T_{k2}—T_f. Intermediate deformation values belong to the intervals T_k—T_{k1} and T_{k1}—T_{k2}. Unlike ordinary glasses, the magnitude of the elastic deformation in the segment T_k—T_f is not greater, but less than the deformation of the segment 20°—T_g. The changes occurring in the interval T_k—T_f make the behavior of crystallizing glasses different from that of ordinary glasses (1,2). In the final analysis the differences amount to an increase in rigidity (a decrease in elastic deformations) in the interval T_k—T_{k1}, to breaks at the points T_k, T_{k1}, and T_{k2}, and, finally, to a very extended interval T_{k2}—T_f; in this last interval the system is no longer a glass but a glassy-crystalline material with gradually changing phase composition and structure.

To clarify the nature of these changes, we carried out an investigation using the quenching method.

The initial glasses were subjected to various heat treatments. One and the same initial glass was heated to the temperatures: T_g, T_g—T_k, T_k, T_k—T_{k1}, T_{k1}—T_{k2}, and T_{k2}—T_f (see Fig. 1). At the indicated temperatures, various holding times were applied, from minutes to hours, after which the specimens were quenched in air.

As a result of microstructural analysis of the experimental specimens, it was found that crystallization does not occur up to the temperature T_g. In the interval T_g—T_k, individual crystallized regions were observed in some glasses.

In specimens held at the temperature T_k, against the background of the glassy phase there were found clearly expressed individual crystallized regions (Fig. 2; see insert to p. 1364), the number and volume of which increased as the holding time was increased. The structure of a completely crystallized glass is shown in Fig. 3 (see insert to p. 1364).

The size of the crystals ranges from 2 to 4 μ. A small amount (approximately 5-7%) of glassy phase is distributed between the crystals. It should be noted that

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[*] T_g–temperature at which softening of the initial glass begins; T_k–temperature of effective crystallization; T_f–temperature of transition to the liquid state; T_g—T_k–temperature interval of the formation of crystallization centers; interval T_k—T_{k1}—T_{k2}–temperature interval of crystallization, in which the interval T_k—T_{k1} is the principal one. T_k—T_f–temperature interval of the glass-crystalline material.

Fig. 4. Dependence of the elastic modulus on temperature. 1 –initial glass, 2 –crystallized glass (glass-crystalline material)

Figure 2: Fig. 4. Dependence of the elastic modulus on temperature. 1 –initial glass, 2 –crystallized glass (glass-crystalline material)

the crystallization process should not be greatly prolonged in time. According to our observations, long holding times are not useful and are even harmful, since they promote the growth of crystals, whose excessive size leads to loosening of the structure and loss of strength. The optimum holding time is established experimentally for each system.

Specimens held in the interval T_{k1}—T_{k2} and T_{k2}—T_f for various times showed no essential difference in structure compared with specimens held at the temperature T_k—T_{k1}. The deformation changes and secondary thermal effects (Figs. 1, 2) in the interval T_k—T_{k2} are apparently associated with crystallization of a second glass phase present in small amounts. It was of great interest to follow the kinetics of crystallization during heat treatment. With the aid of Leonov' s high-temperature microscope (^{3}), we were able to carry out some experiments in this direction.

Glass specimens were heated in the microscope with a slow rise in temperature and were continuously observed in polarized light. Up to the temperature T_g, no changes were detected in them.

At temperatures in the interval T_g—T_k, and especially near the point T_k, the finest bright points–the centers of crystallization (crystal nuclei)–appeared on the surface of the experimental piece from its various sides. Gradually increasing, as the holding time at the given temperature increased, these points grew into separate, finely crystallized regions. The crystallites were anisotropic; when the microscope stage was rotated, extinction was observed.

With a further increase in temperature, the crystallized regions, expanding, drew closer together and joined. The structure (Fig. 3) shows the final stage of crystal formation, when the scattered crystallized regions have merged into a single fine-crystalline structure.

In the interval T_{k^2}—T_f, no substantial changes in the structure were observed.

Figure 4 gives curves of the elastic moduli of the initial glass and of the glass-crystalline material being formed at different stages of their heating. As can be seen, the value of the shear modulus of the crystallized glass under room-temperature conditions is approximately 1.5–2 times higher than that of the initial glass.

Fig. 4. Dependence of the elastic modulus on temperature. 1 –initial glass, 2 –crystallized glass (glass-crystalline material)

This value remains constant also upon heating up to the point T_f of glass-crystalline materials, above which the values of the elastic moduli decrease sharply (plastic deformations and flow begin).

In Fig. 4 we already see the "relaxation well" known for ordinary glasses and the sharp break corresponding to the point T_k (^{1,2}). In the temperature interval of crystallization T_k—T_{k^2}, strengthening is observed. In the interval T_{k^2}—T_f the elastic moduli change hardly at all.

All the samples we obtained with different heat treatments were subjected to bending tests under room-temperature conditions and upon heating.

The greatest strength was shown by samples held in the interval T_k—T_{k1}. The strength (σ in bending) of these samples was 2400 kg/cm^2.

From the experimental materials presented, it is evident that changes in the elastic and strength properties of glass-crystalline materials during their crystallization are closely connected with changes in their structure; the most favorable formation of this structure requires, for each system, a definitely established heat-treatment regime.

The temperature range of increased elastic and strength properties of glass-crystalline materials is significantly expanded not only in comparison with the initial glasses, but also in comparison with a number of well-known ceramic materials (porcelain, fireclay, dinas, magnesite, chromomagnesite, etc.), which places them among the most heat-resistant and thermally stable materials.

The study of the elastic and plastic deformations of the initial glasses as a function of temperature and holding time can serve as a reliable and rapid method for identifying the optimum heat-treatment conditions with the aim of obtaining high-quality glass-crystalline materials.

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