IN-27-CR
OCIT.
65719
p.5

TRANSIENT NUCLEATION IN GLASSES

K. F. Kelton, Department of Physics, Washington University, St. Louis, MO 63130
U.S.A.

ABSTRACT

Nucleation rates in condensed systems are frequently not at their steady state values. Such time dependent (or transient) nucleation is most clearly observed in devitrification studies of metallic and silicate glasses. The origin of transient nucleation and its role in the formation and stability of desired phases and microstructures are discussed. Numerical models of nucleation in isothermal and nonisothermal situations, based on the coupled differential equations describing cluster evolution within the classical theory, are presented. The importance of transient nucleation in glass formation and crystallization is discussed.

I.   INTRODUCTION

Since most first order phase transformations occur by nucleation and growth, the prediction of resulting phases and microstructures requires a precise knowledge of the rates of these processes. In some cases, such as for many silicate glasses, it is possible to measure the nucleation rate directly by counting the number of nuclei per unit volume, N_v, that appear with annealing. N_v is related to the nucleation rate, I, by

$$N_v = \int_0^t I \, dt \quad . \tag{1}$$

Assuming that the nucleation rate is time-independent, given by the steady state nucleation rate, I^s, a plot of N_v vs the time, t, should then be fit by a straight line with slope equal to I^s. Nucleation studies in many glasses, however, find a nonlinear behavior in this plot, generally indicating an initially low nucleation rate that approaches the steady state value only after long annealing times. Such transient nucleation is common, having been reported in metallic glasses, glass-ceramic materials, enamel, and silicate glasses. It is important in many phase

transformations, including nucleation of new crystalline phases within existing crystalline phases, liquid phase separation, crystallization of undercooled liquids, devitrification of glasses, and glass formation.

In this article, I will discuss the origins of transient nucleation and focus on the results of computer studies that directly incorporate transient nucleation to better understand phase transformations. Many phenomenon are incorrectly described if a steady state nucleation rate is assumed. We show that by using simple numeric models, experimental kinetic data can be analyzed in new ways to extract the time dependent nucleation rate, I(t), to verify the kinetic model assumed in the classical theory, and to investigate glass formation. The interested reader is referred to references 1-3 for more comprehensive reviews.

II. CLASSICAL THEORY - STEADY STATE NUCLEATION

For simplicity, spherical clusters with a sharp dividing surface, having the same composition as the parent phase, are assumed. Following Gibbs, the reversible work of formation of a cluster of size n, constructed from n monomers, or molecules, is:

$$\Delta G_n = n\Delta G' + (36\pi)^{1/3} v^{2/3} n^{2/3} \sigma \quad , \tag{2}$$

where $\Delta G'$ is the Gibbs free energy per molecule of the new phase less that of the initial phase, v is the molecular volume and σ is the interfacial energy per unit area. The surface energy penalty is dominant for small clusters, leading to a maximum in ΔG_n at the critical size, n*,

$$n* = \frac{32\pi}{3v} \frac{\sigma^3}{|\Delta G_v|^3} \tag{3}$$

where ΔG_v is the free energy difference per unit volume, $\Delta G'/v$. Since clusters smaller than n* will on average shrink, while those larger than n* will on average grow, the nucleation rate is in a crude sense the production of postcritical clusters.

Clusters are assumed to evolve in size by a series of bimolecular reactions, describing cluster growth by growth or shrinkage in one monomer steps. The time dependent cluster density, $N_{n,t}$, is then determined by solving a system of coupled differential equations of the form

$$\frac{dN_{n,t}}{dt} = N_{n-1,t} \, k^+_{n-1} - [N_{n,t} \, k^-_n + N_{n,t} \, k^+_n] + N_{n+1,t} \, k^-_{n+1} \quad \cdot \tag{4}$$

where k^+_{n-1} and k^-_n are the forward and backward rate constants respectively for a cluster of size n. Typically they are calculated assuming that the atomic mobility is

identical to that describing bulk diffusion. The nucleation rate at a cluster size n, $I_{n,t}$, is the time-dependent flux of clusters past that size, given by

$$I_{n,t} = N_{n,t} \, k_n^+ - N_{n-1,t} \, k_{n+1}^- \quad . \tag{5}$$

Assuming that the cluster distribution reaches steady state, Becker and Döring[4] arrived at the familiar expression for the steady state nucleation rate:

$$I^s = N_o \exp\left[-\frac{\Delta G_{n*}}{kT} \right] k_{n*}^+ \left(\frac{|\Delta G'|}{6\pi k_B T n*} \right)^{1/2} \propto N_{n*}(T) \, k_{n*}^+(T) \quad , \tag{6}$$

where N_o is Avagadro's number, k_B is Boltzmann's constant and $N_{n*}(T)$ is the temperature dependent steady state distribution.

III.   CLASSICAL THEORY - TRANSIENT NUCLEATION

When a glass is rapidly quenched from the melt, there is insufficient time for the cluster distribution to maintain the appropriate steady state distribution. Upon reheating, then, the density at the critical size will be artificially low, giving a nucleation rate lower than expected. With time, the distribution will evolve to the steady state distribution appropriate to the annealing temperature, causing the nucleation rate to rise. As will be seen in subsequent sections, this process can lead to complex nucleation behavior with time.

Assuming that n is continuous, the coupled set of linear differential equations can be written as a single partial differential equation,

$$\frac{\partial N_{n,t}}{\partial t} = \frac{\partial}{\partial n} \left[k_n^+ \, N_n^e \, \frac{\partial}{\partial n} \left(\frac{N_{n,t}}{N_n^e} \right) \right] \quad , \tag{7}$$

where N_n^e is the equilibrium density of clusters of size n. Most expressions for I(t) are obtained by solving Eq. (7), making different approximations for the rate constants and ΔG_n (see ref. 1). All assume that the relaxation to I^s can be characterized by a single time constant, the transient time. Experimental data and a computer calculation by Kelton et al.[5] (discussion following) suggest that the best of these solutions is the one obtained by Kashchiev,[6]

$$I_{n*,t} = I^s \left[1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp\left(-\frac{m^2 t}{\tau_K} \right) \right] \quad , \tag{8}$$

where I^s is the steady state nucleation rate, and τ_K is the transient time,

$$\tau_K = \frac{-24 k_B T n*}{\pi^2 k_{n*}^{\cdot} \Delta G'} \quad . \tag{9}$$

To compare this with experimental data, however, a proper account must be made of the additional time required for a cluster to grow from n* at the nucleating temperature to n* at the growth temperature.[1]

Kelton et al solved Eq. (4) by a numerical method to obtain the transient nucleation behavior, avoiding the usual restrictive assumptions.[5] Dividing the time into a large number of intervals, δt, the number of clusters of size n at the end of each interval is calculated by

$$N_{n,t + \delta t} = N_{n,t} + \delta t \frac{dN_{n,t}}{dt} \quad . \tag{10}$$

Values for I(t) were computed directly from Eq. (5).

Assuming parameters appropriate to lithium disilicate, good agreement was found between the computer generated values for I(t) at n* and those predicted by Eq. (8). Recent theoretical treatments by Wu[7] and Shneidman et al.,[8] however, suggest that this agreement is fortuitous because of the particular parameters chosen. Shneidman argues that the cluster distribution evolution cannot be described by a single relaxation time, making most existing analytical treatments invalid. This is supported by recent studies by Kelton and Greer, of the effects of preannealing treatments on nucleation rates (c.f. Sec. V.A).

Due to its simplicity and more accurate solution of the rate equations, the numerical calculation is easily extended to include nucleation under nonisothermal conditions,[9] heterogeneous nucleation,[10] and compositional effects.[11]

IV. NONISOTHERMAL NUCLEATION AND CRYSTALLIZATION

It is important to assess the importance of transient nucleation in nonisothermal phase transformations, such as are studied by differential scanning calorimetry (DSC) or differential thermal analysis (DTA) for example, and for glass formation. To extend the rate kinetics to large clusters, it is assumed that for sufficiently large n, $N_{n,t} \approx N_{n+1,t}$, giving an average growth rate for a cluster of radius r

$$\frac{dr}{dt} = C \ \frac{16D}{\lambda^2} \left(\frac{3v}{4\pi}\right)^{1/3} \sinh\left[\frac{v}{2k_B T}\left(\Delta G_v - \frac{2\sigma}{r}\right)\right] \quad , \qquad (11)$$

where C is a constant that is generally between 1 and 10, depending on the density of the cluster distribution at the point where the extrapolation is begun. Calculated growth velocities are in excellent agreement with experiment.[12]

     To model a nonisothermal phase transformation, the continuous scan is divided into a series of isothermal anneals of size δT and duration $\delta t = \delta T/S$, where S is the scan rate. At the end of each interval, the total number of nuclei generated during the interval is calculated and stored, and the sizes of the nuclei generated in previous anneals are calculated using the average growth rate given in Eq. (11). Assuming no impingement, the total volume is computed as

$$V_t = \sum_{i=1}^{m} \left(\frac{4\pi}{3}\right) N_i \ r_{i,t}^3 \quad , \qquad (12)$$

where $r_{i,t}$ is the time dependent radius of each nuclei formed in the previous temperature intervals and N_i is the corresponding density. Taking V_o as the sample volume, the actual volume transformed is obtained by the Avrami analysis

$$x(t) = 1 - \exp\left(-\frac{V_t}{V_o}\right) \quad . \qquad (13)$$

     DSC and DTA experiments measure the rate of energy production (dH/dt), which is proportional to the rate of volume fraction transformed. This is easily calculated as a function of temperature as

$$DSC \ signal = \frac{dH}{dt} \propto \frac{x(T_i + \delta T) - x(T_i)}{\delta t} \quad . \qquad (14)$$

V.   EXAMPLES

     Three examples are provided to illustrate the utility of these numerical approaches. Lithium disilicate is used as a model glass in most cases since it is known to nucleate crystals of the same composition by a homogeneous mechanism. The parameters determined by Kelton and Greer from quantitative fits to the steady state and transient data are assumed.[13]

A. VALIDITY OF THE KINETIC MODEL IN CLASSICAL NUCLEATION THEORY

Definitive tests of the classical theory of nucleation do not exist, partially due to the uncertainty in the values for the interfacial energy, σ, and the atomic mobility. Most experimental and theoretical attention has focused on the thermodynamic aspects of the theory. The kinetic model, common to many theories, however, has received little attention.

Kalinina et al.[14] first noticed that a proper annealing schedule for lithium disilicate glass causes the nucleation rate to go through a maximum with time, corresponding to a complicated response of the cluster population to the annealing history. Within the classical theory, this behavior should be predictable, providing a critical test of the cluster dynamics assumed in the kinetic model for nucleation theory. Using the numerical model discussed previously, σ and the atomic mobility were determined by consistently matching the measured temperature-dependent values for I^s and τ. Holding all parameters fixed, then, the number of nuclei, N_v, produced as a function of annealing were computed and compared with experimental data.[13]

Figure 1 shows N_v as a function of annealing time, measured by Kalinina et al. by annealing at 758K and growing at 899K, following preanneals at 713K, 724K, and 756K.
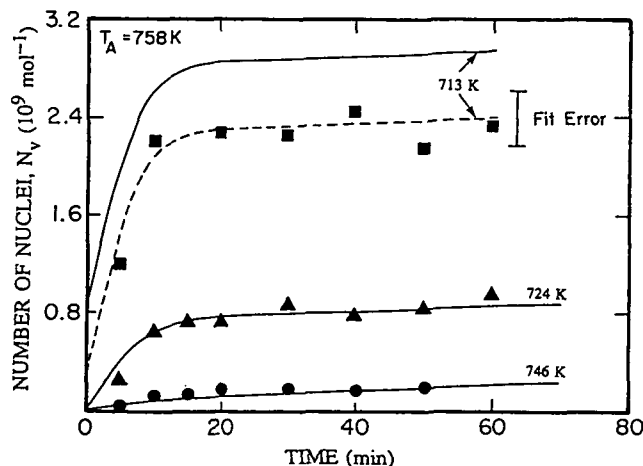

Figure 1 The number of nuclei in lithium disilicate glass as a function of annealing time at 758K after annealing to steady state at 713K, 724K and 746K. (from ref. 13).

Unlike the case for an as-quenched glass the nucleation rate is too high initially, approaching the lower steady state value with time. This demonstrates that the initial concentration of clusters of size n* was too large, reflecting the lower temperature

distribution induced by the preannealing treatment. The solid lines are the predictions from our numerical treatment, showing excellent agreement with the 724K and 756K data. The apparent disagreement with 713K is likely due to an error in the steady state value originally reported at that temperature; the dashed line is the prediction based on a value reported later. In agreement with experimental data, calculations for lower temperature preanneals predicted a peak in the nucleation rate with annealing temperature. Investigations demonstrated that this corresponds to a complicated evolution of the cluster distribution that could not be described by a single relaxation time, in agreement with the theoretical arguments of Wu[7] and Shneidman.[8] Our computer generated results demonstrate for the first time that nucleation proceeds as if there were an actual cluster distribution that evolves with the dynamical model assumed in the classical theory.

B. GLASS FORMATION

Glass formation requires that the liquid be quenched so fast that there is insufficient time for significant nucleation and growth of crystalline phases; a glass is typically assumed to have a crystalline volume fraction, x_c less than 10^{-6}.[15] Calculations of the critical quenching rate for glass formation, Q*, are usually made assuming steady state nucleation rates and macroscopic growth velocities.[16] During a rapid quench, however, it is likely that the steady state distribution will not be maintained, resulting in a nucleation rate that can be significantly lower than expected, making glass formation easier and increasing the stability of the glass to crystallization.

By directly simulating the evolution of the cluster distribution under the nonisothermal conditions of a quench, Kelton and Greer[9] demonstrated that the nucleation rate decreases markedly with increasing quench rate (Fig. 2 left). The effect is even more dramatic when parameters are chosen that are appropriate for $Au_{81}Si_{19}$, a typical metallic glass forming alloy (Fig. 2 right).
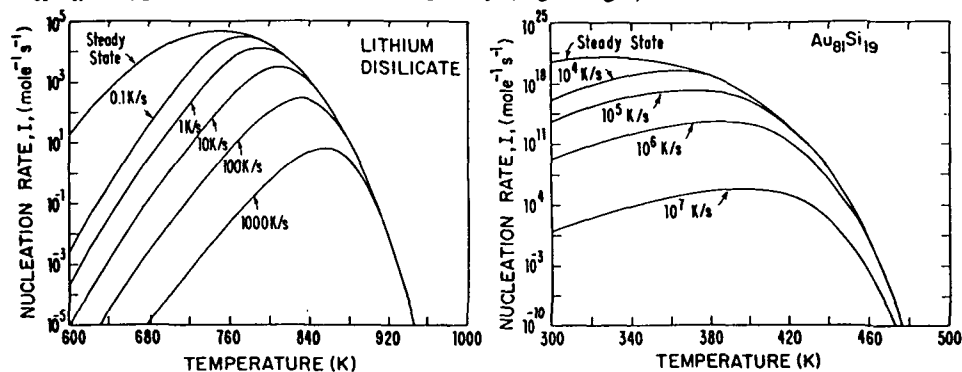

Figure 2 Nucleation rate as a function of quench rate for lithium disilicate (left) and $Au_{81}Si_{19}$ (right) (from ref. 9).

The lower nucleation rate results in a striking decrease in the number of nuclei generated (Fig. 3.a) and in the volume fraction transformed (Fig. 3.b, calculated following Sec. IV) over expectations from steady state calculations in $Au_{81}Si_{19}$. Steady state calculations predict a value for Q^* between 10^7 to 10^8 K/s (for $x_c < 10^{-6}$); transient effects decrease Q^* to $\approx 10^5$ K/s, in agreement with experiment. It is therefore likely that only because of transient nucleation is glass formation possible in some metallic alloys. In lithium disilicate, the predicted values for Q^* are identical, whether transient effects are included or not, resulting from the decreasing crystallization rate for temperatures below that where the nucleation departs significantly from its steady state value.
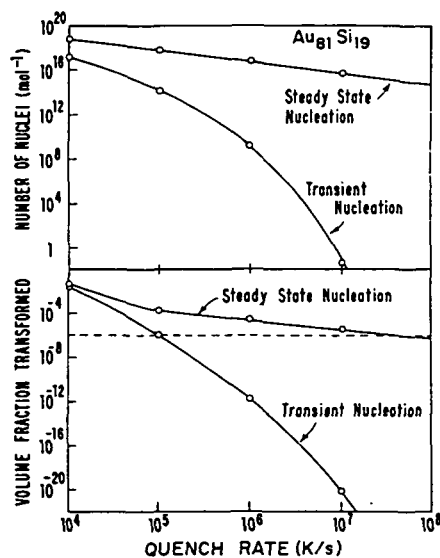

Figure 3 Number of nuclei and volume fraction transformed as a function of quench rate for steady state and transient nucleation in $Au_{81}Si_{19}$ (from ref. 10).

C.   DSC AND DTA MEASUREMENTS OF NUCLEATION RATES

Based on an experimental study of lithium disilicate glass, where I^s is well known, Ray and Day[17] suggested that nonisothermal DSC or DTA experiments could provide a rapid method for obtaining nucleation data, arguing that the temperature of the maximum nucleation rate could be determined by first heating the glass isothermally in the DSC or DTA at a sufficiently low temperature to promote crystal nucleation and subsequently measuring the temperature of the maximum rate of transformation, T_p and the peak height at T_p, δT_p, upon nonisothermal heating. The minimum in a plot of T_p (or the maximum in δT_p) vs the annealing temperature, should correspond to the maximum in the nucleation rate. Using the numerical methods described in Sec. III and IV the experimental procedures were simulated

52   Nucleation and Crystallization in Glasses and Liquids

exactly for lithium disilicate glass.[12] Figure 4.a shows the predicted DSC peak heights (for a scan rate of 15°C/min) as a function of the preannealing temperature (assuming 3 hour preanneals). Values for $I^s(T)$, calculated using the same thermodynamic and kinetic parameters are also shown. As observed experimentally by Ray and Day, a peak is predicted near the peak in the steady state rate. These two peaks are shifted slightly, however. Also in agreement, the peak temperatures and peak widths showed a minimum near the peak in the nucleation rate. More recent calculations on $Na_2O.2CaO.3SiO_2$, a glass with a much larger nucleation rate, produce results that are similar to those for lithium disilicate, but the peak in δT_p is much weaker (Fig. 4.b). Again, the peak in the plot of δT_p vs. annealing time is displaced slightly from the peak in the steady state nucleation rate, although as shown, the location of the peak is sensitive to the duration of the preanneal.
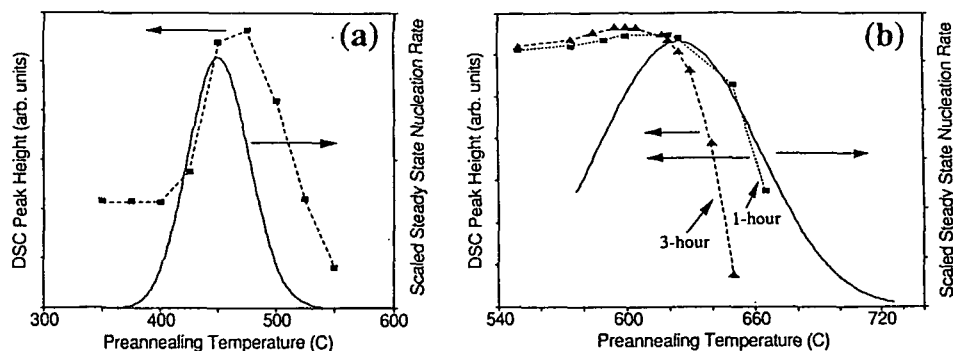

Figure 4 DSC peak heights as a function of preannealing temperature for (a) lithium disilicate and (b) $Na_2O.2CaO.3SiO_2$ glasses. Computed steady state nucleation rates are shown for comparison. Figure (a) is taken from ref. 12.

These results qualitatively support the experimental conclusions of Ray and Day. They depend critically on transient effects. Predicted results from steady state calculations are in poor agreement with experimental data.

VI.   CONCLUSION

In conclusion, transient nucleation is important for a proper understanding of isothermal and nonisothermal phase transformations, it is even essential for glass formation in some cases. Nucleation rates are a strong function of annealing history, often showing complex behavior that verifies the kinetic model of cluster evolution assumed by the classical theory. Using the principles developed in this paper for modeling this cluster evolution on readily available microcomputers, it is now possible to analyze nonisothermal DSC or DTA measurements more accurately than has been possible and to devise new methods for extracting fundamental kinetic parameters such as the nucleation rate.

VI.   REFERENCES

1.   K. F. Kelton, "Crystal Nucleation in Liquids and Glasses," in *Solid State Physics: Advances in Research and Applications*, Vol. 45, pp. 75-177 (H. Ehrenreich and D. Turnbull, eds.) Academic Press, New York, 1991.

2.   P. F. James, in "Glasses and Glass-Ceramics," pp. 59 (M. H. Lewis, ed.), Chapman and Hall, London, 1989.

3.   I. Gutzow, D. Kashchiev, and I. Avramov, J. Non-Cryst. Solids, **75**, 477-99 (1985).

4.   R. Becker and W. Döring, Ann. Phys. **24**, 719-52 (1935).

5.   K. F. Kelton, A. L. Greer, and C. V. Thompson, J. Chem. Phys., **79**, 6261-76 (1983).

6.   D. Kashchiev, surf. Sci., **14**, 209 (1966).

7.   D. Wu, J. Chem. Phys. (submitted).

8.   V. A. Shneidman, J. Chem. Phys., **44**, 2609-11 (1991); V. A. Shneidman and M. C. Weinberg, J. Chem. Phys., **95**, 9148-50 (1991).

9.   K. F. Kelton and A. L. Greer, J. Non-Cryst. Solids, **79**, 295-309 (1986).

10.   A. L. Greer, P. V. Evans, R. G. Hamerton, D. K. Shangguan and K. F. Kelton, Proc. 9th Int. Cryst. Growth Conf., Sendai, Japan, 1989.

11.   P. V. Evans, Ph.D Thesis, University of Cambridge, Cambridge, UK, 1988 (unpublished).

12.   K. F. Kelton, J. Am. Cer. Soc. (in press).

13.   K. F. Kelton and A. L. Greer, Phys. Rev. B., **38**, 10089-92 (1988); A. L. Greer and K. F. Kelton, J. Am. Cer. Soc., **74**, 1015-22 (1991).

14.   A. M. Kalinina, V. N. Filipovich, and V. M. Fokin, J. Non-Cryst. Solids, **38&39**, 723-728 (1980).

15.   D. R. Uhlmann, J. Non-Cryst. Solids, **7**, 337 (1972).

16.   H. Yinnon and D. R. Uhlmann, J. Non-Cryst. Solids, **50**, 189-202 (1982).

17.   C. Ray and D. Day, J. Am. Cer. Soc., **73**, 439-42 (1990).