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Influence of preformed nuclei on crystal nucleation kinetics in soda–lime–silica glass

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ABSTRACT

An unusual form of the time-dependence of the number $N(t, T_n)$ of nucleated at a temperature T_n crystals was obtained for a soda–lime–silica glass of the composition $22.4Na_2O \cdot 28.0CaO \cdot 49.6SiO_2$ (mol.%). The crystals are solid solutions based on the $Na_2O \cdot 2CaO \cdot 3SiO_2$ compound. The analysis of the nucleation kinetics was performed for a nucleation temperature T_n located well below the temperature of the maximum of the steady-state crystal nucleation rate. Following to the development method, supercritical clusters formed at the temperature T_n have been developed at a temperature $T_d > T_n$ in order to reach measurable sizes. A large number of crystals, $N(t, T_n, T_d) = N_o$, was detected by this method already at $t = 0$. With an increasing nucleation time, the number of developed crystals gradually increases with a temporary tendency towards saturation. After this transient stage, the crystal number gradually increases again and a linear $N(t, T_n, T_d)$-dependence corresponding to the steady state nucleation rate is established. These uncommon features are the consequence of the growth at the nucleation temperature of the nuclei preformed in the course of glass preparation with sizes between critical sizes corresponding to the nucleation T_n and development T_d temperatures.

1. Introduction

Studying crystal nucleation in silicate glasses one usually assumes that the process of nucleation starts from monomeric units supposing that critical and supercritical crystal nuclei are absent in the glass samples at the initial moment of time $t = 0$ when the nucleation temperature T_n is reached. In other words, it is assumed that the process of crystal nucleation takes place only at the given nucleation temperature T_n. Under such conditions, the dependence of the cluster number $N(t, T_n)$ formed at a temperature T_n versus time t has a shape as shown in Fig. 1. A non-linear increase of the crystal number with time observed in the initial stage of the process gradually approximates a linear one. Accordingly, the crystal nucleation rate, $I(t) = dN/dt$, increases with time and approaches its stationary value I_{st}.

Such behavior can be easily interpreted in terms of classical nucleation theory (see e.g. [1]) and is confirmed as a rule by experimental results [2]. In the first stage of the process (denoted as transient nucleation), a steady-state cluster size distribution is established in the range up to the critical cluster size. Once this process is completed, nucleation proceeds further with the time-independent steady-state nucleation rate I_{st} resulting in a linear time-dependence of the number of supercritical clusters, i.e. $N(t, T_n) \approx I_{st}(T_n)t$. The intersection point of the prolongation of the linear part of the $N(t, T_n)$-curve with the time axis determines the induction period t_{ind} (or the time lag in nucleation $\tau = 6t_{ind}/\pi^2$). An illustration of these features of the $N(t, T_n)$-curves is given in Fig. 1. The experimental data for the number of the supercritical nuclei, the $N(t)$-curve shown there, can be described theoretically by Eq. (1) [3,4]

$$N(t, T_n) = I_{st}\tau\left[\frac{t}{\tau} - \frac{\pi^2}{6} - 2\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}\exp\left(-m^2\frac{t}{\tau}\right)\right]. \tag{1}$$

At large times, from Eq. (1) the asymptotic dependence for $N(t)$

$$N(t, T_n) = I_{st}\left(t - \frac{\pi^2}{6}\tau\right) \tag{2}$$

as given by Eq. (2) is obtained as a special case. To estimate the number of nucleated crystals the development method was employed. According to this method supercritical clusters formed at the temperature T_n have been developed at a temperature $T_d > T_n$ in order to reach measurable sizes. Note, that the experimentally observed curve $N(t, T_n, T_d)$ is shifted along the time axis relative to $N(t, T_n)$ by period of time

$$t_o(T_n, T_d) = \int_{r^*(T_n)}^{r^*(T_d)} \frac{dr}{U(T_n, r)} \tag{3}$$

(where $U(T_n, r)$ is the growth rate of a cluster of size r at nucleation temperature and $r^*(T_n)$ and $r^*(T_d)$ are the sizes of critical nuclei at indicated

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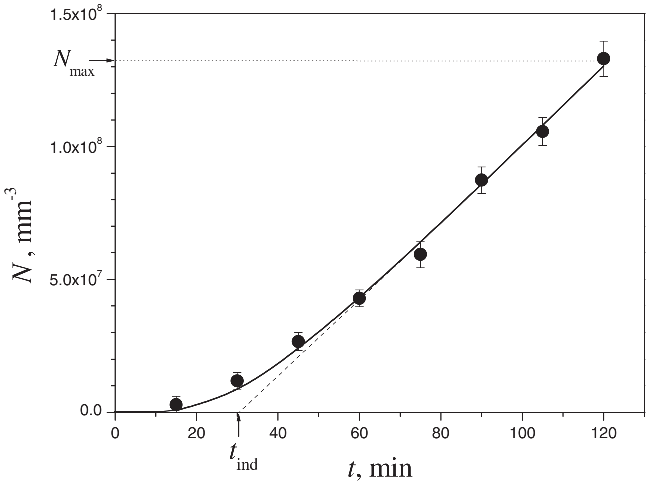

Fig. 1. The typical $N(t)$-curve for the number of nucleated crystals in a silicate glass of composition $22.4Na_2O\cdot 28.0CaO\cdot 49.6SiO_2$ (mol.%) at a temperature $T_n = 557$ °C ($T_d = 650$ °C). The solid and dashed lines are plotted with Eqs. (1) and (2), respectively ($I_{st} = 2.50\cdot 10^{13}$ m^{-3} s^{-1}, $\tau = 20$ min).

temperatures) since only crystals that achieve at T_n the critical size corresponding to T_d could be developed via deterministic growth (see e.g. [2]).

In the present paper, we report experimental results and develop a theoretical interpretation of the time-dependence of the number $N(t, T_n)$ of nucleated crystals in a soda–lime–silica glass of the composition $22.4Na_2O\cdot 28.0CaO\cdot 49.6SiO_2$ (mol.%). The clusters have bulk properties of solid solutions based on the $Na_2O\cdot 2CaO\cdot 3SiO_2$ compound. The analysis of nucleation kinetics was performed for a nucleation temperature T_n well below the temperature T_{max} of the maximum of the steady-state crystal nucleation rate. In contrast to described above conventional dependencies $N(t, T_n)$ vs t (illustrated in Fig. 1) we obtained in the experiments an unusual step-like curve on the first stage of nucleation heat treatment. The present paper is devoted to an analysis of the origin of this unusual shape of the $N(t, T_n, T_d)$-curve.

The paper is structured as follows: In Section 2 a brief outline is given on materials and methods employed in order to establish the dependence of the crystal numbers formed at the temperature T_n on time t. In Section 3, an overview on the main experimental results is given. Section 4 is devoted to a theoretical analysis of these data. Both the origin of the conventional course of the $N(t, T_n)$ vs t dependencies (illustrated in Fig. 1) is discussed as well as the possible cause for deviations from such kind of dependence and an explanation of our experimental results are given. The paper is completed by conclusions.

2. Material and methods

The soda–lime–silica glass under investigation was synthesized from chemically pure reagents Na_2CO_3, $CaCO_3$ and SiO_2. The components were thoroughly mixed. The glass was melted in an electric furnace, using a platinum–rhodium crucible, by keeping it at a temperature of 1400 °C for 3 h. The melt was cast then onto a cold steel plate. According to the chemical analysis, the composition of the obtained glass was $22.4Na_2O\cdot 28.0CaO\cdot 49.6SiO_2$ (mol.%). This glass composition belongs to the metasilicate section $CaO\cdot SiO_2$–$Na_2O\cdot SiO_2$ of the ternary soda–lime–silica system. According to the phase diagram of this section [5], the glass composition lies in the interval between the compositions $Na_2O\cdot 2CaO\cdot 3SiO_2$ and $Na_2O\cdot CaO\cdot 2SiO_2$, where solid solution on the basis of $Na_2O\cdot 2CaO\cdot 3SiO_2$ is crystallized. It was shown [2] that in glasses with compositions in this interval the crystal nuclei of solid solutions enriched by sodium oxide as compared with stoichiometric crystal $Na_2O\cdot 2CaO\cdot 3SiO_2$ are formed. According to Ref. [2] in the glass under study the critical nuclei have the composition close to $Na_2O\cdot CaO\cdot 2SiO_2$.

The temperature dependence of the steady-state nucleation rate, $I_{st}(T)$, has as a rule a dome shape with a maximum at the temperature T_{max} close to the glass transition temperature, T_g. This shape is determined by the interplay of an increase of the viscosity and an increase of the thermodynamic driving force for crystallization with decreasing temperature [2], i.e. by the interplay between the kinetic and thermodynamic barriers for nucleation. In the present analysis, we performed the nucleation experiments at a temperature $T_n = 515$ °C. This temperature is located well below the glass transition temperature $T_g = 540$ °C and the temperature $T_{max} = 571$ °C of the maximum steady-state nucleation rate [6].

The number of nucleated crystals was determined by the double-stage (development) method. According to this method crystals nucleated at the temperature T_n, are grown up to microscopic sizes at higher temperature T_d (development temperature). In our experiments, $T_d = 650$ °C is located well above the maximum of the steady-state nucleation rate. Therefore, the nucleation rate at this temperature is small and the number of crystals nucleated for the short time $t_d = 3$ min of heat treatment at this temperature could be neglected.

The quenched glass pieces had a maximum size about 5–6 mm. After the heat treatments the surface layer of the samples was removed by grinding. Then the sample surfaces were polished. To enhance the image contrast the samples were etched into a solution of 0.01 normal hydrochloric acid for 10 s.

Sample sections were analyzed by optical microscopy in reflected light (Neophot 32, Carl Zeiss Jena). Since at $T_d = 650$ °C the crystals grew as spherulites with spherical shape and their size distribution was close to a monodisperse one, N was estimated via the following stereological formula [7]

$$N = n_s/d_{max}, \tag{4}$$

where n_s is the number of crystal traces per unit area of the sample section and d_{max} is the diameter of the largest crystal traces that is equal to the real diameter of crystals.

Then the dependence of the crystal number $N(t, T_n, T_d)$ on time of heat treatment at the given temperature of nucleation T_n was determined.

The heat treatments of the glass samples were performed in an electrical shaft furnace at temperatures maintained within ±1 °C. A substantial stainless steel cylinder equalized the temperature throughout the space around the samples.

3. Results

The experimentally observed kinetic dependence of the number $N(t, T_n, T_d)$ of crystals nucleated at the temperature of 515 °C is shown in Fig. 2a. Its shape is qualitatively different from the usually obtained curves as shown in Fig. 1. A large number of crystals is observed already at $t = 0$ ($N_o \equiv N(t = 0, T_n, T_d) \cong 360{,}000$ mm^{-3}). Further, with increasing nucleation time an increase in the number of crystals is observed with a tendency to achieve a constant value N_s, approximately equal to 870,000 mm^{-3} (the interval a–d in Fig. 2b). With a further increase of heat treatment time ($t > 1000$ min) at the nucleation temperature T_n, an increase in the number of crystals is resumed and the dependence of the crystal number on time is approaching a linear one (the interval d–e in Fig. 2b). The two parts of the $N(t, T_n, T_d)$ curve described above (a–d and d–e) are shown in more detail separately also in Fig. 2c and d, respectively. A theoretical interpretation of these results will be given in the subsequent section.