Journal of Non-Crystalline Solids 442 (2016) 34–39

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

On the variation of the maximum crystal nucleation rate temperature with glass transition temperature

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ARTICLE INFO

Article history:
Received 20 February 2016
Received in revised form 26 March 2016
Accepted 30 March 2016
Available online 9 April 2016

Keywords:
Nucleation
Glass transition temperature
Oxide glass-formers
Crystallization
Fragility

ABSTRACT

The variation of the maximum nucleation rate temperature (T^*) with respect to the glass transition temperature (T_g) is analyzed as a function of system parameters such as fragility. Calculated values are compared with experimental results for six stoichiometric oxide systems that are known to exhibit homogeneous nucleation. An examination of $T^*(T_g)$ relation supports the experimental observation that liquids having $T^* > T_g$ tend to exhibit homogeneous nucleation whereas only heterogeneous nucleation is observed in other systems.

1. Introduction

Below the melting temperature (T_M), a liquid is metastable against the stable crystal state. The crystal nucleation rate in a super-cooled liquid shows a maximum at some temperature (T^*) before vanishing at low temperatures [1]. There is considerable interest in understanding how T^* varies with various system parameters [2,3]. The maximum nucleation rate temperature plays an important role in the design of nano-structured glass-ceramics [4]. More importantly, as observed by James [5] and by Zanotto [6], it is a signature of the nucleation ability of a liquid. Systems having T^* greater than the glass transition temperature (T_g) tend to exhibit (in commonly accessible laboratory time/sample-size scales) homogeneous (internal or volume) nucleation while others, having $T^* < T_g$, show only heterogeneous (surface) nucleation. This suggests that the glass forming ability is better for systems having $T^* < T_g$. This paper reports an analysis of the variation of T^* with T_g as a function of system parameters such as fragility. The calculations are compared with experimental data in six stoichiometric oxide glass formers. These are the only (to our knowledge) stoichiometric oxide systems where homogeneous nucleation has been documented and for which sufficient thermodynamic and kinetic data are available to make the necessary calculations.

Similar to previous reported efforts in the literature [5–8] the present analysis uses a formalism based on the classical nucleation theory (CNT) in combination with the Stokes–Einstein (SE) equation for the atomic transport involved in nucleation, the Vogel–Fulcher–Tammann (VFT) expression for the temperature dependence of viscosity, and the Turnbull expression for the thermodynamic driving force for crystal nucleation. As has been pointed out [9], there are some fundamental issues with this phenomenology. While the failures of CNT in predicting absolute values of nucleation rates are well known [10,11], several investigations [5,7,12] have reported that the temperature dependence of the nucleation rate is well described by CNT, at least in the temperature range above T^*. Similarly, the SE and Turnbull equations are questionable approximations [13] but have been used frequently [2,7,8] to provide qualitative (i.e., generic) description of nucleation kinetics. The validity of VFT is also controversial (especially at very low temperatures, $T < T_g$) despite the fact that it fits the viscosity data well above T_g [14,15]. In spite of these shortcomings, several investigators [5,7] have successfully used this formalism to examine the temperature dependence of the nucleation kinetics in stoichiometric oxide melts. Our motivation to use this formalism lies in the fact that it permits quantitative results about the variation of T^* with T_g with a mathematical rigor (i.e., with no subsequent mathematical simplifications or approximations) that has not been reported in previous works. In principle, the present treatment can be extended to more complex formalisms (non-SE, non-VFT and non-Turnbull) but not without a significant loss of clarity and rigor.

2. Literature review

As early as 1986, Weinberg [16] analyzed the dependence of T^* on system parameters using CNT. Weinberg showed that in general $T^* \geq T_M/3$ (where T_M is the melting temperature of the crystal phase).

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.03.024

This analysis showed that two dimensionless parameters (a reduced activation energy of viscous flow and the ratio of the difference in specific heat between the liquid and the crystal to the entropy of fusion) control the location of T*. In addition, he showed that T* is dominated by (and increases with increase in) the activation energy of viscous flow. However, Weinberg's analysis used an Arrhenius temperature dependence of the viscosity that is limited to strong liquids and employed an approximate form of the Stokes–Einstein equation to account for the atomic rearrangements controlling crystal nucleation in the liquid. The effects of these approximations are not clear on his results.

Later, Zanotto and Weinberg (ZW) [8] used the Stokes–Einstein equation in combination with the non-Arrhenius VFT temperature dependence of viscosity to calculate (numerically) the values of T* for selected stoichiometric oxide glass compositions. Based on these results, ZW made the important observation: only glasses having $T^* > T_g$ exhibited internal (homogeneous) nucleation in laboratory time/size scales. However, ZW did not perform an analytic variation of T* as a function of system parameters.

Fokin et al. [2] reported experimental evidence that, in silicate melts that undergo internal nucleation, T* is typically close to (equal or greater than) T_g. Unfortunately, they also used an approximate form of the Stokes–Einstein equation to rationalize the dependence of T* on T_g.

Recently, Schmelzer et al. [3] have analyzed the variation of T* (as well as the temperatures of maximum growth rate and that of overall crystallization rate). While their calculated results for T* are similar to the results reported in this paper, they did not use the Stokes–Einstein or the VFT equations. Further, they introduced an unconventional definition of fragility that makes their results difficult to compare with the conventional fragility data. To our knowledge, a rigorous analysis of T* as a function of T_g and fragility is not available in the literature.

3. Analysis

i). The VFT expression for the T-dependence of viscosity, η(T):

The VFT expression [17–19] is an empirical non-Arrhenius equation that exhibits viscosity divergence at a finite temperature T_0 — called the VFT temperature. Using a reduced temperature, x, that is normalized with respect to the melting temperature, T_M of the crystal phase:

$$x \equiv \frac{T}{T_M}, \tag{1}$$

the VFT equation can be expressed as follows:

$$\ln(\eta) = A + \frac{C_2}{x - x_0}, \tag{2}$$

where A, C_2 (the dimensionless activation energy), and $x_0 = T_0/T_M$ (the reduced VFT temperature) are the three VFT parameters. The VFT equation can also be expressed in terms of experimentally accessible system parameters, such as the reduced glass transition temperature and fragility. Using Eq. (2), the reduced glass transition temperature, x_g (defined as the temperature where the value of viscosity, η_g, is 10^{12} Pa·s) is given by:

$$x_g = x_0 + \frac{C_2}{D}. \tag{3}$$

Here, the constant $D \equiv [\ln(\eta_g) - A]$ has a fixed value of approximately 37. Using Eq. (3), the VFT eqn can be expressed in terms of x_g:

$$\ln(\eta) = A + D\frac{x_g - x_0}{x - x_0}. \tag{4}$$

It is also possible to write the VFT eqn in terms of the fragility (m) of the system, which is defined [20] as:

$$m = \left.\frac{\partial \log_{10}(\eta)}{\partial\left(\frac{x_g}{x}\right)}\right|_{x=x_g}. \tag{5}$$

Using Eq. (4), it can be readily shown that

$$x_0 = x_g\left[1 - \frac{m_0}{m}\right], \tag{6}$$

where m_0, the minimum value of fragility (corresponding to the strongest liquid), is about 16 and is related to D as follows:

$$D = m_0(\ln(10)). \tag{7}$$

Eliminating x_0 between Eqs. (4) and (6) gives the VFT eqn that has m_0, x_g, and m as the three VFT parameters:

$$\ln(\eta) = A + \frac{m_0^2 \ln(10)}{m\left(\frac{x}{x_g} - 1\right) + m_0}, \tag{8}$$

where A and m_0 are related as follows:

$$A = (12 - m_0)(\ln(10)). \tag{9}$$

ii). Expression for the T-dependent steady state nucleation rate:

When combined with the Stokes–Einstein equation, CNT gives the following expression for the steady state nucleation rate, I(T):

$$I(T) = \frac{KT}{\eta(T)} \exp\left[-\left(\frac{W(T)}{k_B T}\right)\right]. \tag{10}$$

Here K is a constant and k_B is the Boltzmann constant. For a spherical nucleus, the thermodynamic barrier, W, is given by:

$$W(T) = \frac{16\pi\sigma^3}{3\Delta G_V^2(T)}. \tag{11}$$

Here σ is the surface energy density of the crystal-liquid interface. According to the Turnbull expression [21], which gives an upper bound for the free energy change per unit volume, ΔG_V, is expressed in terms of the molar enthalpy of melting, ΔH_M:

$$\Delta G_V = \frac{\Delta H_M}{V}\left[1 - \frac{T}{T_M}\right]. \tag{12}$$

Here V is the molar volume. Combining Eqs. (1), (11), and (12), one can rewrite W as follows:

$$\frac{W}{k_B T} = \frac{C_1}{x(1-x)^2}, \tag{13}$$

where the dimensionless positive parameter C_1, representing the thermodynamic barrier for nucleation, is given by

$$C_1 = \left(\frac{16\pi}{3}\right)\frac{\sigma^3 V^2}{k_B T_M (\Delta H_M)^2}. \tag{14}$$