PHASE TRANSITIONS, NUCLEATION, AND NANOCHEMISTRY

The Kinetics of Crystallization of Solid Solutions in a Glass of the Stoichiometric Composition Na₂O · 2CaO · 3SiO₂

V. M. Fokin[1], O. V. Potapov[2], V. L. Ugolkov[2], E. D. Zanotto[3], and F. M. Spiandorello[3]

[1] Vavilov State Optical Institute, Birzhevaya liniya 12, St. Petersburg, 199034 Russia

[2] Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, ul. Odoevskogo 24/2, St. Petersburg, 199155 Russia

[3] San Carlos Federal University, San Carlos, Brazil

Abstract—The crystallization of a glass of the stoichiometric composition Na₂O · 2CaO · 3SiO₂ was shown to proceed with the nucleation and growth of solid solution crystals whose composition was enriched in sodium compared with the initial glass and approached the stoichiometric composition during the phase transition. Crystal growth was accompanied by changes in the composition of the glass in a partially crystallized sample, which in turn caused nucleation termination at the early phase transition stages and slowed down the growth of nuclei. The reason for the nucleation of crystals with a shifted composition is discussed within the framework of the classic nucleation theory.

When strongly cooled glass-forming melts crystallize, nucleated crystals are difficult to identify because most of the methods for measuring nucleation rates deal with crystals whose size is 2–3 orders of magnitude larger that the critical nucleus size, which is on the order of several dozen angstrom units. Because of a series of unsuccessful attempts at applying the classic nucleation theory to quantitatively describe the rate of crystal nucleation in silicate glasses, the possibility of formation of metastable phases that catalyze the nucleation of the stable phase observed in experiments has been broadly discussed in recent years [1].

The formation of solid solutions typical of silicate systems allows another possible reason for the difference in properties between the critical nucleus and the macrophase to be considered. This is a continuous change in the composition of crystals during their isothermal growth from the critical size to a macroscopic phase. In this work, we present experimental evidence in favor of such a mechanism.

The composition of the glass that we studied, 17Na₂O · 33.2CaO · 49.8SiO₂ (mol %, analytic data), was close to the stoichiometric composition 16.7Na₂O · 33.3CaO · 50SiO₂ (mol %). The temperature dependences of the stationary nucleation rate obtained by the "development" method [2, 3] and of the rate of the growth of nuclei at the early phase transition state, when the crystallized volume fraction (α) does not exceed 0.05–0.10, are shown in Fig. 1. According to the X-ray data, the crystals represent a solid solution based on the Na₂O · 2CaO · 3SiO₂ metasilicate structure [3]. Changes in the a parameter of the hexagonal unit cell depending on (1) the crystallized volume fraction and (2) the content of sodium oxide are shown in Fig. 2. Dependence 2 was obtained for completely crystallized

glasses of various compositions [2, 3]. Comparing dependences 1 and 2 leads us to suggest that a decrease in the a parameter with increasing α is caused by a decrease in the content of sodium in the crystals.

This suggestion is substantiated by the X-ray spectral microanalysis data shown in Fig. 3. Dashed lines 1 and 2 correspond to the Na and Ca contents in the crystalline phase calculated from the experimental data on glass composition changes. Compared with the glass, the crystals are enriched in sodium and depleted of calcium. The composition of the crystals approaches the stoichiometry of the initial glass as α increases. The dependence of the composition of the crystals on the crystallized volume fraction allows us to suggest that
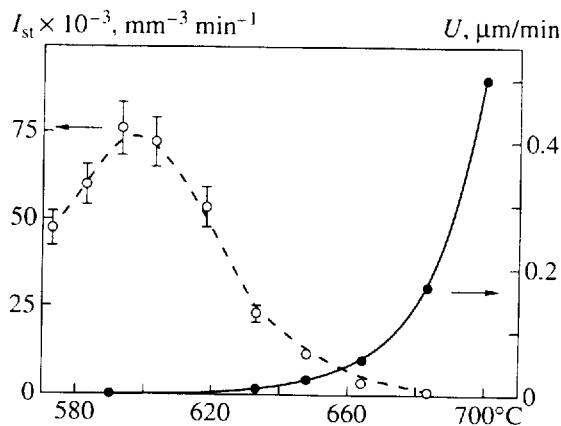

Fig. 1. Temperature dependences of the rates of nucleation I_{st} and growth U of crystals in the glass of the Na₂O · 2CaO · 3SiO₂ stoichiometric composition [2, 3]. The dashed line is given for clarity. The solid line approximates the experimental data according to the exponential law.
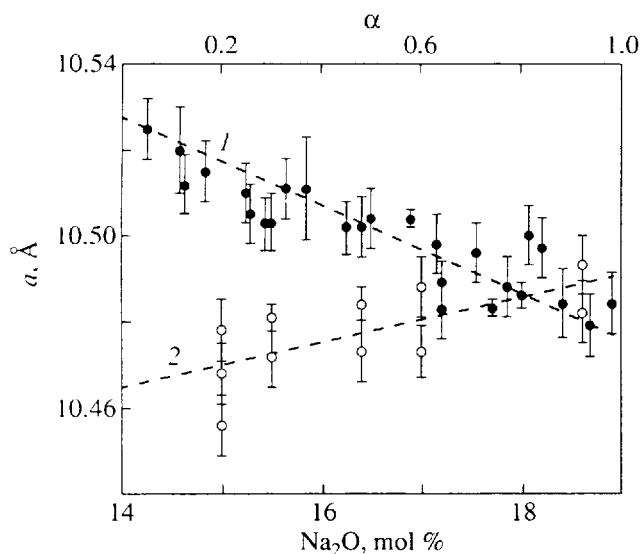
Fig. 2. Dependences of the *a* hexagonal unit cell parameter on (*1*) the fraction of crystallized volume and (*2*) the content of sodium oxide. The straight lines are drawn through the experimental points by the method of least squares.

Fig. 3. Dependences of glass and crystal compositions on the crystallized volume fraction at 650°C. The contents of the elements (M) in the glass were determined by X-ray spectral microanalysis. The solid straight lines were drawn through the experimental points by the method of least squares. Dashed lines *1* and *2* are the contents of Na and Ca in the crystalline phase calculated from the experimental data on glass composition changes. Dashed lines *3* and *4* are the contents of Si and O in the initial glass.

the crystals of the critical size are also enriched in sodium. The contents of Si and O virtually do not change in the glass (and, therefore, in the crystals); that is, composition changes during crystallization do not affect the silicon–oxygen carcass and only involve redistribution of Na and Ca. According to the slopes of linear dependences *1* and *2*, changes in the composition of the crystals occur with the replacement of Ca by 2Na, which corresponds to a series of $Na_{4+2x}Ca_{4-x}[Si_6O_{18}]$ solid solutions with $0 \leq x \leq 1$ [4].

Changes in the composition of the crystals during glass crystallization strongly shift the reversible polymorphic phase transition temperature T_{pm}, which is substantially lower than the glass transition temperature T_g (570°C). According to the differential scanning calorimetry and dilatometry data, an increase in α from 0.5 to 1 is accompanied by a decrease in the content of sodium in the crystals and increases the T_{pm} temperature by ~150 K [3].

The difference between the composition of the crystals and that of the glass in a partially crystallized sample causes the formation of diffused zones depleted of sodium around the crystals. The rate of nucleation rapidly decreases as the content of sodium oxide in the glass lowers [2, 3], and new crystals virtually do not form in the diffused zones, whereas nucleation and crystal growth continue in glass regions situated fairly far from the crystals already formed [3, 5]. It is natural to expect that nucleation in the system should stop when the diffused zones surrounding the growing crystals coalesce. This conclusion follows from an analysis
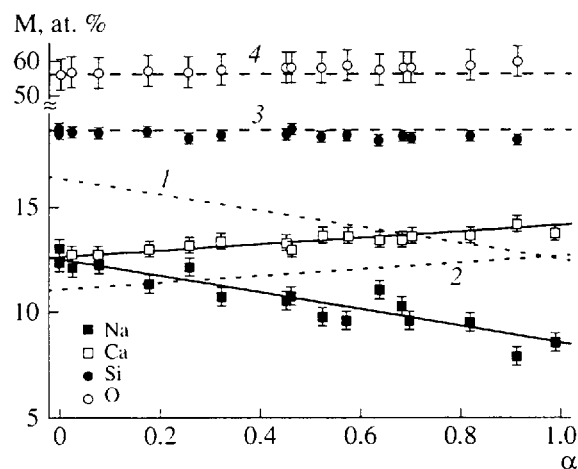
of the kinetics of isothermal mass crystallization, which is often described by the Avrami equation [6]

$$\alpha(t) = 1 - \exp(-Kt^n), \qquad (1)$$

where K includes such parameters as the rate of crystal growth and the rate of nucleation (or the number of growing crystals when the number of crystals is constant) and n is the so-called Avrami coefficient, which can be determined from the slope of the dependence of $\ln[-\ln(1 - \alpha(t))]$ on $\ln t$. For three-dimensional growth, the Avrami coefficient can be written in the form

$$n = k + 3m, \qquad (2)$$

where k and m are the exponents with which time enters into the equation for the number $(N \sim t^k)$ and size $(R \sim t^m)$ of crystals.

When n and m are determined from experimental $\alpha(t)$ and $R(t)$ dependences, the k value characterizing nucleation can easily be found. The dependences of the crystallized volume fraction and the size of the largest crystals on the time of thermal treatment at 650°C are shown in Fig. 4 in the corresponding coordinates. These dependences can conventionally be divided into two approximately linear regions corresponding to the following n and m values: $n \approx 4$ and $m \approx 1$ up to $t \approx 150$ min and $n \approx 1$ and $m \approx 0.33$ at t exceeding 150 min. It follows that, according to (2), k changes from 1 to 0. This means that, at the early phase transition stage ($\alpha < 0.2$), nucleation and crystal growth occur at constant rates, whereas, at $\alpha > 0.2$, the number of crystals does not change, and the kinetics of mass crystallization is only determined by crystal growth. It follows that, starting with $\alpha \approx 0.2$, the nucleation rate becomes negligibly
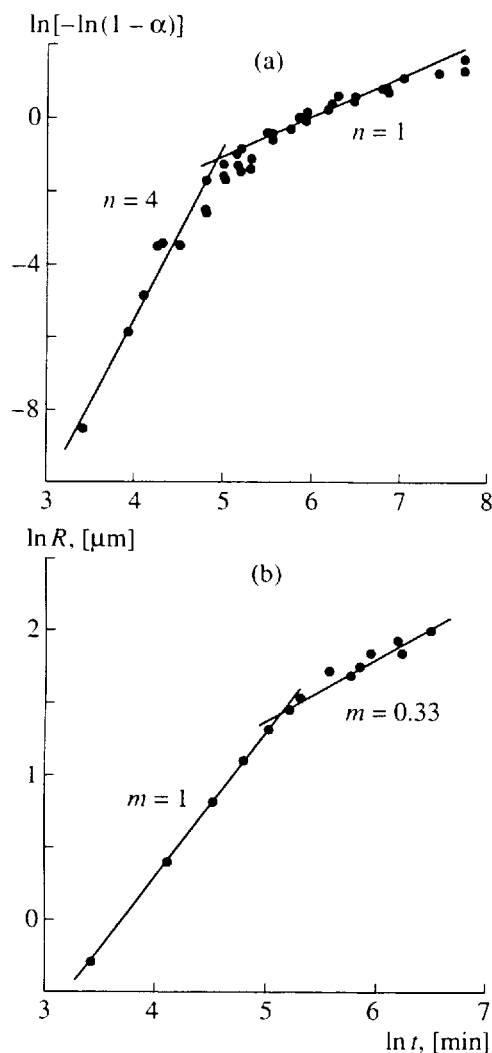
Fig. 4. Dependences of (a) $\ln[-\ln(1-\alpha(t))]$ and (b) $\ln R$ on $\ln t$ (α is the crystallized volume fraction, R is the size of the largest crystals, and t is the time of thermal treatment at 650°C). The straight lines are drawn through the experimental points by the method of least squares.

$$W^* = \frac{16\pi}{3}\frac{\sigma^3}{\Delta G_V^2}, \qquad (4)$$

where W^* and ΔG_D are the thermodynamic and kinetic nucleation barriers, respectively, and σ is the specific Gibbs energy of the crystal/liquid interface.

A deviation of the critical nucleus composition from the stoichiometric composition of the glass can only increase the kinetic barrier. Nucleation with the formation of crystals of a shifted composition therefore occurs as a result of a lowering of the thermodynamic barrier caused by their enrichment in sodium. This leads us to suggest that a decrease in the thermodynamic driving force ΔG_V is balanced by a decrease in surface energy σ [see (4)].

The conclusion of a decrease in surface energy caused by an increase in the content of sodium oxide was also made in [2, 3] based on an analysis of the concentration dependence of the rate of nucleation in glasses of compositions close to $Na_2O \cdot 2CaO \cdot 3SiO_2$.

The suggested interpretation of the nucleation of solid solution crystals in the $Na_2O \cdot 2CaO \cdot 3SiO_2$ stoichiometric glass is in conformity with the Ostwald step rule generalized in [7]: "In phase transitions, the properties of a critical nucleus can qualitatively differ from the properties of not only the initial but also the final macrophases. The transformation process is determined by those critical nuclei to which a minimum work of formation corresponds (compared with other alternative structures and compositions that can form under given thermodynamic conditions)."

low. Nucleation termination is observed even at the temperature corresponding to a maximum nucleation rate ($\approx$590°C) when α reaches 0.1–0.15 [3].

The described results are a consequence of a substantial deviation of the composition of the crystals from the stoichiometric composition of the initial glass, evidently starting with crystals of the critical size. Such a deviation should decrease the thermodynamic driving force of crystallization (ΔG_V). Nevertheless, the formation of solid solution crystals enriched in sodium is an experimental fact. According to theory (e.g., see [6]), the stationary homogeneous nucleation rate in a supercooled liquid can be written in the following general form:

$$I_{st} = A\exp\left[-\frac{W^* + \Delta G_D}{k_B T}\right], \qquad (3)$$

REFERENCES

1. Burgner, L.L., Lucas, P., Weinberg, M.C., Soares, P.C., Jr., and Zanotto, E.D., *J. Non-Cryst. Solids*, 2000, vol. 274, p. 188.

2. Potapov, O.V., Fokin, V.M., Ugolkov, V.L., Suslova, L.Ya., and Filipovich, V.N., *Fiz. Khim. Stekla*, 2000, vol. 26, no. 1, p. 39.

3. Potapov, O.V., Kinetics of Nucleation and Growth of $Na_2O \cdot 2CaO \cdot 3SiO_2$ Crystals in Glasses of the Composition Close to Stoichiometry: Effect of Water and Variations in Composition, *Cand. Sci. (Chem.) Dissertation*, St. Petersburg, 2001.

4. Ohsato, H., Takeuchi, Y., and Maki, I., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1990, vol. 46, p. 125.

5. Fokin, V.M., Potapov, O.V., Chinaglia, C.R., and Zanotto, E.D., *J. Non-Cryst. Solids*, 1999, vol. 258, p. 180.

6. Christian, J., *The Theory of Transformations in Metals and Alloys*, part 1: *Equilibrium and General Kinetic Theory*, Oxford: Pergamon, 1975. Translated under the title *Teoriya prevrashchenii v metallakh i splavakh*, Moscow: Mir, 1978.

7. Schmelzer, J.W.P., Schmelzer, J., Jr., and Gutzow, I.S., *J. Chem. Phys.*, 2000, vol. 112, no. 8, p. 3820.