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Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Heating rate effects in time-dependent homogeneous nucleation in glasses

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ARTICLE INFO

Keywords:

Homogeneous crystal nucleation
 Induction time
 Transient nucleation
 Heating rate effect
 Lithium disilicate
 Glass

ABSTRACT

Nucleation kinetics of glass-ceramics is frequently determined using Tammann's double-stage heat-treatment. This method requires a complex deconvolution of the experimentally observed induction time (t_{ind}), i.e. the intercept of the linear part of the crystal number density curve with the nucleation time axis, into two components. In this paper, double-stage heat treatments were performed, with heating rates between the nucleation and development temperatures covering two orders of magnitude, in samples of a homogeneously nucleating glass-forming system, lithium disilicate. Our results show that t_{ind} increases with increasing heating rates with cubic root dependence. In accordance with the theory, t_{ind} was split into the intrinsic time required to establish a steady-state cluster size distribution, τ (time-lag) at the nucleation temperature and an incubation time (t_i), which is a size, heating rate and development temperature (T_d) dependent growth time. We demonstrate that the Collins-Kashchiev nucleation model performs poorly if t_i is approximated by the time needed to experimentally detect the first crystal. In contrast, the Shneidman approach is consistent with theory. We found that at any given nucleation temperature, t_i is a strong function of the heating rate, and is proportional to t_{ind} , whereas τ is a constant, as expected.

1. Introduction

Since the pioneering work of Tammann [1], double-stage heat treatments have been used to provide experimental access to the nucleation kinetics of undercooled glass forming liquids, especially for compositions showing small overlap between the nucleation and the crystal growth rate curves. This method has been extensively used for decades for the study of the crystal nucleation rates of oxide glasses, as reviewed by Fokin et al. [2]. Especially in the case of deeply undercooled silicate glass compositions, such as lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) [3–9], Tammann's method has been used to allow nucleation during the first treatment at a nucleation temperature (T_{nuc}) and to grow these nuclei to observable crystal sizes during the second hold at a development temperature (T_d), $T_d > T_{\text{nuc}}$ (Fig. 1A). Consequently, only supercritical clusters that have reached the critical size at the development temperature ($r^*(T_d)$), which are nucleated at T_{nuc} are able to grow at T_d , whereas the clusters that are smaller than $r^*(T_d)$ dissolve back into the glass matrix. As a result, the typical number density curves obtained from Tammann's double-stage heat treatment method show a time (t_0) which is required to detect the first crystal, then a prolonged non-stationary period, where the number density increases quasi exponentially over time, finally reaching the stationary nucleation regime, that is a linear increase of the crystal number density (N_v) with

nucleation time (t_{nuc}) [4,5,8,10]. From the stationary behaviour at long-time durations, the steady-state nucleation rate per unit volume ($I_0 = \text{slope of a } N_v \text{ versus } t_{\text{nuc}} \text{ curve}$) and the experimental induction time ($t_{\text{ind}} = \text{intercept with the } t_{\text{nuc}} \text{ axis}$) can be determined free of any theoretical assumptions (Fig. 1B).

The experimental induction time, t_{ind} , consists of three contributions: First, the intrinsic “time-lag”, τ , defined as the time the system takes to establish a steady-state cluster size distribution for clusters with sizes up to the critical cluster size at T_{nuc} ; second, the average time of formation of the first supercritical nucleus at steady-state nucleation, t_{ss} ; and finally a growth time, which is called herein incubation time t_i [2,11], correlated with the time for the growth of supercritical clusters to detectable sizes (depends on T_d). Following these considerations, t_{ind} can be approximated by [12]:

$$t_{\text{ind}}(T_{\text{nuc}}, T_d) \cong \tau(T_{\text{nuc}}) + t_{\text{ss}}(T_{\text{nuc}}) + t_i(T_d). \quad (1)$$

We note that the experimental induction time is called “lag-time”, i.e. $\tau_{\text{lag-time}}$ in Ref. [12]. To avoid confusion with the “time-lag” τ of Eq. (1), we use the name experimental induction time with the label t_{ind} instead. We will show in Section 4 that the incubation time and thus t_{ind} depend on T_d , and also on the heating rate between T_{nuc} and T_d . However, only the temperature dependencies of t_i and t_{ind} are stated in Eq. (1).

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Received 1 June 2017; Accepted 22 July 2017

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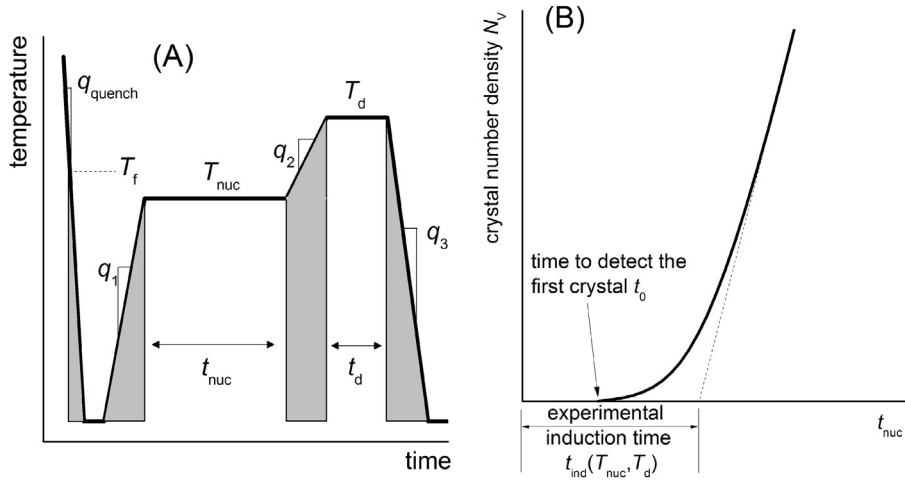


Fig. 1. Scheme of a double-stage heat treatment after Tammann (A). The grey areas indicate non-isothermal conditions. (B) Crystal number density vs. nucleation time.

For t_{ss} , the following relation holds [12]

$$t_{\text{ss}}(T_{\text{nuc}}) = (I_0 V)^{-1} \quad (2)$$

where V is the volume of the glass specimen and I_0 the steady-state nucleation rate. Using small sample sizes and temperature below the liquidus, where growth rates are very high but nucleation rates are generally small, t_{ind} of Eq. (1) can be governed by t_{ss} . Under these conditions, the incubation time is negligible and the inclusion of t_{ss} in τ can only be considered as a rough approximation of t_{ind} [13]. However in this study, regular sized samples (10^{-7} – 10^{-8} m³) and nucleation temperatures close to the maximum of the nucleation rate curve ($I_{0\text{max}} = 10^9$ – 10^{10} m⁻³ for lithium disilicate [3–9]) were used. Thus, t_{ss} is very small (10^{-1} – 10^{-3} s) and its contribution to t_{ind} can be neglected. Under these conditions, t_{ind} is approximated by [12]:

$$t_{\text{ind}}(T_{\text{nuc}}, T_d) \cong \tau(T_{\text{nuc}}) + t_i(T_d). \quad (3)$$

Eq. (3) shows that the time scale of the crystal number density curve (Fig. 1B) displays contributions of T_{nuc} as well as T_d . For deconvolution of these contributions, nucleation models have to be applied. In particular, a correction of the time scale is required, if such models only cover the on-going phenomena at the nucleation temperature. On the other hand, the uncorrected $N_V(t)$ curve can be used when the nucleation model includes the incubation time, t_i , which strongly depends on the development process (heating rate and T_d). In Section 4, both approaches will be analyzed. Furthermore, t_0 of the crystal number density curve (Fig. 1B) is not defined by Eqs. (1)–(3). Thus, it is unclear if t_0 can be used to correct the time scale of the double-stage heat treatment.

The overlap of the nucleation and growth rate curve of the liquid-to-crystal transition in lithium disilicate glasses to affect the induction times determined from double-stage heat treatments has been discussed [14–17]. In well-designed experiments, the typical development temperatures are chosen so the crystal nucleation at T_d is negligible (dwell times at T_d are only a few minutes and the nucleation rates are rather low), but the growth of supercritical clusters at the typical nucleation temperatures must be taken into account due to the prolonged heating times (several hours) normally used to reach steady-state conditions. Supercritical clusters can grow during that time period at T_{nuc} and also during the subsequent heating period from T_{nuc} to T_d . As a consequence, the number of supercritical clusters that have reached the critical size at the development temperature, $r^*(T_d)$, is the sum of those grown to that size during the treatment at T_{nuc} and during the subsequent heating period to T_d . They all contribute to the density of crystals counted after the development stage. For the latter, the heating rate q_2 from T_{nuc} to T_d (Fig. 1A) plays an important role because the critical cluster size is only governed by thermodynamics and increases with increasing temperature. Thus, supercritical clusters can become

sub-critical again and dissolve for certain heating rates when the temperature-dependent increase in critical size (due to heating with q_2) exceeds their growth rate [18]. This phenomenon has been named the “flushing effect” [14,15].

To tackle this problem, a few numerical and analytical calculations have been performed. Numerical calculations have been done by Kelton and Greer [19–21] who used the Becker-Döring equations to describe crystal nucleation in lithium disilicate glasses with a gain coefficient (frequency at which a cluster gains a molecule) based on the reaction rate theory. They pointed out that the induction time increases when the size of the supercritical clusters increase, which are used to detect nucleation (by increasing the development temperature). Davis [14,15] performed numerical simulations using the same Becker-Döring equations and gain coefficients, but showed that due to the flushing effect, an effective critical size (“survival” size) can be expected, which is lower than the critical size at the growth temperatures, but larger than the critical size at nucleation temperatures. A crucial point of their numerical analysis arises from the assumption made for the growth of supercritical clusters: In studies carried out by Kelton and Greer [19–21], a Turnbull-Fisher model for the size-dependent growth of supercritical clusters was used, and their numerical calculations predicted cluster sizes equal to 20 times that of the critical one in Ref. [22], which is much larger than the sizes covered by usual double-stage heat-treatments. On the other hand, Keding and Rüssel [17] used growth rates of micron (macroscopic) sized crystals, U_0 (a comprehensive data collection of these rates can be found in Ref. [23]).

An analytical expression for the transient nucleation flux as a function of the post nucleation heating rate (as in two-step nucleation/development treatments) was derived by Shneidman [24–27]. The heating rate dependence enters the solution through a survival size (r_s), which may or may not be close to the critical size at the development temperature.

Although the above discussed theoretical analyses have indicated a significant influence of the heating rate on the number density of crystals (Fig. 1B), most experimentalists and theoreticians neglect the effect of heating rates on the nucleation induction times and, in addition, experimental work is lacking. To the best of our knowledge, and to our great surprise, induction time and steady-state nucleation rate data for defined heating rates in double-stage thermal experiments have not been reported so far. This paper therefore aims at providing experimental evidence for this effect, and to shed some light on to what extent the induction times are affected by the experimental conditions of thermal treatment, especially by the heating rate from T_{nuc} to T_d .

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