Glass-formation and crystallization kinetics[1]

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Abstract

A review is presented of several aspects of crystallization processes in glass and their impact on glass-forming ability. Herein, both isothermal and non-isothermal processes are considered. For isothermal crystallization processes, generalizations of the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory are described and the status of certain features of nucleation rate and crystal growth calculations in glasses are given. For non-isothermal crystallization, some features of DTA/DSC analyses and critical cooling rate calculations for glass-formation are discussed, and generalizations of the standard theory for computation of the fraction crystallized are presented.

Keywords: Crystallization; Glass; Isothermal; Kinetics; Non-isothermal

1. Introduction

The topic of crystallization kinetics is of essential importance for glass formation and glass-ceramic synthesis. According to the kinetic viewpoint of glass formation [1,2], the glass-forming ability of a composition may be assessed by its reluctance to undergo crystallization. Hence, glass formation may be considered in terms of a competition between crystallization and cooling. These notions have been formulated in a quantitative manner, and critical cooling rates for glass formation have been calculated for simple systems [3–5].

The existing descriptions of isothermal and non-isothermal crystallization processes in glasses are based upon two fundamental theories: classical nucleation theory (CNT) [6–8], and the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory [9–12]. The former provides a means for the computation of crystal cluster size distributions and

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[1] Dedicated to Professor Hiroshi Suga.

cluster growth rates, while the latter allows one to calculate the volume fraction crystallized in terms of crystal nucleation and growth rates. Thus, CNT provides the input parameters for the formal theory of transformation kinetics expressed by JMAK theory. However, within the past couple of decades, it has been recognized that both CNT and JMAK formalisms have certain limitations and must be modified or generalized in order to be applicable to crystallization processes in glasses [13–15]. Herein, some of these generalizations will be discussed.

Crystallization processes can be studied under isothermal or non-isothermal conditions. Although isothermal crystallization is easier to describe, most recent studies have been performed non-isothermally due to the widespread availability of DTA/DSC instruments. Often the analyses of the latter class of experiments have not been executed critically, and hence many of the DSC/DTA studies which have been published provide little insight into the crystallization mechanisms which are operative in various compositions. Although Yinnon and Uhlmann [16] have given a critical evaluation of the analysis of non-isothermal DTA/DSC experiments in the not too distant past, some discussion of this topic will be presented in this paper.

In the next section, the isothermal crystallization of glass will be considered. In particular, the calculation of the volume fraction crystallized as a function of time, $X(t)$, will be reviewed and discussed for several different cases. In addition, theoretical expressions commonly used for crystal nucleation and growth rates will be assessed. In the section thereafter, non-isothermal crystallization processes will be analyzed. Several issues relating to calculation of critical cooling rates and analysis of DTA/DSC experiments will be discussed. The final section will present some concluding remarks.

2. Isothermal crystallization

For isothermal crystallization, $X(t)$ is usually computed from the JMAK equation

$$\ln(1 - X(t))^{-1} = CIU^n t^{n+1}/(n+1) \tag{1}$$

where U is the crystal growth rate, I is the steady-state crystal nucleation rate, C is a geometric factor dependent upon crystal shape, and n is an integer and corresponds to the dimensionality of the crystallization process. Although it is not always explicitly stated, Eq. (1) is limited by the following conditions: (a) I is time-independent, (b) U is size-independent, (c) nucleation occurs randomly and uniformly, and (d) growth is interface-controlled.

Zanotto and coworkers [17, 18] and Weinberg [19] have evaluated the accuracy of the JMAK equation. However, from the work of Bradley [20] it is clear that the JMAK equation is precise in the limit of large nucleation statistics. In other words, if boundaries can be ignored and nucleation densities are sufficiently large, then the JMAK equation is virtually exact. However, Eq. (1) is not applicable if conditions (a)–(d) are not satisfied, and in such cases other transformation equations must be employed. Below, two examples are considered where generalizations of Eq. (1) are required.

Weinberg and Kapral [21] derived expressions for $X(t)$ for systems in which finite size as well as inhomogeneous nucleation effects were present. The theory was developed for both the cases of initial nucleation and continuous nucleation. A simple discrete space and time model was used to compute the kinetics, and analytical results were obtained for $X(t)$. The validity of the analytical results were tested by comparisons with numerical simulations of the nucleation and growth processes for a two-dimensional version of the model. The numerical and analytical results were in precise agreement, confirming the theoretical formulae given for $X(t)$.

Weinberg [14] employed a continuum version of the approach given in Ref. [21] to derive the transformation laws for 2- and 3-dimensional surface-nucleated processes and for the crystallization kinetics of spherical particles where combined surface and bulk nucleation occur. For the analyses of the purely surface-nucleated transformations, initial seeding (nucleation) was assumed. Analytical expressions were given for $X(t)$ and the influence of sample geometry on transformation rate was explored. It was found that 2-D samples of equal area but different shape transformed at nearly equal rates if their perimeter lengths were similar. Standard JMAK theory, e.g. Eq. (1), indicates that a plot of $\ln(-\ln(1 - X(t)))$ vs. $\log t$ should be linear. However, it was demonstrated that such plots need not be linear for surface-nucleated crystallization. In considering the transformation kinetics of particles with surface and bulk nucleation, a model system was used which satisfied the following conditions: (a) particles are spherical, (b) surface nuclei are present at initial times (with seeding density/unit area $= P_r$), but nucleation occurs continuously and at a constant rate I in the bulk, (c) crystal growth rate U is constant and follows a spherical growth law for crystals nucleated on the surface or in the bulk. Explicit expressions were derived for $X(t)$, and the relative importance of surface and bulk crystallization kinetics was assessed. For small surface-seeding probability, it was found that the crystallization kinetics were nearly those of a bulk-nucleated sample. However, a plot of $\ln(-\ln(1 - X(t)))$ vs. $\log t$ did not have a slope of 4 due to finite particle size effects. For comparable values of I/U and P_r, the crystallization kinetics were found to be quite similar to those from a purely surface-nucleated crystallization process. This feature followed from the fact that at the initial time all surface nuclei were present while the bulk was free of seeds. Although for many conditions linear $\ln(-\ln(1 - X(t)))$ vs. $\log t$ plots were obtained (with integer values of n), it was shown that such plots did not provide information regarding crystallization mechanism.

The second generalization of JMAK theory deals with the influence of transient effects upon the crystallization rate. For 3-D spherical growth, Eq. (1) may be rewritten as

$$\ln(1 - X(t))^{-1} = (4\pi/3) \int_0^t I(t') R^3(t; t') \, dt' \tag{2}$$

in order to account for time-dependent effects. In Eq. (2), I is the nucleation rate, and $R(t; t')$ is the radius of a particle at time t which nucleated at a time t'. For interface-controlled crystal growth, most previous investigators have treated the time dependence of the nucleation rate, while assuming U constant, e.g. see Ref. [22] and references cited therein. However, Shneidman and Weinberg [14] have shown that it is an

inconsistent procedure to allow the nucleation rate to be time-dependent without taking into account the size dependence of the growth rate. When this time-dependent problem is treated in a consistent manner, one finds that the corrections to the JMAK equation (Eq. (1)) are larger than anticipated [23, 24]. Shneidman and Weinberg found that corrections to the JMAK equation are particularly significant for moderate to small barrier heights ($W^*/kT < 30$, where W^* is the free energy barrier to form a critical nucleus) where nucleation rates are large. For large nucleation barriers, corrections to the usual t^4 law occur only in the time regime where the total volume-fraction crystallized is very small, and thus such corrections are unimportant. Furthermore, it was shown that at long times the corrections to the t^4 law cannot be expressed solely in terms of powers of τ/t (where τ is the relaxation time) since the correction contains a term dependent upon the logarithm of this ratio.

Hence, for isothermal crystallization processes there are at least two situations where the standard JMAK equation must be generalized. For the case of small barriers to nucleation, transient effects will be important, and time-dependent nucleation and radius-dependent growth must be taken into consideration. In this situation, Eq. (1) will give the leading order contribution for the volume fraction crystallized. If nucleation occurs non-uniformly throughout the sample (such as in surface crystalliza-tion), then other expressions are needed for $X(t)$. Such expressions can be derived using the same statistical arguments needed for the derivation of the JMAK equation. Finally, it should be noted that even if nucleation is uniform and transient effects are unimportant, corrections to Eq. (1) can arise from finite sample size effects. However, except for special cases where the surface area is unusually large, these corrections are quite small.

In order to compute $X(t)$, one must be able to calculate the steady-state nucleation rate I. About 15 years ago, comparisons were made between calculated values of I, using CNT, and experimental measurements for crystal nucleation in lithium disilicate (LS2) glass [25, 26], and a huge discrepancy was discovered. Although the temperature dependences of the nucleation rate was described reasonably well by CNT, the predicted magnitude of I was many orders of magnitude too small. Subsequently, James and coworkers (see Ref. [13] and references cited therein) found that the temperature dependences of the crystal nucleation rates in several additional silicate glasses were described quite precisely by CNT. Also, James demonstrated that if the liquid-crystal surface tension was allowed to have a weak temperature dependence, then calculated values of the nucleation rate (using CNT) could be made to agree quite well with experimental data. However, Weinberg and coworkers have found certain difficulties with the application of CNT to problems of nucleation in glass [27–29]. For example, Smith and Weinberg [27] found that CNT could not fit the magnitude or the temperature dependence of the measured nucleation rates in lithium diborate glass. Weinberg and Zanotto [28] indicated that the kinetic prefactor in CNT could be obtained without the use of the Stokes–Einstein assumption if transient nucleation data were employed. They used this procedure to re-examine the temperature depend-ence of the crystal nucleation rate in LS2 glass and several other silicate glasses. They discovered that in all cases differences between CNT and experimental data appeared in the region of large undercoolings. Thus, they concluded that the temperature

dependence of the classical nucleation rate was still a matter of controversy. Shneidman and Weinberg [29] used an asymptotic solution of the transient nucleation equation to compute the barrier to nucleation in LS2 glass. In this manner they were able to asses various kinetic models of nucleation. They found systematic deviations between experimental data and the predictions of all models, which they interpreted as either indicating the presence of pre-existing nuclei or the failure of CNT.

The crystal growth rate U must be known as a function of temperature, too, in order to calculate the fraction crystallized at various temperatures. Unlike metallic systems where crystal growth is governed by thermal diffusion, the kinetics of crystal growth in glasses is most often interface- or diffusion-controlled. Three models have been used to describe interface growth in glasses [30]: normal growth, screw dislocation growth, and surface nucleation controlled growth. For normal growth, the growth rate may be expressed as

$$U = va[1 - \exp(-\Delta S_f \Delta T/T) \tag{3}$$

where a is the unit distance advanced by the interface, v is the jump frequency at the interface, and ΔS_f is the molar entropy of fusion in units of the gas constant. In normal growth, the interface is rough on an atomic scale and the crystal–liquid interface is non-faceted. According to the work of Jackson [31, 32], normal growth will occur for small entropy of fusion materials. The growth rate for screw dislocation growth is

$$U = f\, va[1 - \exp(-\Delta S_f \Delta T/T) \tag{4}$$

where f is the fraction of preferred growth sites. In screw dislocation growth, the interface is smooth and faceted, and growth occurs preferentially on the steps of the dislocation defect. Screw dislocation growth is expected in high entropy of fusion materials. Finally, for surface nucleation growth, the growth rate is given by

$$U = Cv \exp(-B/T\Delta T) \tag{5}$$

where B and C are constants. Surface nucleation growth refers to a growth mechanism in which two-dimensional nuclei form on a crystal surface and grow along the surface. Surface nucleation growth is anticipated in high entropy fusion materials, and it is characterized by a smooth faceted interface.

The status of crystal growth in glasses has been reviewed recently by Uhlmann and Uhlmann [33]. From Ref. [33], one observes that a limited number of quantitative comparisons have been made between the experimentally determined and theoretically predicted crystal growth rates as a function of temperature, and that for only two systems which are predicted to exhibit normal growth (GeO_2 and SiO_2) do the measured temperature dependences of the growth rates agree well with theory. However, the experimental and theoretical magnitudes of the growth rates in these systems differ by about an order of magnitude. For systems with high entropies of fusion, there is little agreement between theory and experiment. For example, for systems in which growth occurs by a 2-D nucleation mechanism, a plot of the log of the growth rate times the viscosity vs. $1/(T(T_m - T)$ should be linear (where T_m is the melting temperature). This relationship has been experimentally tested for several glass-forming compositions which are believed to exhibit 2-D nucleation crystal

growth [30, 33], and in nearly all cases the observed temperature dependence of the growth rate does not conform to the above-mentioned functional form although the magnitudes of the predicted growth rates are within an order of magnitude of those measured. A notable exception to these observations is the case of crystal growth in lithium diborate where the temperature dependence of the experimental growth rates at large undercoolings is described well by the 2-D nucleation crystal growth model, but the computed values of the growth rates are found to be many orders of magnitude too small [34].

In summary, although the basic theory required for the computation of $X(t)$ for isothermal transformations is in place, a number of "loose ends" exist which make crystallization calculations for glasses somewhat suspect.

3. Non-isothermal crystallization

There have been numerous studies of non-isothermal crystallization kinetics, many of which are related to interpretation of non-isothermal DTA/DSC experiments [35–44]. For non-isothermal transformations, the fraction transformed as a function of time can be written in the form of Eq. (2), where now the time dependence arises from the temperature dependence of the nucleation and growth rates [44]. Additional time-dependent effects may arise if transient nucleation effects are important [46], but herein we focus on situations where steady-state nucleation and size-independent growth rates can be utilized. For such circumstances, and for constant cooling rates, one may transform Eq. (2) into the following expression which involves temperature integrals

$$X(T) = (4\pi S^{-4}/3) \int_{T_i}^{T_f} I(T') \, \mathrm{d}T' \left[\int_{T_i}^{T_f} U(T'') \, \mathrm{d}T'' \right]^3 \tag{6}$$

In Eq. (6), S is the magnitude of the cooling rate, $I(T')$ is the steady-state nucleation rate, $U(T'')$ is the crystal growth rate, and T_i, T_f are the initial and final temperatures.

If one chooses T_i as the melting temperature and T_f as room temperature (or some sufficiently low temperature where crystallization does not occur) and selects $X < 10^{-06}$ as a criterion for glass formation [2], then S_c, the critical cooling rate for glass formation, can be obtained by using these parameters in Eq. (6). Although this equation provides a precise expression for S_c (within the framework of the quasi-steady scheme), several approximate methods have been utilized for critical cooling rate calculations. Most notably, it has been shown that reasonably good estimates of S_c may be obtained by the "nose method", which relies upon computing the cooling curve which just passes through the nose of a T–T–T (time–temperature–transformation) diagram [47, 48]. If T_n, t_n designate the temperature and time, respectively, at the nose of a T–T–T diagram corresponding to $X = 10^{-06}$, then the critical cooling rate is given by

$$S_c = (T_m - T_n)/t_n \tag{7}$$

where T_m is the melting temperature. It has been observed that critical cooling rates computed by the "nose method" were generally greater than those calculated by other

methods. Weinberg and coworkers [49] have provided an explanation for this finding. Also, an assessment of the various factors involved in critical rate calculations has been made [48]. In this analysis the following three ingredients were considered: (1) the selection of a kinetic model, e.g. use of Eq. (6) or Eq. (7), etc., (2) the choice of the nucleation and growth expressions, and (3) the selection of the values of several parameters which enter into the nucleation and growth equations. Calculations were performed using parameters appropriate for SiO_2 and GeO_2 glasses. It was shown that S_c is fairly insensitive to the kinetic model, but is quite dependent upon the material parameters which enter into the crystal nucleation and growth expressions. In particular, the critical cooling rate is a strong function of the value of the liquid-crystal surface tension, or the Turnbull parameter [50] which approximately characterizes the latter. Also, S_c was shown to be quite sensitive to the value of $\Delta C_p/\Delta S_f$ (where ΔC_p is the difference between crystal and liquid specific heats).

The critical cooling rate calculations for glass formation described above assume that crystallization initiates homogeneously. However, it is known that most compositions devitrify by a surface crystallization mechanism, and thus traditional critical cooling rate calculations are limited to a particular class of compositions. Recently, a description of surface-initiated non-isothermal crystallization kinetics was given and applied to SiO_2- or GeO_2-type glasses [51]. Calculations were performed to elucidate the effects of surface nuclei density and cooling rates on the crystallization kinetics. Also, the cooling rates required for the avoidance of a specific value crystallized were computed. It was demonstrated that, unlike the situation for bulk nucleation, critical cooling rates for glass formation in surface-initiated transformations are size-dependent. Thus, glass-formation depends not only on the cooling rate, but also upon the sample dimensions.

As mentioned, about a decade ago Yinnon and Uhlmann [16] provided a detailed analysis of the myriad of mathematical methods proposed for the analysis of DTA/DSC experiments. In the abstract of Ref. [16] it is stated, "All these methods are based on the Avrami treatment of transformation kinetics and define an effective crystallization rate coefficient having an Arrhenian temperature dependence. Several different ways of mathematically treating the data have been proposed. Most are shown to be based on an incorrect neglect of the temperature dependence of the rate coefficient." The authors go on to say, "It is further argued that in general the overall crystallization rate coefficient is not Arrhenian in character. Thus, in general, non-isothermal transformation cannot be treated analytically." In view of these comments, Weinberg [52] undertook an effort to delineate those cases where an Arrhenian assumption might be justified. The condition of site saturation was imposed, and the three standard models of crystal growth were utilized. It was shown that for the case of normal growth, the requirement of an Arrhenian form for K, the reaction rate coefficient, could be satisfied by imposing a minimum value to a parameter which is proportional to the number of particles nucleated and inversely proportional to the heating rate. For surface nucleated or screw dislocation crystal growth, though, it was demonstrated that an Arrhenian form for K is not valid. However, even for the latter growth models if a similar parameter exceeds a critical value, then it was shown that the equations which describe non-isothermal DTA/DSC

experiments are quite close in form to those derived using an Arrhenian assumption for K.

The latter analysis was limited in two respects. First, site saturation was assumed without discussing the anticipated domain of validity of this approximation. Also, only the Kissinger [53] method was considered. Thus, in a more recent work [54], the generality of the site saturation assumption was evaluated, and the validity of an Arrhenian assumption for K using other mathematical models for evaluation of experimental data was tested. The site saturation approximation is accurate if homogeneous nucleation and growth curves are reasonably well separated. It was demonstrated that this is the case for most simple inorganic oxide glass-forming systems, and hence site saturation is a good approximation if one restricts attention to sufficiently high temperatures in a DTA/DSC heating experiment. Also, it was concluded that although plots of $(1/3)\ln(\ln(1-X)^{-1})$ vs. $1/T$ are often found to be linear, only for certain values of the parameters which control crystallization may the slope be associated with an activation energy.

4. Conclusions

Although much information has been compiled regarding crystallization of glasses and supercooled liquids, difficulties still exist in producing reliable crystallization calculations for isothermal or non-isothermal transformations. In the case of isothermal transformations, the basic theory is "in place", but problems arise due to the inadequacy of the nucleation and crystal growth expressions. For non-isothermal transformations, there is a larger gap in knowledge since no theoretical framework exists for the treatment of problems where transient effects are of importance.

Acknowledgements

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