CRYSTAL NUCLEATION OF Li2O·2SiO2 GLASS REVISITED

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Detailed nucleation, growth and overall crystallization data has been obtained for a Li2O·2SiO2 glass treated at 500°C. It was shown that apparent “induction” periods of 1 to 3 hours, detected in single-stage treatments, are mostly due to the time required for growth of the critical nuclei to sizes detectable by optical microscopy. As the “induction” times determined by three distinct kinetic parameters are similar, it can be concluded that, any metastable phase that might nucleate in the early crystallization stages has no significant influence on the overall crystallization kinetics.

Introduction

The failure of the classical nucleation theory to describe crystal nucleation rates in glasses could, in principle, be assigned to the birth of metastable phases in the early crystallization stages. The case of lithium disilicate (LS2) glass is particularly interesting. For instance, in 1964, Kalinin et al.[1] observed spurious XRD peaks in substoichiometric LS2 glasses treated at 480°C. Kinser & Hench [2,3] in 1971 suggested the existence of a metastable phase in similar glasses, treated at 500°C, based on their SAXS patterns and electrical behavior. Interest on the subject was reawakened by the report of Deubener et al.[4]. These authors observed a difference of two orders of magnitude between the induction periods for nucleation and crystal growth at 490 °C, concluding that this was due to the nucleation of a metastable phase, which was confirmed by electron diffraction patterns of glasses treated at 454 °C. However, Deubener [5] later mentioned that due to fast degradation of the crystals under the electron beam, his diffraction data were subjected to some uncertainty. Hence, most evidence for appearance of metastable phases in lithium-silica glasses are indirect. Additionally, from nucleation rate determinations, Barker & James [6] concluded that no metastable phase appears in glasses with 31-36 mole % Li2O. Thus a long standing discrepancy exists concerning the nucleation mechanism of LS2 glass and should be clarified. The objective of this paper is to check Deubener’s proposition [4] for the early nucleation of a transient phase in LS2 glass, as inferred from the large difference between the induction times for crystal nucleation and growth. This will be accomplished by carefully measuring the apparent induction times from nucleation, growth and overall crystallization curves.

Theory

When a liquid is cooled below its melting point, crystal nucleation (see the classical nucleation theory [7]) followed by crystal growth of the nuclei, can lead to a polycrystalline material. The overall crystallization kinetics can be described by a theory
derived independently, by Kolmogorov [8], Johnson and Mehl [9] and Avrami [10-12], hereafter called KJMA theory. Avrami [10-12] has assumed that: (i) nucleation is random, (ii) nucleation occurs from a certain number of embryos (N) which are gradually exhausted; (iii) the growth rate (U) is constant, until the growing regions impinge on each other and growth ceases at the common interface, although it continues normally elsewhere. In these conditions, the volume fraction transformed, $\alpha$, can be easily calculated for two limiting situations. When the number of embryos is not exhausted until the end of the transformation (homogeneous nucleation) it is given by:

$$\alpha = 1 - \exp(-g I U^3 t^4/4), \tag{1}$$

where $g$ is a shape factor, equal to $4\pi/3$ for spherical grains, and $t$ is the time period.

For small $N$ (fast heterogeneous nucleation):

$$\alpha = 1 - \exp(-g N U^3 t^3) \tag{2}$$

If the induction periods, $t'$, for crystallization are significant, then $t$ should be replaced by $(t-t')$ in equations (1-2).

The KJMA theory can be shown to be exact within the framework of its assumptions. Hence, any violation must be a result of applying it to situations where its assumptions are not followed. Recently, Zanotto and co-authors[13-15] demonstrated that if accurate $I$ and $U$ data are obtained, the general theory predicts well the glass-crystal transformation for both homogeneous and heterogeneous nucleation.

**Experimental**

The glass was melted at 1350°C in a Pt crucible [16], and contained 33.2 mole% $\text{Li}_2\text{O}$ as well as 0.02 wt% “water” and 0.01 wt% $\text{Na}_2\text{O}$, as the main impurities; the levels of Fe and Al being much lower. The heat treatments were carried out in an electric furnace with a temperature control within 1°C. All specimens were heated at 500°C for periods from 5 to 95 hours. The samples treated from 5 to 20 hours were also subjected to a “development” treatment at 600°C for 10 minutes, so the majority of the crystals could be seen under an optical microscope. After standard polishing and etching the specimens were characterized by both transmitted (TLM) and reflected light microscopy (RLM) in a Neophot -Carl Zeiss- microscope equipped with a 25X objective for RLM and with a 100X objective lens for TLM. About 700 crystals were counted and measured per specimen, which led to an statistical scatter of $\pm$15%, within 95% confidence limits. Standard stereological procedures were employed for the determination of average number of crystals per unit volume, $N_v$, largest crystal dimensions and volume fraction crystallized.

Depending on the heat treatment conditions, specially for single-stage treatments, many crystals (and their two-dimensional planar cuts seen in the RLM micrographs) may still be smaller than the resolution limit of the microscope. This may cause underestimated nucleation densities and volume fraction transformed, and superestimated induction periods. Due to this problem all data were corrected by the equations derived by Zanotto & James [17] for reflected light microscopy.
The correct value of $N_v$ for transmitted light microscopy is simple given by

$$N_v \sim N_v e^{+l_e \Delta t}, \quad (3)$$

where $\Delta t = e/(2U_a)$ is the ratio between the resolution limit of the microscope used ($e \sim 1 \mu\text{m}$ for the $25X$ objective) and $U_a$ an estimate of the linear growth rate from length versus time curves. $l_e$ is an estimate of the steady-state nucleation rate from the uncorrected $N_v e$ versus time curves. In this work, the TLM data were underestimated by less than $3\%$, while the RLM data were underestimated by $6$ to $14\%$. Hence, these data were corrected in the way described above.

**Results and Discussions**

Figure 1 shows the crystal nucleation density data of LS2 glass specimens ($T_g \sim 450^\circ\text{C}$) nucleated at $500^\circ\text{C}$ for periods up to $20h$ and subjected to a development treatment at $600^\circ\text{C}$ for $10$ min., the well known double stage treatment. The resulting microstructures were analyzed by reflected light microscopy (RLM-DT). Figure 1 also shows the data obtained from specimens heated for longer periods (single-stage treatments), measured by both reflected (RLM-ST) and transmitted light microscopy (TLM-ST). Single-stage treatments are possible when crystal growth is sufficient to render the crystals large enough to be measured by optical microscopy, although crystals nucleated at the latest stages might still be below the resolution limit of the microscope.

It is worth mentioning that the linearity of the plot was maintained throughout the extensive range of treatment times and that the coincidence of the data points obtained by the two techniques (TLM-ST and RLM-ST) was excellent. This detail was essential to infer the steady-state nucleation rates from the line slopes ($784-799 \text{ /mm}^3\text{h}$), and the induction periods from the intercept on the time axis, $t^* = 3.0-2.4\text{hours}$ ($r^2 = 0.994$), for TLM-ST and RLM-ST, respectively. For RLM-DT, $I = 770 \text{ /mm}^3\text{h}$ and $t^* = 0.027h$ ($r^2 = 0.95$) resulted. If *uncorrected* RLM-ST data are used (not shown in the figure) an apparent induction time of 5.0 hours comes out from the time axis intercept. Thus, it is clear that the steady-state nucleation rates obtained with the three techniques coincide, while there is a pronounced difference in the induction periods determined by single-stage and double-stage treatments. This point will be discussed later.

The crystal growth curves for the minor and major half-axis of the ellipsoidal crystals, obtained with single-stage treatments at $500^\circ\text{C}$, with both techniques (RLM and TLM) are shown in Figure 2. The composite plots (using TLM+RLM data) are good straight lines which yield a growth rate $U_a = 0.00038 \text{ mm/h}$ from the slope and an apparent “induction” period $t^* = 2.0h$ ($r^2 = 0.94$) from the time axis intercept for the major axis, and $U = 0.00020 \text{ mm/h}$ and $t^* = 0.7h$ ($r^2 = 0.96$) for the minor axis. Obviously, these different values reflect the uncertainty related to the extrapolations from long time data to $t = 0$, and this defines the accuracy limits of our data.

The volume fraction crystallized of the Li$_2$O 2SiO$_2$ phase in the LS2 glass was also followed in the same specimens. As an “induction” period was observed in the nucleation and growth curves (for single-stage treatments), $t$ was substituted by $(t-t^*)$ in the
calculations of Equation (1). A straightforward way to analyze the time evolution of crystallinity is to use double-log plots. Hence, a \( \ln(1/(1-\alpha)) \) versus \( \ln(t-t') \) plot, shown in Figure 3, gives a straight line of slope 4.0, as predicted by Equation (1), with \( r^2=0.991 \), if \( t'=2 \text{hours} \) is used. For smaller values of \( t' \), the slope increases, being 4.17 for \( t'=0 \) Thus, this independent test confirmed that the induction period is in between 1 and 3 hours.

It is well established that nucleation curves often display an induction period, necessary to establish a steady-state distribution of embryos, as shown by Gutzow et al. [18] several years ago. The induction times for growth, however, do not have a clear connection to the first (see Wemberg [19]) but, instead, can be related to the early appearance of metastable phases (as shown by Ramsden & James for Baria-Silica glasses [20]) and/or to experimental limitations of the techniques. For instance, if the times required to grow super-critical nuclei (nm-range) to sizes detectable by optical microscopy (\( \mu \)-range) are significant, they manifest as apparent induction times in length versus time plots. We will demonstrate that this is the case for LS2 glass treated at 500°C. The calculation of such period, i.e., \( \tau = \int dr/U(\tau) \), integrated from the critical radius (8A) to a microscopic size can be performed through the expression of Kelton & Greer [21] which take into account a size dependent growth rate, \( U(\tau) \). However, their equation requires a knowledge of several unknown parameters, such as the diffusion coefficient and the surface energy. A detailed discussion about this problem will be presented elsewhere. Here, instead, a reasonable lower bound for \( \tau \), was estimated using the experimental growth rate (\( \partial D/\partial t=2.1 \times 10^{-10} \) m/s) and a resolution limit of 1\( \mu \)m, giving \( \tau \sim 1.3 \text{h} \).

Therefore, as the apparent experimental “induction” times determined by nucleation, growth and overall crystallization experiments are \( \sim 1-3 \text{ hours} \), one can conclude that the time needed for the first crystal to grow to detectable sizes is the main component of the observed “induction” periods.

When one examines the nucleation plots obtained from single-stage treatments, the experimental induction time is \( 2.4 - 3.0 \text{ hours} \), while that from the double treatment curve is only a few minutes. Thus, the induction periods obtained from nucleation, growth and overall crystallization experiments are quite similar (\( \sim 1-3 \text{ hours} \)), when they are measured using the same method (single-stage treatment); and reflect the period for the first crystal to grow to detectable sizes. Hence, the apparent discrepancy found by Deubener et al.[4], and confirmed here, when \( \tau \) is measured from nucleation (double-stage) and growth (single-stage) experiments, merely reflects the differences in the experimental techniques and has no bearing to the possible birth of a metastable phase.

**Concluding Remarks**

Detailed nucleation, growth and overall crystallization data has been obtained for a LS2 glass treated at 500°C, using both single-stage and double-stage heat treatments, employing reflected light and transmitted light microscopy. It was clearly demonstrated that apparent “induction” periods of 1 to 3 hours are mostly due to the time required for growth of the critical nuclei to sizes detectable by optical microscopy methods in single-stage treatments. When double-stage treatments are used, the development of small crystals during the second treatment reduces the induction period to only a few minutes at 500°C, which is close to the real incubation time for nucleation at this temperature. Hence, any metastable phase that might nucleate in the early crystallization stages has no significant role on the overall crystallization kinetics.
Figure 2. Principal axis of the largest ellipsoidal crystals of the distribution in a LS2 glass treated at 500°C measured by RLM-ST (□, φ) and TLM-ST (■, φ).

Figure 3. $\ln \ln \left(1 - \alpha \right)^{-1}$ versus $\ln \left(t - t' \right)$ for LS2 treated at 500°C. A value of $t' = 2h$ was used.
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References

5. J. Deubener- Personal communication, Jena, July (1994).

Figure 1. Crystal nucleation curves for LS2 glass at 500°C.