



Identification of the onset crystallization time in metallic glasses at isothermal conditions



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ABSTRACT

An approach for determination of the onset crystallization time (t_{ons}) at isothermal annealing of metallic glasses similar to that used in the DSC analysis for the onset crystallization temperature is proposed. The analysis performed in the framework of the Kolmogorov-Johnson-Mehl-Avrami model has shown that the volume fraction transformed at t_{ons} (X_{ons}) increases from 0 to 0.05 with the Avrami exponent increasing from 1.5 to 12. It has been found that the values of X_{ons} determined from the experimental kinetic crystallization curves for the $\text{Fe}_{85}\text{B}_{15}$ glass at 628 K, for the $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ glass at 662, 649 and 617 K and for the $\text{Fe}_{40}\text{Co}_{40}\text{P}_{14}\text{B}_6$ glass at 695 K are in good agreement with the calculated ones. New possibilities for analysis of nucleation behavior in glasses using the relation established between the kinetic and structural data are discussed.

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1. Introduction

The studies of the thermal stability of metallic glasses are of prime importance not only when determining the stability of the amorphous phase and producing controlled microstructures with enhanced physical properties, but also in the course of fundamental studies of crystal nucleation and growth. The most studies focus on the crystallization onset as a measure of kinetic stability of glass under heat treatment. In practice, the stability is characterized by the onset crystallization temperature, T_{ons} , at continuous heating or by the onset crystallization time, t_{ons} , at isothermal annealing. However, in contrast to the widely used quantity T_{ons} , the term “onset crystallization time” is not so popular [1]. In the isothermal studies of metallic glass stability, the onset of crystallization is considered as the moment when the crystals become first detectable by transmission electron microscopy [2,3] or at the moment when the crystallization exotherm starts in the differential scanning calorimetry (DSC) experiments (e.g., [4,5]). The time interval between the start of annealing and the moment of detection of signs of crystallization is called “incubation time”, τ_{inc} , and this quantity is often used in the analysis of crystallization kinetics (e.g., [4]). However, it is evident that such determined incubation time has no real physical

meaning because the value of τ_{inc} is crucially dependent both on the technique used and on its sensitivity.

Besides, according the commonly used model developed by Kolmogorov [6], Johnson and Mehl [7] and Avrami [8] (the KJMA model)

$$X(t) = 1 - \exp[-(Kt)^n] \quad (1)$$

crystallization starts directly at $t > 0$. (Here, K is a kinetic constant that depends on the temperature and on the rates of crystal nucleation and growth, while the so-called Avrami exponent, n , gives information of the dimensionality of the growth and depends on the nucleation rate behavior as well as on the fact whether the transformation is interface or diffusion controlled [9]). Note, that Eq. (1), which is a partial solution of the equation obtained by Kolmogorov [6,10], has been derived for polymorphic (interface controlled) transformations in which the initial phase is completely transformed to the final phase without a compositional change. However, it was shown that the KJMA model could be expanded to description of eutectic crystallization of metallic glasses [2–4, 12] and even (as a first approximation) to the transformations involving the diffusion-limited growth occurring with continuously lowering rate [1,13,14].

The KJMA model gives the values of n between 4 and 3 for interface-controlled growth and between 2.5 and 1.5 for diffusion-limited three-dimensional growth assuming constant or decreasing nucleation rate, respectively. These crystallization mechanisms are typical for metallic

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glasses. To classify the mechanism, the experimentally measured kinetic crystallization curves $X(t)$ are plotted as $\ln\{-\ln[1 - X(t)]\}$ vs. $\ln(t)$ which should give a straight line with the slope of n . Numerous studies (e.g., [1,4,5,11,12,15–17]) have shown that the KJMA model satisfactory describes crystallization kinetics of metallic glasses. In many cases, the Avrami exponents estimated from the $X(t)$ experimental curves within Eq. (1) are in accordance with the microscopically established crystallization mechanisms. However, in a number of studies, very low (~ 1) [16] and very high (about 11) [11] values of n compared with those mentioned above are reported. These discrepancies are explained by the failure of the KJMA equation for primary nanocrystallization [16], by incorrect choice of the onset crystallization time [4] or by the transient behavior of nucleation rate [11] such indicating that the KJMA model applicability requires further clarification.

From both physical and technical points of view, it is reasonable to determine the value of t_{ons} as the time required to form a specified volume fraction crystallized. Besides, determination of the onset crystallization time has to be experimentally convenient and relatively independent on the technique used for crystallization kinetics study. In particular, it can be done by finding the intersection of the baseline on the left side of the dX/dt isotherm peak and the extrapolated tangent at the inflection point of the leading edge of the peak similarly to determination of the onset crystallization temperatures in the DSC scans at continuous heating [17]. It should be noted that the values of such determined t_{ons} may be calculated using Eq. (1) and compared with those estimated from the experimental data. The aim of this article is to present an analytical model for calculation of the onset crystallization time and to compare the results of calculations with the experimental data for evaluation of the validity of the simple KJMA model for description of the isothermal crystallization of glasses occurring via different mechanisms.

2. Description of the model

For convenience of the subsequent analysis, let us replace the kinetic constant K in Eq. (1) by certain crystallization time τ_c ($=K^{-1}$) and rewrite it with using a dimensionless parameter $\xi = t/\tau_c$ as

$$X(\xi) = 1 - \exp[-(\xi)^n]. \tag{2}$$

The isothermal transformation rate, $dX(\xi)/d\xi$, can be easily derived by differentiating Eq. (1) with respect to dimensionless time

$$dX/d\xi = Y(\xi) = n\xi^{n-1}[1-X(\xi)]. \tag{3}$$

In order to estimate the effect of the crystallization mechanism, the dimensionless time dependences of $dX(\xi)/d\xi$ for different values of n are calculated using expression (3). As evident in Fig. 1, as n increases, the calculated crystallization peaks become higher and narrower and their positions shift to larger values of ξ .

The effect of n on the peak position ξ_{max} and the volume fraction crystallized at this moment can be estimated from equation

$$dY/d\xi|_{\xi_{max}} = \left\{ [(n-1) - n\xi^n] n\xi^{n-2} [1-X(\xi)] \right\} \Big|_{\xi_{max}} = 0 \tag{4}$$

Solving Eq. (4) for ξ_{max} , we obtain

$$\xi_{max} = [(n-1)/n]^{1/n} \text{ and } t_{max} = \tau_c [(n-1)/n]^{1/n} \tag{5}$$

The volume fraction crystallized corresponding to t_{max} is expressed as

$$X(t_{max}) = 1 - \exp[-(n-1)/n]. \tag{6}$$

It follows from Eqs. (5) and (6) that both ξ_{max} and $X(t_{max})$ grow fast with n up to near saturation. In particular, the calculation shows that the

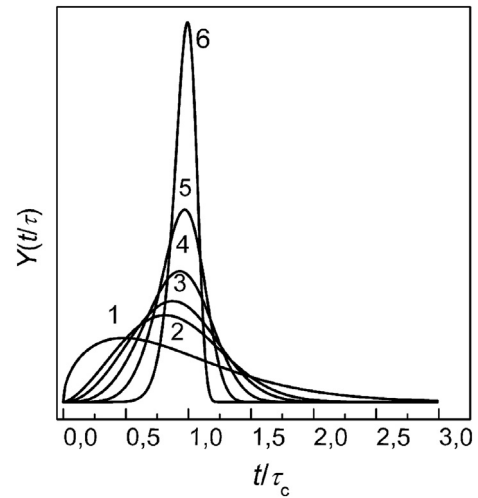


Fig. 1. The isothermal crystallization rates calculated according to Eq. (3) for different values of the Avrami exponent: 1–1.5, 2–2.5, 3–3.0, 4–4.0, 5–6.0, 6–12.

increase of n from 1.5 to 12 results in the increase of ξ_{max} from 0.48 to 0.99 while the value of $X(t_{max})$ increases from 0.28 to 0.6 (Fig. 2).

In order to calculate the onset crystallization time t_{ons} as the intercept of the extrapolated tangent at the inflection point of the leading edge of the crystallization peak, $Y(t)$, on the x -axis, the coordinates of the inflection points are found from the known condition obtained by differentiating of Eq. (4) with respect to ξ

$$\frac{d^2 Y/d\xi^2}{d\xi} \Big|_{\xi_i} = \left\{ [n^2 \xi^{2n} - 3n(n-1)\xi^n + (n-1)(n-2)] n\xi^{n-3} [1-X(\xi)] \right\} \Big|_{\xi_i} = 0. \tag{7}$$

In view that the $Y(t)$ function has the inflection points on the left and right sides, it seems reasonable to estimate the time of the end of crystallization, t_{end} , additionally to t_{ons} . Solving Eq. (7) for ξ gives the coordinates of the inflection points

$$\xi_{iL,iR} = \left[\frac{3n-1}{2} \frac{n-1}{n} \left(1 \mp \sqrt{1 - \frac{4n-2}{9n-1}} \right) \right]^{1/n}, \tag{8}$$

where ξ_{iL} and ξ_{iR} are coordinates of the left and right inflection points, respectively. It follows from Eq. (8) that the solutions of Eq. (1) are in the range of $n \geq 2$. Otherwise the left side of the calculated crystallization

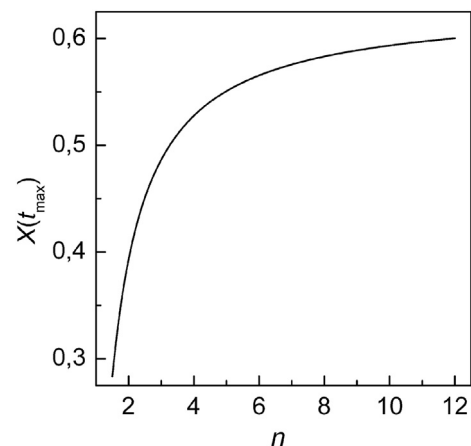


Fig. 2. The volume fraction crystallized at the time corresponding to the maximum crystallization rate as a function of the Avrami exponent.

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