

Crystallization of Liquids and Glasses

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Received February 10, 1992

The scientific and technological importance of advanced materials are summarized. The governing theories of glass transition, crystal nucleation and crystal growth are combined with the overall theory of transformation kinetics to clarify the phenomenon of glass formation from the liquid state. Finally, examples of novel glasses as well as glass-ceramics obtained from the controlled crystallization of certain liquids are given.

I. Introduction

The contemporary, technology intensive, age with its high technology industries and services demands the use of novel materials with improved properties. For instance, in the opinion of the presidents of one hundred Japanese industries the following were the most innovative new technologies in the last two decades: VLSI, Biotechnology, Optical Fibers, Robotics, Special Ceramics, Interferon, Office Automation, New Materials, Super-Computers and Space Technology¹. It is obvious that most of them are directly related to advanced materials.

The study and development of useful materials demands highly interdisciplinary efforts from physicists, chemists, materials scientists and engineers. Materials Science emphasizes the relationships between the *structure* and *properties* of materials, providing a link between the fundamental sciences and applications, while Materials Engineering focus the study of the relationships between the *processing* techniques and the *applications*. A schematic view of the scope of the various segments of science and materials engineering is presented in Figure 1.

Materials can be classified in several ways; i.e., by:

- i. *The general behavior*: metals, ceramics, polymers and composites;
- ii. *Chemical nature*: covalent, ionic, metallic, van der Waals, hydrogen, mixed bonding;
- iii. *Some property, e.g.*: insulator, semi-conductor, conductor, superconductor, or;
- iv. *Structure*: single crystal, polycrystal, vitreous, etc.

This article deals with the controlled crystallization of liquids or glasses of any type as a technique to obtain novel materials.

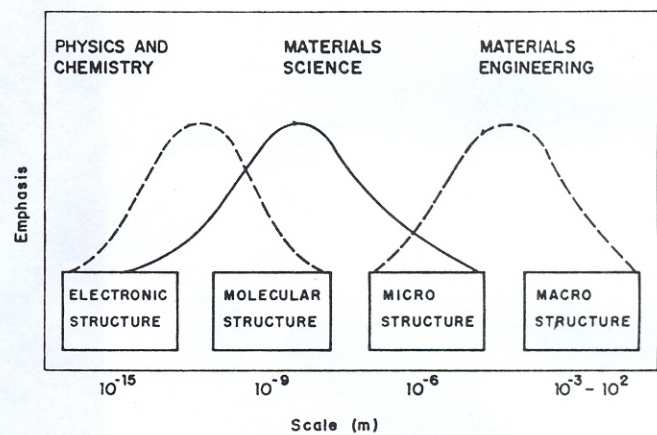


Figure 1: Scope of the basic sciences and materials engineering².

II. Types and applications of materials obtained via crystallization

The most obvious crystallization process is that frequently employed by chemists for the synthesis of purer or new compounds, i.e. the precipitation of powder particles from super-saturated solutions.

The geologists rely on the *post-mortem* study of crystallization to understand the formation of minerals and solidified magmas.

Many solid-state physicists depend on crystal growth from seeded melts to obtain a plethora of single-crystal specimens as well as commercially important materials such as silicon and lithium niobate.

Ceramicists and materials scientists dedicate a lot of time to the synthesis of novel ceramics and glasses employing the sol-gel technology. In this case the avoidance (or lack) of crystal nucleation and growth in the gel, during the sintering step, can lead to a glass.

Finally, the catalyzed crystallization of glass objects

can lead to a wide range of pore-free *glass-ceramics*, with unusual microstructures and properties, such as transparency, machinability and excellent dielectric, chemical, mechanical and thermal – shock behaviour. Many commercial glass-ceramic products are available for domestic uses, e.g. vision-TM, rangethops, feed-throughs, electronic substrates, artificial bones and teeth, radomes, etc.

III. The glass transition

Glasses are amorphous substances which undergo the glass transition. The most striking feature of the glass transition is the abrupt change in the properties of a liquid, such as the thermal expansion coefficient (α) and heat capacity (c_p), as it is cooled through the range of temperature where its viscosity approaches 10^{12} Pa.s. In that range the characteristic time for structural relaxation is of the order of a few minutes, so the effects of structural reorganization are easily detected by human observers.

Figure 2 shows the change in volume, V , of a glass forming liquid during cooling through the transition region.

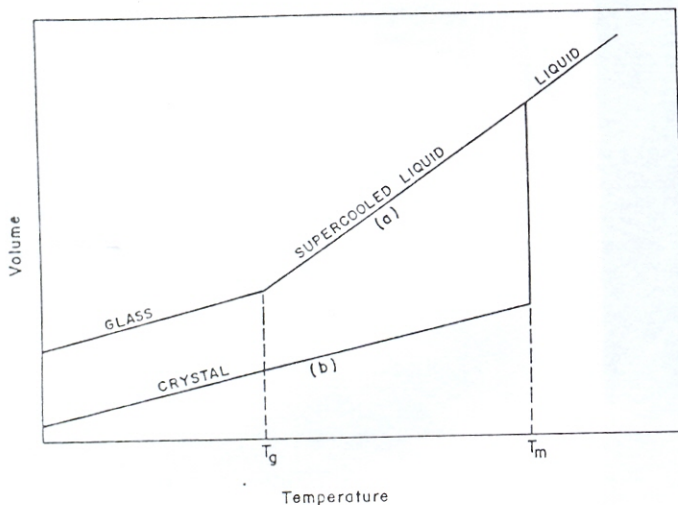


Figure 2: Schematic representation of glass transition (a) and crystallization of a liquid (b).

If the liquid is cooled slowly (path b) it may crystallize at the melting point, T_m . If the cooling rate is fast enough to avoid crystal nucleation and growth, a supercooled liquid would be produced (path a). As the temperature drops, the time required to establish the equilibrium configuration of the liquid increases, and eventually the structural change cannot keep pace with the rate of cooling. At that point a transition temperature, T_g , is reached below which the atoms are frozen into fixed positions (only thermal vibrations remain) and a glass is formed.

Thus, glass formation from the liquid state is feasible if path (a) is followed. On the other hand, all

glasses heated to a temperature between T_g and T_m tend to crystallize to achieve thermodynamical equilibrium. If crystallization occurs from a large number of sites in the bulk, useful, fine grained, glass-ceramics can be produced. When crystallization occurs in an uncontrolled way (devitrification) from a few surface impurity sites, damage and cracking of the specimen may take place. In the following sections the relevant theories and experimental observations leading to controlled crystallization in the volume of glasses or supercooled liquids will be described.

IV. Crystal nucleation

When a liquid is cooled below its melting point, crystal nucleation can occur homogeneously (in the volume), by heterophase fluctuations. The Classical Nucleation Theory (CNT) was derived in the late 50s by Turnbull and Fischer³. The homogeneous nucleation rate I in condensed systems is given by

$$I = n_v \nu (n_s^*/n^*) (W^*/3\pi kT)^{1/2} \times \exp[-(\Delta G_D + W^*)/kT], \quad (1)$$

where:

- n_v = the number of molecules or formula units of nucleating phase per unit volume of parent phase (typically $10^{28} 10^{29} m^{-3}$);
- ν = vibration frequency ($10^{13} s^{-1}$);
- n_s^* = number of molecules on the surface of a critical nucleus;
- n^* = number of molecules in the critical nucleus;
- W^* = Thermodynamic barrier for nucleation;
- ΔG_D = Activation energy for transport across the nucleus/matrix interface;
- k = Boltzmann's constant;

The quantity $(n_s^*/n^*)(W^*/3\pi kT)^{1/2}$ is within one or two powers of ten for all nucleation problems of interest. Therefore, eq. (1) may be written with sufficient accuracy as

$$I = n_v \nu \exp[-(\Delta G_D + W^*)/kT], \quad (2)$$

where the pre-exponential factor $A \simeq (n_v \nu)$ is typically $10^{41} - 10^{42} m^{-3} s^{-1}$.

Assuming that the molecular re-arrangement for the nucleation process can be described by an effective diffusion coefficient, D , we have

$$D = \nu \lambda^2 \exp(-\Delta G_D/kT), \quad (3)$$

where λ is the jump distance, of the order of atomic dimensions. D can be related to the viscosity (η) by means of the Stokes-Einstein equation:

$$D = kT/3\pi\lambda\eta. \quad (4)$$

Combining eqs. (2), (3) and (4) we have

$$I = (n_v kT / 3\pi\lambda^3 \eta) \exp(-W^*/kT). \quad (5)$$

For spherical nuclei

$$W^* = 16\pi\sigma^3 V_m^2 / 3\Delta G^2,$$

where V_m is the molar volume of the crystallizing phase, ΔG the thermodynamic driving force and σ the surface energy. Therefore, eq. (5) can be rewritten in the form

$$\ln(I\eta/T) = (n_v k / 3\pi\lambda^3) - (16\pi\sigma^3 V_m^2 / 3k\Delta G^2 T) \quad (6)$$

Hence, a plot of $\ln(I\eta/T)$ versus $1/\Delta G^2 T$ should yield a straight line, with σ and the pre-exponential factor given by the slope and intercept, respectively.

To test the classical theory, accurate data for the thermodynamic driving force for the glass to crystal transformation (ΔG) are required. ΔG for a single component system, at temperature T below the melting point T_m , is given by

$$\Delta G = -\Delta H_{fM}(T_m - T)/T_m - \int_T^{T_m} \Delta C_p dT + T \int_T^{T_m} (\Delta C_p/T) dT, \quad (7)$$

where ΔH_{fM} is the heat of fusion per mole and $\Delta C_p (< 0)$ is the difference in specific heats between the crystalline and liquid phases at constant pressure at temperature T .

Classical Nucleation Theory has been used extensively by materials scientists for prediction of nucleation rates. However, the steady-state crystal nucleation rates (I) calculated with CNT are many orders of magnitude smaller than the experimental values for inorganic glasses^{4,5}.

Recently, Manrich and Zanotto⁶ recalculated the crystal nucleation rates in six silicate glasses: $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (LS_2), $\text{Li}_2\text{O} \cdot \text{SiO}_2$ (LS), $\text{CaO} \cdot \text{SiO}_2$ (CS), $\text{BaO} \cdot \text{SiO}_2$ (BS_2), $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ ($\text{N}_1\text{C}_2\text{S}_3$) and $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ ($\text{N}_2\text{C}_1\text{S}_3$). The nucleation parameters σ , as well as the maximum experimental (I_{ex}) and predicted (I_{th}) nucleation rates, obtained from the mathematical fittings, are listed in Table I. The differences between (I_{th}) and (I_{ex}) are as large as 55 orders of magnitude!

Two main assumptions of CNT could be responsible for its failure to accurately predict experimental nucleation rates:

i) The activation energy for atomic jumps at the nucleus/matrix interface, the kinetic part of the classical expression, is normally associated with that of ordinary diffusion, and is eliminated in favor of the shear viscosity through the use of the Stokes-Einstein equation. However, this procedure has not been justified. Recently, a more rigorous approach, which makes use

Table I

Nucleation parameters and rates using CNT⁶

System	σ (Jm^{-2})	$\log(I_{\text{ex}})$ ($\text{m}^{-3} \text{s}^{-1}$)	$\log(I_{\text{th}})$ ($\text{m}^{-3} \text{s}^{-1}$)
LS	0.21	11.45	-36.70
LS ₂	0.21	9.63	-25.51
CS	0.28	6.22	-14.36
BS ₂	0.14	12.17	-19.78
N ₁ C ₂ S ₃	0.18	11.75	-43.41
N ₂ C ₁ S ₃	0.31	13.63	-41.78

of the induction times for nucleation instead of viscosity, was suggested and tested⁷. Neither the magnitude nor the temperature dependence of the nucleation rates were well described by theory when the latter procedure was used. A good fit could be obtained only in the temperature range above the temperature of the maximum nucleation rate. Therefore, discrepancies between theory and experiment were found with both approaches implying that other problems exist with CNT;

ii) The capillarity approximation is the assumption that the free energy of a nucleus can be written as the sum of a bulk and surface free energy and that the surface tension (surface energy/area) is that of a flat interface and is independent of nucleus size. However, use of a constant liquid-crystal surface tension produces large discrepancies between measured and predicted I . James⁴ observed that CNT could be made to agree with experimental data by employing a temperature dependent interfacial surface tension whose parameters were fixed by fit to experimental data. Although this procedure has been used by others for different types of materials, the use of a temperature dependent surface tension has been criticized by Oxtoby⁸.

If the critical nucleus is small, then its surface free energy could be quite sensitive to its radius. Tolman⁹ and others¹⁰ have developed theories to account for this size dependence and applied it to liquid droplet nucleation from the vapor. Thus Manrich and Zanotto⁶ have fitted experimental data to a modified form of CNT employing a radius dependent surface tension. The agreement between theory and experiment was better than that achieved with CNT, but still several orders of magnitude disagreement was found.

To summarize, CNT or its modifications are useful for qualitative understanding of the nucleation phenomenon. However, they are not capable of quantitatively predicting nucleation rates.

V. Standard Models of Crystal Growth

It is now generally accepted that the nature of the crystal-liquid interface has a decisive influence in the kinetics and morphology of crystallization. Theoretical treatments of crystal growth have therefore directed close attention to the nature of the interface and its relation to predicted behavior. It is useful to review briefly the standard models for crystal growth from the melt.

Three standard models¹¹ used to describe crystal growth and their respective predictions of kinetic behavior are:

a) *Normal growth*: Here the interface is pictured as rough on an atomic scale, with a sizable fraction of the interface sites being step sites where growth takes place. Assuming that this fraction does not change appreciably with temperature, the growth rate, u , is expressed by

$$u = \nu\lambda[1 - \exp(-\Delta H_{fM}\Delta T/RTT_m)]. \quad (8)$$

Here ν is the frequency of atom jumps at the interface, λ is the distance advanced by the interface in a unit kinetic process (usually taken as a molecular diameter), ΔH_{fM} the molar heat of fusion, ΔT the undercooling, and T_m the melting point.

b) *Screw dislocation growth*: This model views the interface as smooth but imperfect on an atomic scale, with growth taking place at step sites provided by screw dislocations intersecting the interface. The growth rate is given by:

$$u = f\nu\lambda[1 - \exp(-\Delta H_{fM}\Delta T/RTT_m)], \quad (9)$$

where f is the fraction of preferred growth sites (at the dislocation ledges) on the interface, given approximately by:

$$f \simeq \frac{\Delta T}{2\pi T_m}. \quad (10)$$

c) *Surface nucleation growth*: According to this model, the interface is smooth on an atomic scale and also perfect (free of intersecting screw dislocation). Growth takes place by the formation and growth of two-dimensional nuclei on the interface. The growth rate is expressed by

$$u = C\nu\exp(-B/T\Delta T), \quad (11)$$

where C and B depend on the time required for the formation of the nucleus relative to that for its propagation across the interface. When the nucleus propagates across the interface in a time short compared with the time between nucleation events (small crystal case),

$$C \simeq \lambda N_s A_0, \quad (12)$$

and

$$B = \frac{\pi\lambda V_M T_m \sigma_E^2}{k\Delta H_{fM}}, \quad (13)$$

where N_s is the number of atoms per unit area at the interface, A_0 the cross-sectional area of the interface, V_M the molar volume, σ_E the edge surface energy of the nucleus.

For the more generally applicable case where the lateral propagation rate of the surface nucleus must be considered (large crystal case),

$$C \simeq \frac{(\pi/3)^{1/3}}{\Gamma(4/3)} N_s^{1/3} a^{5/3} \times [1 - \exp(-\Delta H_{fM}\Delta T/RTT_m)]^{2/3}, \quad (14)$$

$$B = \frac{\pi\lambda V_M T_m \sigma_E^2}{3k\Delta H_{fM}}, \quad (15)$$

where Γ is the gamma function.

In his now-classic treatment of interface roughness, Jackson¹² used a single-layer Bragg-Williams model to describe the change in free energy of an initially plane interface on adding molecules at random to the interface. This free energy change, ΔF_s , was expressed:

$$\frac{\Delta F_s}{NkT_m} = -\frac{\Delta H_{fM}\Delta T}{RTT_m} X + f'X(1-X) + \frac{T}{T_m} [X \ln X + (1-X) \ln(1-X)] \quad (16)$$

Here N is the number of sites on the interface; X is the fraction of sites which are occupied and

$$f' = (\Delta S_{fM}/R)\xi, \quad (17)$$

where ΔS_{fM} is the molar entropy of fusion, and ξ is the number of nearest-neighbor sites in a layer parallel to the surface divided by the total number of nearest-neighbor sites. The factor ξ is largest for the most closely-packed planes of the crystal, for which it is $\simeq 0.5$.

For $f' < 2$, the minimum free energy configuration corresponds to half the available sites being filled ($X = 1/2$) and represents an atomically rough surface. In contrast, for $f' > 2$, the lowest free energy configuration corresponds to a few surface sites filled and a few molecules missing from the completed layer and represents an atomically smooth interface. Hence, for materials with $\Delta S_{fM} < 2R$, the most closely-packed interface planes should be small. For materials with $\Delta S_{fM} > 4R$, the most closely-packed surfaces should be smooth, the less-closely-packed faces should be rough, and the growth rate anisotropy should be large.

The above described theories describe reasonably well the experimentally measured growth rates at low undercoolings in glass forming liquids¹¹.

VI. Overall crystallization

The overall crystallization of a liquid occurs by the combination of nucleation and growth. The kinetics

of such processes is usually described by a theory derived in the period 1937-1939 by Kolmogorov¹³, Johnson and Mehl¹⁴ and Avrami¹⁵⁻¹⁷, best known as the Kolmogorov-Avrami or Johnson-Mehl-Avrami (JMA) theory. Since that time this theory has been intensively used by materials scientists to study the various mechanisms of phase transformations in metals. More recently, the JMA theory has been employed by polymer and glass scientists. Examples of technological importance include the study of stability of glass metals, curing of odontological plasters, devitrification time of rad-wast glasses, glass-ceramics and kinetics calculations of glass formation¹⁸.

Avrami¹⁵⁻¹⁷ has assumed that: (i) nucleation is random, i.e. the probability of forming a nucleus in unit time is the same for all infinitesimal volume elements of the assembly; (ii) nucleation occurs from a certain number of embryos (\bar{N}) which are gradually exhausted. The number of embryos decreases in two ways; by growing to critical sizes (becoming critical nuclei) with rate v per embryo and by absorption by the growing phase; (iii) the growth rate (u) is constant, until the growing regions impinge on each other and growth ceases at the common interface, although it continues normally elsewhere.

Under these conditions Avrami^{15,17} has shown that the transformed fraction volume, α' , is given by

$$\alpha' = 1 - \exp \left[\frac{-6g\bar{N}u^3}{v^3} \times \left(\exp(-vt) - 1 + vt - \frac{(vt)^3}{2} + \frac{(vt)^3}{6} \right) \right], \quad (18)$$

where g is a shape factor, equal to $4\pi/3$ for spherical grains, and t is the time period.

There are two limiting forms of this equation, corresponding to very small or very large values of vt . Small values imply that the nucleation rate, $I = \bar{N}v \exp(-vt)$, is constant. Expanding $\exp(-vt)$ in eq. (1) and dropping fifth and higher order terms gives

$$\alpha' = 1 - \exp(-gu^3 I_0 t^4 / 4), \quad (19)$$

where $I_0 = \bar{N}v$.

This is the special case treated by Johnson and Mehl² and is valid for \bar{N} very large when the number of embryos is not exhausted until the end of the transformation (homogeneous nucleation). Large values of vt , in contrast, means that all nucleation centers are exhausted at an early stage in the reaction. The limiting value of eq. (18) is then

$$\alpha' = 1 - \exp(-g\bar{N}u^3 t^3). \quad (20)$$

Eq. (20) applies for small \bar{N} , when there is a rapid exhaustion of embryos at the beginning of the reaction (instantaneous heterogeneous nucleation). Avrami has proposed that for a three-dimensional nucleation and

Table II

Avrami parameters, m , for several mechanisms
(Spherical Growth)

	Interface Controlled Growth	Diffusion Controlled Growth
Constant I	4	2.5
Decreasing I	3-4	1.5-2.5
Constant number of sites	3	1.5

growth process, the following general relation should be used

$$\alpha' = 1 - \exp(-Kt^m), \quad (21)$$

where $3 \leq m \leq 4$. This expression covers all cases where I is some decreasing function of time, up to the limit when I is constant. Eq. (21) also covers the case of heterogeneous nucleation from a constant number of sites, which are activated at a constant rate until becoming depleted at some intermediate stage of the transformation. In the more general case, where I and u are time dependent

$$\alpha' = 1 - \exp \left(-\frac{4\pi}{3} \int_0^t I(\tau) \times \left[\int_\tau^t u(t') dt' \right]^3 d\tau \right), \quad (22)$$

where τ is the time of birth of particles of the new phase. Table II shows values of m for different transformation mechanisms. Thus, if spherical particles grow in the internal volume of the sample then m should vary from 1.5 to 4. If growth proceeds from the external surfaces towards the center (collunar shape) then m will be different.

The above treatment, whilst including the effects of impingement neglects the effect of the free surfaces. This problem was recently treated by Weinberg¹⁹.

Eq. (21) is usually written as:

$$\ln \ln(1 - \alpha')^{-1} = \ln K + m \ln t. \quad (23)$$

This expression is intensively employed by materials scientists to infer the mechanisms of several classes of phase transformations from the values of m , that is the slope of $\ln \ln(1 - \alpha')^{-1}$ versus $\ln t$ plots. The linearity of such plots is taken as an indication of the validity of the JMA equation. It should be emphasized, however, the $\ln - \ln$ plots are insensitive to variations of α' and t and that the value of the intercept K is seldom compared to the theoretical value. This is mainly due to the great

difficulty in measuring the high nucleation and growth rates in metallic and ceramic (low viscosity) systems.

VII. Application to glass crystallization

The JMA theory can be shown to be exact within the framework of its assumptions. Hence, any violation must be a result of applying it to situations where its assumptions are violated, which may be the case in many crystallization situations.

In an extensive number of studies the JMA theory has been employed to analyze experimental data for crystallinity versus time in both isothermal and non-isothermal heat treatments of glass systems. Emphasis was usually given to values of m obtained from the slopes of experimental $\ln \ln(1 - \alpha')^{-1}$ versus $\ln t$ plots. In²⁰⁻²⁴ for instance, m ranged from 1 for surface nucleation to 3 for internal nucleation. In no case has the intercept been compared with the theoretical value.

Recently, Zanotto and Galhardi²⁵ carried out a series of experiments to test the validity of the Johnson-Mehl-Avrami theory.

The isothermal crystallization of a nearly stoichiometric $\text{Na}_2\text{O} \cdot 0.2\text{CaO} \cdot 3\text{SiO}_2$ glass was studied at 627°C and 629°C by optical microscopy, density measurements and X-ray diffraction. Both nucleation and growth rates were measured by single and double stage heat treatments up to very high volume fractions transformed and the experimental data for crystallinity were compared with the calculated values at the two temperatures. The early crystallization stages were well described by theory for the limiting case of homogeneous nucleation and interface controlled growth. For higher degrees of crystallinity, both growth and overall crystallization rate decreased due to compositional changes of the glassy matrix and the experimental kinetics could be described by theory if diffusion controlled growth was assumed. It was also demonstrated that the sole use of numerical fittings to analyse phase transformation kinetics, as very often reported in the literature, can give misleading interpretations. It was concluded that if proper precautions are taken the general theory predicts the glass-crystal transformation well.

VIII. Glass formation

Turnbull²⁶ noted that there are at least some glass formers in every category of material based on bond type (covalent, ionic, metallic, van der Waals, and hydrogen). The cooling rate, density of nuclei and various material properties were suggested as significant factors which affect the tendency of different liquids to form glasses.

This approach leads naturally to posing the question not whether a material will form an amorphous solid when cooled in bulk form from the liquid state, but rather how fast must a given liquid be cooled in order that detectable crystallization be avoided. In turn,

the estimation of a necessary cooling rate reduces to two questions: (1) how small a volume fraction of crystals embedded in a glassy matrix can be detected and identified; and (2) how can the volume fraction of crystals be related to the kinetic constants describing the nucleation and growth processes, and how can these kinetic constants in turn be related to readily-measurable parameters?

In answering the first of these questions, Uhlmann^{18,27} assumed crystals which are distributed randomly through the bulk of the liquid, and a volume fraction of 10^{-6} as a just-detectable concentration of crystals. In answering the second question, Uhlmann adopted^{18,27} the formal theory of transformation kinetics described in this section.

In this paper I shall be concerned with single-component materials or congruently-melting compounds, and will assume that the rate of crystal growth and the nucleation frequency are constant with time. For such a case, the volume fraction, α' , crystallized in a time t , may for small α' be expressed by a simplified form of Eq. (19):

$$\alpha' \simeq \frac{\pi}{3} I_0 u^3 t^4. \quad (24)$$

In identifying I_0 as the steady-state rate of homogeneous nucleation, I shall neglect heterogeneous nucleation events—such as at external surfaces—and will be concerned with minimum cooling rates for glass formation. Clearly, a glass cannot be formed if observable amounts of crystals form in the interiors of samples. I shall also neglect the effect of transients during which the steady-state concentrations of subcritical embryos are built up by a series of bimolecular reactions. Neglect of transients in the present analysis is justified whenever the time required to establish the steady-state nucleation rate is small relative to the total transformation time.

The cooling rate required to avoid a given volume fraction crystallized may be estimated from eq. (24) by the construction of so-called T-T-T (time-temperature-transformation) curves, an example of which is shown in figure 3 for two different volume fractions crystallized. In constructing these curves, a particular fraction crystallized is selected, the time required for that volume fraction to form at a given temperature is calculated and the calculations is repeated for other temperatures (and possibly other fractions crystallized).

The nose in a T-T-T curve, corresponding to the least time for the given volume fraction to crystallize, results from a competition between the driving force for crystallization, which increases with decreasing temperature, and the atomic mobility, which decreases with decreasing temperature. The transformation times t_1 , are relatively long in the vicinity of the melting point as well as at low temperatures; and for purposes of the present paper, I shall approximate the cooling rate re-

quired to avoid a given fraction crystallized by the relation

$$\left(\frac{dT}{dt}\right)_c \approx \frac{\Delta T_N}{\tau_N}, \quad (25)$$

where $\Delta T_N = T_m - T_N$; T_N is the temperature at the nose of the T-T-T curve; τ_N is equal to the time at the nose of the T-T-T curve, and T_m is the melting point.

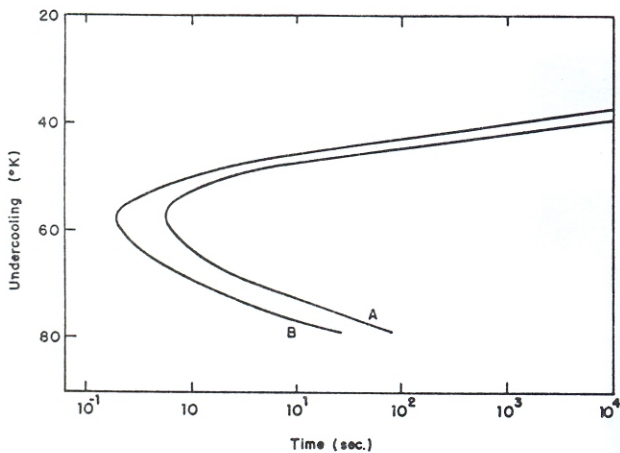


Figure 3: Time-temperature transformation curves for salol: (A) $\alpha' = 10^{-6}$; (B) $\alpha' = 10^{-8}$.

From the form of eq. (24), as well as from the curves shown in figure 3 which were calculated therefrom, it is apparent that the cooling rate required for glass formation is rather insensitive to the assumed volume fraction crystallized, since the time at any temperature on the T-T-T curve varies only as the one-fourth power of α' .

An alternative estimate of the glass-forming characteristics of materials may be obtained by considering the thickness of sample which can be obtained as an amorphous solid. Again using the criterion of a volume fraction crystallized less than 10^{-6} , and neglecting problems associated with heat transfer at the external surfaces of the sample, the thickness, y_c , of sample which can be formed without detectable crystallization should be of the order of²⁷

$$y_c \approx (D\tau_N)^{1/2}, \quad (26)$$

where D is the thermal diffusivity of the sample.

To estimate the critical conditions to form a glass of a given material, one can in principle to employ the measured values of the kinetic factors to calculate the T-T-T curves. In practice, however, information on the temperature dependence of the nucleation frequency is seldom available; and in only a portion of the cases of interest there are adequate data available on the variation of the growth rate with temperature.

IX. Concluding remarks

The kinetic approach of glass formation allows one to conclude that *all* materials are capable of forming amorphous solids when cooled in bulk form from the liquid state. The question to be answered is how fast must a given liquid be cooled in order that crystallization be avoided. Thus novel materials such as *metallic alloys*, with unusual properties, have been successfully obtained by very fast quenching²⁸. On the other hand, if crystal nucleation is controlled to occur uniformly in the bulk of certain glasses, a variety of advanced *glass-ceramics* can be and, indeed, are being commercially produced²⁹.

Deeper insights on the crystallization process, such as precise predictions of TTT curves, and consequently of critical cooling rates for glass formation, based solely on materials properties, will depend critically on new developments concerning the nucleation theory. One interesting attempt on that issue was recently advanced by Meyer with his Adiabatic Nucleation Theory³⁰.

Acknowledgements

The author thanks his co-workers and students who collaborated in several phase-transformations problems in the past fifteen years namely: A. Craievich, M. Weinberg, E. Meyer, P. James, E. Müller, C. Kiminami, A. Galhardi, N. Mora, M. Leite, E. Belini, E. Wittman, E. Ziemath.

Thanks are also due to PADCT (New Materials), contract n^o 620058/91-9, for financial support.

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