ELSEVIER Thermochimica Acta 280/281 (1996) 73–82

thermochimica
acta

The applicability of the general theory of phase transformations to glass crystallization[1]

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Abstract

The general theory of phase transformation kinetics, derived independently by Kolmogorov, Johnson and Mehl, and Avrami (KJMA), has been used intensively by materials scientists to study various mechanisms of phase transformations in metals, polymers and glasses, especially in kinetic calculations of glass formation. The theory is certainly valid within the framework of its assumptions, and thus its violation in certain cases can be used to infer hidden details of the crystallization mechanisms of supercooled liquids. In this paper the applicability of the KJMA theory to glass crystallization is discussed for three transformation mechanisms: (i) volume crystallization of single crystals, (ii) volume crystallization of branched crystals, and (iii) surface crystallization, in the following silicate glasses: $Na_2O.2CaO.3SiO_2$; $Li_2O.2SiO_2$ and $CaO.MgO.2SiO_2$.

Keywords: Crystallization; General theory; Glass; Phase transformation

1. Introduction—the importance of crystallization and the theory of phase transformations

The most obvious crystallization process is that frequently employed by chemists for the synthesis of new compounds, i.e. the precipitation of powder particles from supersaturated solutions. Geologists rely on the "post-mortem" study of crystallization to understand the formation of minerals and solidified magmas. Many solid-state physi-

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[1] Dedicated to Professor Hiroshi Suga.

SSDI 0040-6031(95)02636-3

cists depend on crystal growth from seeded melts to obtain single-crystal specimens as well as commercially important materials such as silicon and lithium niobate. Ceramicists and materials scientists dedicate a lot of effort to the synthesis of novel ceramics and glasses employing sol-gel technology. In this case the avoidance of crystal nucleation and growth in the gel, during the sintering step, can lead to a glass. The final microstructure and properties of metals obtained by solidification depend on the crystallization kinetics of the cooling path.

In the glass field, the catalyzed crystallization of vitreous materials 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 behavior. Finally, the glassy state is only attainable when crystallization (the thermodynamically favorable path) can be avoided during fabrication! Thus the scientific and technological importance of understanding and controlling the crystallization kinetics of glasses is clear. Hence, the use of phase transformation theories can be of substantial help. In addition, this theory is frequently employed to infer phase transformation mechanisms from both isothermal and non-isothermal (DTA or DSC) experiments [1a, 1b].

2. Nucleation, growth and overall crystallization

When a liquid is cooled below its melting point, crystal nucleation can occur homogeneously or heterogeneously in the volume or on the surface. The classical nucleation theory (CNT) was derived in the late 50's by Turnbull and Fisher [2], and in spite of its limitations it has been used intensively. The subsequent step, crystal growth of the nuclei, leads to a polycrystalline material.

The overall crystallization of a liquid occurs by a combination of nucleation and growth. The kinetics of such a process is usually described by a theory derived independently, in the late 30's, by Kolmogorov [3], Johnson and Mehl [4] and Avrami [5-7], best known as the Kolmogorov-Avrami or Johnson-Mehl-Avrami theory, hereafter called the KJMA theory. This theory has been used intensively by materials scientists to study various mechanisms of phase transformations in metals, polymers and glasses. Examples of technological importance include the study of the stability of glassy metals, the curing of odontological plasters, the devitrification time of radwast glasses, the development of glass-ceramics, and kinetics calculations of glass formation [8].

Avrami [5-7] 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) at a 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 [5–7] has shown that the volume fraction transformed α in isothermal conditions is given by

$$\alpha = 1 - \exp\left[\frac{-6g\bar{N}U^3}{v^3}\left(\exp(-vt) - 1 + vt - \frac{(vt)^2}{2} + \frac{(vt)^3}{6}\right)\right] \tag{1}$$

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

$$\alpha = 1 - \exp(-gI_0U^3t^4/4) \tag{2}$$

where $I_0 = \bar{N}v$. This is the special case treated by Johnson and Mehl [4] and is valid for very large $\bar{N}$, when the number of embryos is not exhausted until the end of the transformation (**homogeneous nucleation**).

Large values of vt, in contrast, mean that all nucleation centers are exhausted at an early stage in the reaction. The limiting value of Eq. (1) is then

$$\alpha = 1 - \exp(-g\bar{N}U^3t^3) \tag{3}$$

Eq. (3) applies for small $\bar{N}$ (**fast heterogeneous nucleation**).

Avrami has proposed that for a three-dimensional nucleation and growth process, the following general relation should be used

$$\alpha = 1 - \exp(-Kt^m) \tag{4}$$

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. (4) 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. Table 1 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 (columnar shape) then m will be different.

In the more general case, where I and U are time-dependent, one can write

$$\alpha = 1 - \exp\left(-\frac{4\pi}{3}\int_0^t I(\tau)\left[\int_\tau^t U(t')\,\mathrm{d}t'\right]^3\mathrm{d}\tau\right) \tag{5}$$

Table 1
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

where τ is the time of birth of the new phase particles. The above treatment, whilst including the effects of impingement, neglects the effect of free surfaces (thin specimens). This problem was treated by Weinberg [9]

Eq. (4) is usually written as

$$\ln \ln (1-\alpha)^{-1} = \ln (K) + m \ln t \tag{6}$$

This expression is used intensively by materials scientists to infer the mechanisms of several classes of phase transformations from the experimental values of m, i.e. 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 KJMA equation. It should be emphasized, however, that 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.

3. Application to glass crystallization

The KJMA 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 KJMA 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. In Refs. [10–14] 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 co-authors [15–17] carried out a series of experiments to test the applicability of the Kolmogorov–Johnson–Mehl–Avrami theory to several cases of glass crystallization. These inlcuded volume nucleation of single crystals and branched crystals as well as surface nucleation of single crystals. Some of these studies will be summarized below.

3.1. *Volume nucleation in $Na_2O.2CaO.3SiO_2$ glass*

In 1988, Zanotto and Galhardi [15] determined the isothermal crystallization kinetics of a nearly stoichiometric $Na_2O.2CaO.3SiO_2$ glass at 627 and 629°C ($T_g \sim 570$°C) by optical microscopy, density measurements and X-ray diffraction. Both nucleation (I_0) and growth (U) rates were measured by single- and double-stage heat treatments, up to high volume fractions transformed ($\alpha \sim 0.5$).

Fig. 1 shows the experimental data for crystallinity, measured up to 0.97, compared with the calculated values, using the independently measured values of I_0 and U, and $m = 4$, in Eq. (2). The experimental points initially (up to 15–20% crystallinity) coincide with the theoretical curve but drop for longer times (higher crystallinities). A possible explanation for this behavior is as follows. The large majority of crystalline phases

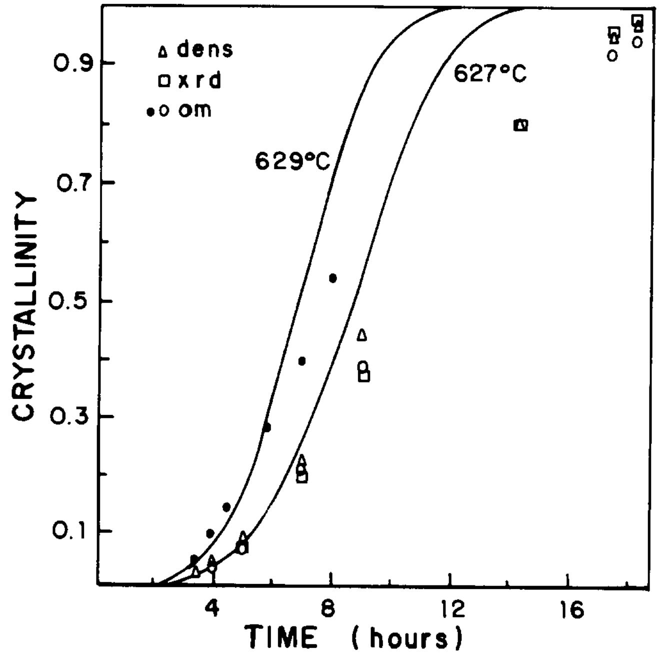

Fig. 1. Volume fraction crystallized as a function of time for specimens heated at 627 and 629°C: optical microscopy (●, ○), X-ray diffraction (□) and density (Δ) measurements, respectively.

growing in viscous liquids are spherulitic (only partially crystalline). In such cases the "crystallinity" values measured depend on the experimental technique employed. The good agreement between the values determined by the three techniques used in Ref. [15] (XRD, density and optical microscopy) indicates that the NC_2S_3 particles are **single crystals**, in agreement with the electron diffraction determinations of Gonzalez-Oliver [18]. Thus, the decrease in the overall crystallinity with time (when compared with the predicted values) could be due to rejection of impurities at the growth fronts. Indeed, a semi-quantitative EDS analysis (Fig. 2) indicated an increase in Si and a decrease in Na and Ca in the glassy matrix with respect to the crystalline particles. Therefore, it is probable that this would locally increase the viscosity, lowering the crystallization rate. If the particles were spherulites this effect probably would not be so drastic since the rejected impurities could be engulfed between the crystalline arms of the spherulites.

In summary, 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 only if diffusion-controlled growth was assumed. It was also demonstrated that the sole use of numerical fittings to analyze phase transformation

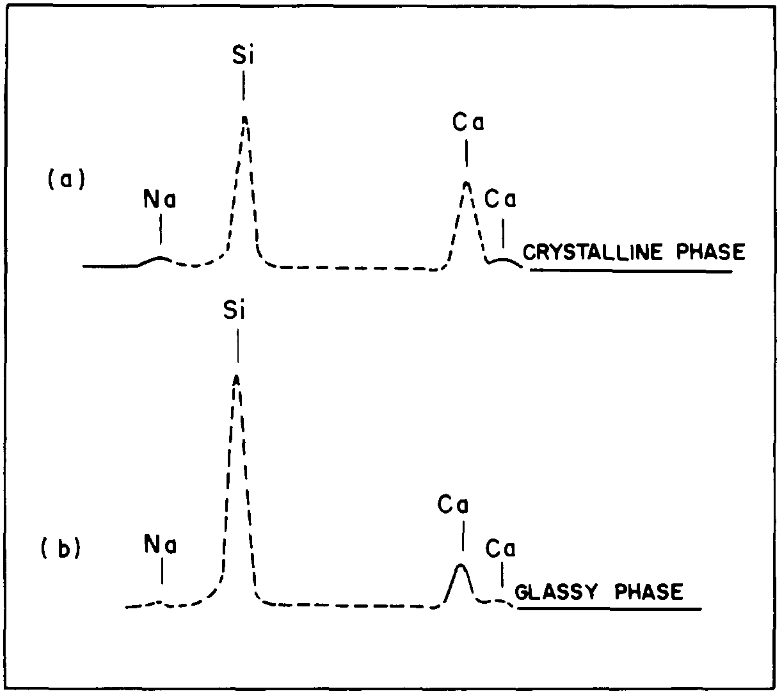

Fig. 2. EDS scan of both glassy and crystalline phases in a sample heated at 627°C for 14.3 h ($\alpha \sim 0.7$).

kinetics via Eq. (6), as very often reported in the literature, can give misleading interpretations [15]. It was concluded that if proper precautions are taken, the theory predicts well the initial stages of the glass–crystal transformation for the case of homogeneous nucleation of single-crystal particles.

3.2. Surface nucleation in CaO.MgO.2SiO$_2$ (diopside) glass

In 1991, the present author [16] tested the applicability of the KJMA theory to the case of nucleation of single crystals on free glass surfaces. A diopside glass containing 5% Al_2O_3, with polished surfaces heat-treated at 820°C ($T_g \sim 720$°C), was used. Figs. 3a, b, c show the time dependence of the average number of crystals per unit area of glass N_s, the maximum crystal dimension, R_m, and the fractional area crystallized, respectively.

Fig. 3a shows a large statistical scatter around an average value ($N_s \sim 79\,000$ crystals per mm^2) which is independent of heat treatment time. This behavior is typical for surface nucleation and has been recently reported for a number of glasses [19]. Therefore, surface nucleation saturates in the early crystallization stages. Fig. 3b shows that the growth rate ($U = 0.001$ mm h^{-1}) is constant up to 4 h at 820°C ($\alpha \sim 0.65$).

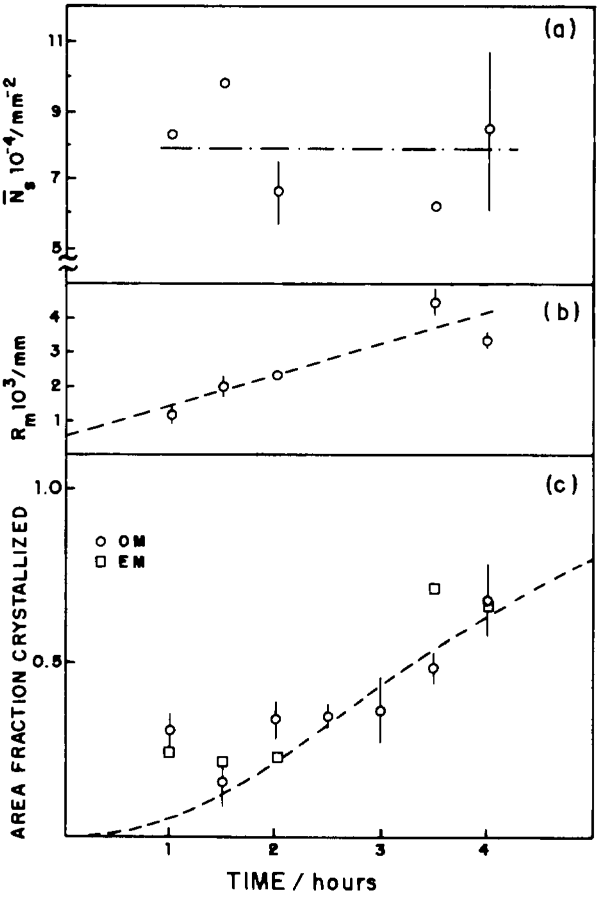

Fig. 3. Time dependence of (a) the average number of crystals per unit area, N_s; (b) maximum edge size; and (c) fractional area crystallized determined by optical microscopy (○) and by scanning electron microscopy (□). The dotted line is the theoretical curve calculated by Eq. (6).

For the special case under study, i.e. fast nucleation of square-shaped crystals from a constant number of sites on a glass surface,

$$\alpha_s = 1 - \exp(-N_s U^2 t^2) \tag{6a}$$

where α_s is the fractional area crystallized.

Fig. 3c shows that, despite the statistical scatter, and taking into account the extreme sensitivity of the exponential expression to small errors in N_s and, especially in U, the evolution of the fractional area crystallized is reasonably well described by Eq. (6a) up to 65% crystallization, the limit of experimental evaluation. In summary, the KJMA describes well the case of rapid heterogeneous nucleation from a fixed number of sites at the glass surface. Thus, in the case of surface crystallization, the possible rejection of impurities at the crystal/glass fronts did not occur or did not affect significantly the crystallization rate up to 65% crystallinity.

3.3. *Volume nucleation of branched crystals in $Li_2O.2SiO_2$ glass*

In a recent study [17], the volume crystallization of $Li_2O.2SiO_2$ (LS_2) branched crystals in an LS_2 glass was followed at 500°C ($T_g \sim 450°C$). This composition is of special interest because it is the canonical system for crystallization studies and a controversy concerning its nucleation behavior (homogeneous versus heterogeneous) was recently resuscitated by Deubener et al. [20]. As the LS_2 spherulites are prolate ellipsoids, the general equation reduces to [17]

$$\alpha = 1 - \exp(-\pi I_0 U_a U_b^2 t^4/3) \tag{7}$$

where U_a and U_b are the growth rate of the largest and smallest dimensions of the crystals, respectively, as shown by Fig. 4. In this case it is assumed that $U_b = U_c$.

Table 2 and Fig. 5 show the experimental volume fraction crystallized, determined by optical microscopy, and the values calculated by Eq. (7), using the independently determined values of crystal nucleation (I_0) and growth (U) rates and induction time (τ) by both reflected light (RLM) and transmitted light (TLM) microscopy.

In this case, an induction period (τ) of approximately 3 h was observed in the nucleation (N_v versus time) and growth (length vs. time) curves, and thus t was substituted by $(t - \tau)$ in the calculations of Eq. (7). Taking into account the difficulty in precisely defining and measuring τ, and the exponential sensitivity of Eq. (7) to τ, U_b, U_a

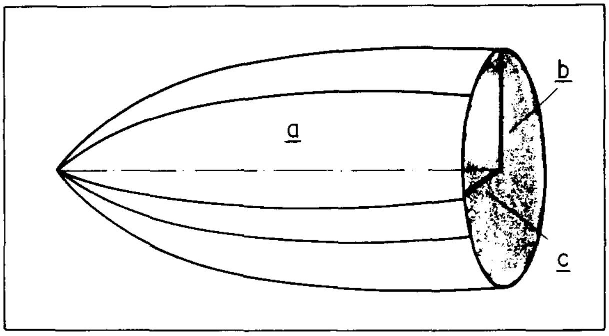

Fig. 4. Cross section of an LS_2 crystal showing the principal axes.

Table 2
Crystallization parameters for LS_2 glass at 500°C [17]

	I_0/mm^{-3} h^{-1}	U_a/mm h^{-1}	U_b/mm h^{-1}	τ/h
TLM	784	383×10^{-6}	231×10^{-6}	3
RLM	794	378×10^{-6}	206×10^{-6}	3

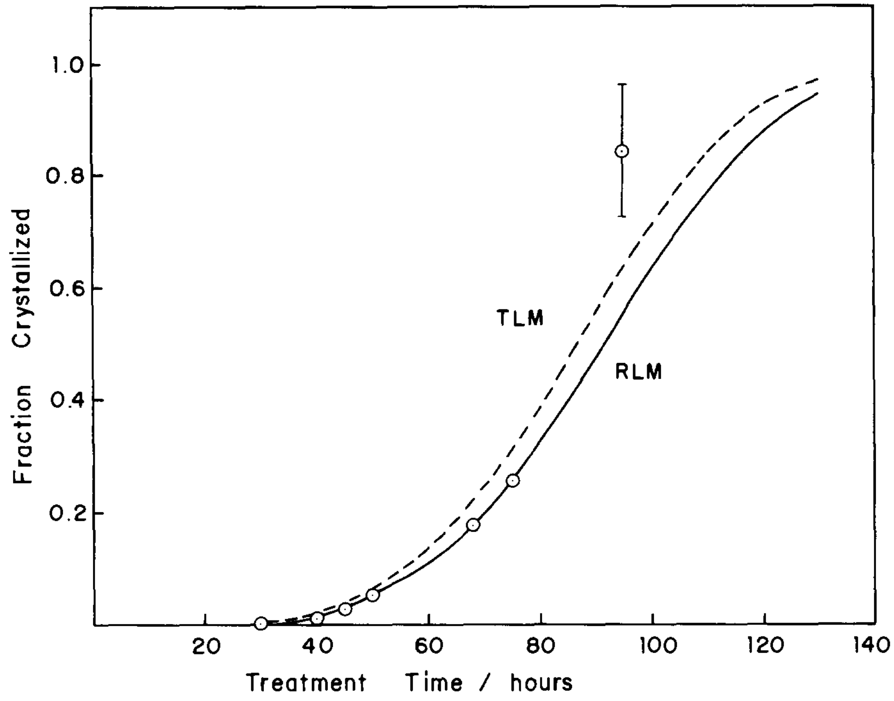

Fig. 5. Experimental (○) and calculated values of crystallinity of $Li_2O.2SiO_2$ at 500°C: TLM, values of *I* and *U* obtained by transmitted light; RLM, values of *I* and *U* obtained by reflected light.

and I_0, it can be concluded that the agreement between the calculated and experimental crystallinity is remarkably good up to 25% crystallinity. Further experiments are being carried out in our laboratory for longer treatment times to reach more advanced crystallinity degrees. Fig. 5 also shows that the predicted crystallinity using the RLM data is in better agreement with experiment than that using the TLM data.

4. Concluding remarks

The general theory of phase transformation kinetics was tested for three crystallization cases without any adjustable parameter. The theory was shown to describe remarkably well the evolution of crystallinity up to ~ 20–25% transformation, for volume nucleation in two glasses which nucleate homogeneously, $Na_2O.2CaO.3SiO_2$ and $Li_2O.2SiO_2$. In the first glass, whose grains are single crystals, the predicted crystallinity is underestimated for more advanced stages due to impurity rejection at the growth fronts. For the other glass, whose grains are branched crystals, no data is yet available for the latter crystallization stages. For a $CaO.MgO.2SiO_2$ glass, which nucleates heterogeneously on the external surfaces, the theory predicted well the time evolution of crystallinity up to the highest crystallinity measured (~ 65%). In summary, the KJMA theory can be used confidently to infer the crystallization mechanism of glasses, but carefully determined data are needed, at least for the initial crystallization stages (up to 20% crystallinity). The more advanced stages can often be influenced by compositional changes in the matrix phase. In addition, it can definitively be concluded that **homogeneous nucleation** is the predominant mechanism for the overall crystallization of LS_2 glass at 500°C.

Acknowledgements

The author thanks his former students A.C. Galhardi, R. Basso and M.L.G. Leite for obtaining most of the experimental data presented in this paper. Thanks are also due to PADCT (New Materials), contract no. 620058/91–9, and CNPq, contract no. 301549/85–0 for financial support.

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