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Letter to the Editor

Stochastic nature of the liquid-to-crystal heterogeneous nucleation of supercooled lithium disilicate liquid

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ABSTRACT

The inherent stochastic nature of the liquid-to-crystal heterogeneous nucleation of lithium disilicate is demonstrated by repeatedly supercooling the liquid of a single sample below melting temperature and reheating after crystallization inside a platinum container. Using this technique allowed us to determine the mean lag time τ_{av} ($=1769$ s) to nucleation of the survival curve, at which the half of 332 runs nucleated and the spread of the nucleation times δ ($=384$ s) with statistical significance. The evidence of a lag time distribution shows that crystal nucleation is a stochastic event, as predicted by classical nucleation theory, even when it is occurring at the same favorable site.

1. Introduction

Lithium disilicate glass is known to nucleate in the volume when annealed in the glass transition (T_g) range [1–6] (see also review in [7]), while at relative low degrees of supercooling (when the liquid is supercooled from the melting temperature T_m) the contact with platinum metal (container wall [8], thermojunction [9–11], and particles [12]) provokes heterogeneous nucleation. This is mainly a consequence of the thermal dependence of the nucleation and crystal growth rates (named as Tammann curves) with their maxima located at temperatures close to T_g (nucleation rate) and T_m (growth rate). Thus, heating-up a lithium disilicate glass will first allow nucleation and later (at higher temperatures) growth of each nucleus. The transformation of the entire ensemble of nuclei by the latter process is accompanied by an exotherm in differential thermal analysis (DTA) [13,14] and differential scanning calorimetry (DSC) [15]. On the other hand, the first critical nucleus (in the volume or at a surface) will grow fast and induces an exothermal signal alone if the lithium disilicate liquid is supercooled from T_m [8–12]. In any case crystal nucleation in the lithium disilicate liquid is expected to occur stochastically, which is usually masked by analyzing ensembles of at least a few hundred nuclei after annealing glasses for certain time intervals at a nucleation temperature and developing these nuclei to observable size at a higher temperature of negligible nucleation (double stage heat-treatment). Under these conditions the first time derivative of the crystal number density, i.e. the stationary nucleation rate, is constant, while for shorter times transient effects are evident and the nucleation rate is time-dependent. Further shortening of the nucleation hold will define the time required to nucleate the first crystal. This time is the lag time τ to nucleation. Lag time and transient nucleation have been explained by the classical nucleation theory (CNT) as the time required to “collect” enough energy via fluctuations to pass the near-critical size space and to establish a steady state nuclei distribution, respectively.

For supercooling the liquid below T_m, however, the first nucleus (most likely at the wall, if a container is used) will grow fast, which impedes the formation of a nuclei ensemble in the volume (the nucleation rate is extremely low at temperatures close to T_m). Thus, the analysis of this single nucleation event by its lag time will provide insights into the stochastic nature of nucleation if repeated for several times. Hereby, one assumes that for relative small degrees of supercooling the ergodicity of the system is valid. The ergodic hypothesis says that the volume average is equal to the time average [16]. By this approach a set of lag time data will be achieved, which again represents an ensemble of nucleation events. But now lag time of each event should be different if the stochastic nature of the nucleation process holds. A lag time distribution has been reported for freezing hydrous systems [16–18], but to the best of our knowledge such repeated supercooling experiments have not been performed in glass-forming silicate liquids. Here the question arises: Is a lag time distribution fundamental to the liquid-to-crystal transformation as predicted by CNT and, thus, also an observable phenomenon in the high-temperature viscous lithium disilicate liquid? The primary work motivation of the present study was therefore to explore lag times of crystal nucleation in a single lithium disilicate volume when cooled repeatedly from T_m. Further, the occurrence of a lag time distribution in the lithium disilicate liquid would have a tremendous consequence on the validity of critical cooling rates reported from single cooling runs [8–12] as well as calculations of continuous-cooling-transformation (CCT) and isothermal time-temperature-transformation (TTT) curves from these data [11,19].

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The present study has been inspired by the work of Barlow & Haymet [16] and Heneghan & Haymet [17,18], who developed an automated lag time apparatus (ALTA) for repeatedly supercooling a hydrous liquid. Using an automated feed-back control (reheating upon freezing), which is based on the change in optical transmittance through a water filled cell substantial time savings were achieved in conducting an experiment of several hundred cooling–heating cycles. Besides freezing pure and seeded water [16,18,20] ALTA has been used to study the stochastic nature of nucleation of tetrahydrofuran/water mixtures [21] and gas hydrates [22,23]. Their findings pointed out that freezing results from a random formation of a critical sized cluster and the presence of foreign particles (seeds) increases the probability of the nucleation, i.e. decreasing the mean lag time, without disturbing its stochastic nature. Further, these studies showed that the linear supercooling regime results in the same curve dependence than dwelling at a fixed supercooling temperature, with the drawback of eventually long times to capture nucleation using the latter method [17,18,24].

In order to access the time dependence of heterogeneous nucleation from repeatedly supercooling a single sample of lithium disilicate and analyzing the lag time with statistical significance the ALTA concept has been adopted by introducing a high-temperature differential scanning (DSC) calorimeter. In our experiment the cell is a Pt/Rh-pan and crystallization is detected by the characteristic change in the heat flow while crystallizing. In order to speed up the very time consuming experiment and in absence of an automated feed-back control a fixed temperature range (47 K above T_m and 233 K below T_m) was preset to run the experiment of 332 cycles automatically without further adjustment of the system.

2. Experimental

A high-temperature differential scanning (DSC) calorimeter (Netzsch DSC 404 F3 Pegasus, Selb, Germany) was equipped with Pt/Rh20 containers and lids. In one crucible a lithium disilicate glass chip (≈22 mg) was placed, which was split from a glass cylinder of a previous study (33.5 ± 0.4 Li_2O, 66.5 ± 0.4 SiO_2 (mol.%) [25], 130 ppmw H_2O [26]). The DSC experiment was performed in a characteristic way of repeatedly running heating–dwelling–cooling cycles under flowing nitrogen gas (Fig. 1). In particular the glass chip was heated to 1353 K (47 K above the melting temperature of lithium disilicate $T_m = 1306$ K [27]), dwelled 300 s and then supercooled to 1073 K, (first heating–dwelling–cooling run), subsequently heated to 1353 K, dwelled 300 s, supercooled again to 1073 K (second and all subsequent runs, see red dashed-dotted line in Fig. 1). The cyclic runs were repeated 332 times ($= N_0$) using a heating rate of 0.17 K s^{-1} but a cooling rate of $q = 0.083$ K s^{-1} before cooled finally to room temperature. For each run N the DSC protocol (blue solid line in Fig. 1) recorded the endothermic melting event (to ensure all crystals are melted during heating above T_m) and the onset temperature of the first exothermic crystallization peak (during supercooling below T_m). The latter was assigned to the nucleation temperature T as

$$\Delta T = T_m - T = q \times \tau \tag{1}$$

with $\Delta T =$ supercooling and $q =$ cooling rate. Hereby we consider τ as the lag time to form the first critical nucleus of the crystal phase within the supercooled liquid since the growth time during which this crystal nucleus consumes a large fraction of the entire DSC sample is many orders of magnitude smaller than τ [16]. Fig. 1 illustrates schematically the read-out of the DSC protocol of two subsequent cooling runs (N and $N + 1$) obtained under the experimental conditions described above. In particular from each cooling run a single lag time τ to nucleation was determined using the onset temperature of the crystallization peak and Eq. (1). The onset temperature T (= nucleation temperature) was obtained from the crossover of two tangents, which were aligned to the baseline and high-temperature flank of the peak, respectively. To determine ΔT the onset temperature was subtracted from T_m.

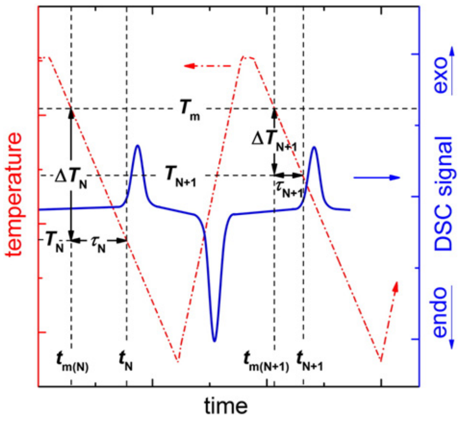

Fig. 1. Scheme of the DSC protocol capturing two subsequent cooling runs (N and $N + 1$). The red dashed-dotted line is the temperature of the heating–dwelling–cooling cycle. The black horizontal dashed lines are the melting temperature T_m, the nucleation temperature of run N (T_N) and the nucleation temperature of run $N + 1$ (T_{N+1}), respectively. The black vertical dashed lines are the times of passing the melting T_m ($t_{m(N)}$ for N and $t_{m(N+1)}$ for $N + 1$) and the nucleation temperature T (t_N for N and t_{N+1} for $N + 1$). The nucleation temperatures correspond to the crystallization onset of the DSC signal (blue solid line) of corresponding supercooling ΔT_N and ΔT_{N+1} (black vertical double arrow lines) and lag times τ_N and τ_{N+1} (black horizontal double arrow lines).

3. Results

Fig. 2 shows as the basic result of our experiment: lag time τ versus the run number N, (so-called "Manhattan" histogram [20–23,28–30]) as it is obtained from the read-out of the DSC protocol. Firstly, for each N crystal nucleation was recorded ($T_m > T > 1073$ K). Secondly, a noticeable spread of τ with N is evident and thirdly the silhouette of "Manhattan" appears to be horizontally, which indicates that during thermal cycling of lithium disilicate nucleation sites (probably at the container walls) continue to be affective and compositional effects (due to possible lithium evaporation and nitrogen gas solubility in the liquid) are negligibly small. Fig. 3 (upper part) shows the temperature at nucleation T as a function of the cooling rate × lag time for the data ($N_0 = 332$). The thin line is the actual recorded temperature of the first run during cooling. The symbols indicate T of each run. The lower part of Fig. 3 shows the survival curve, which we define according to Heneghan et al. [18] as the number of runs uncrystallized after lag time τ, $N(\tau)$ divided by the total number of runs N_0. To calculate the survival curve the lag times were sorted in the order from the lowest to the highest value. Then the uncrystallized fraction was calculated as

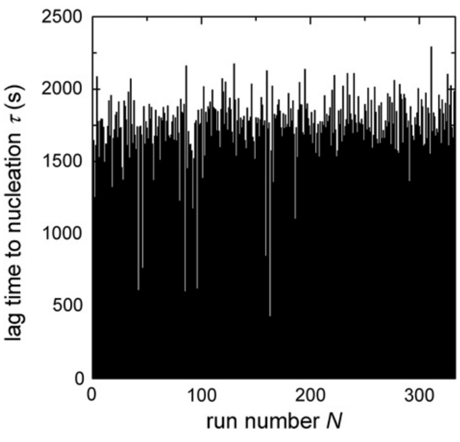

Fig. 2. Lag time τ as function of run number N ("Manhattan" histogram).