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CRYSTALLIZATION KINETICS BY THERMAL ANALYSIS

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Abstract

Thermal Analysis techniques are widely used to study the crystallization kinetics in amorphous solids. Such experimental data are frequently interpreted in terms of the Johnson-Mehl-Avrami (JMA) nucleation-growth model. This paper discusses the limits of such approach. A simple method is proposed to verify the applicability of the JMA model as well as the basic assumptions in kinetic analysis. It is shown that the autocatalytic model includes the JMA model and it is a plausible description of the crystallization kinetics. The main advantage of the autocatalytic model is the possibility to describe quantitatively the kinetics of complex crystallization processes. The experimental data for crystallization of a chalcogenide glass analyzed in this paper clearly demonstrate rather complex nature of these processes. As a consequence it is very difficult to explore real kinetic mechanism of the crystallization process unless some complementary studies are made.

Keywords: autocatalytic model, crystallization kinetics, Johnson-Mehl-Avrami model

Introduction

The crystallization kinetics based on thermal analysis data (such as DTA or DSC) is usually interpreted in terms of standard nucleation-growth model formulated by Johnson and Mehl [1], and Avrami [2]. A similar method was also developed by Kolmogorov [3] and Erofeev [4]. The nucleation-growth model describes the time dependence of the fractional extent of crystallization α, written as:

$$\alpha = 1 - \exp[-(Kt)^{m}] \qquad (1)$$

where K and m are constants with respect to time, t. The kinetic exponent m depends on the crystal growth morphology [5]. The rate equation can be obtained from Eq.(1) by differentiation with respect to time:

$$\left(\frac{d\alpha}{dt}\right) = Km(1-\alpha)[-\ln(1-\alpha)]^{1-1/m} \qquad (2)$$

Equation (2) is usually referred to as the JMA equation and is frequently used for the formal description of TA crystallization data. It should be emphasized, however, that

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the JMA equation is valid in isothermal conditions for homogeneous or heterogeneous nucleation at randomly dispersed second phase particles [6, 7]. The growth rate of new phase should be controlled by temperature and independent of time, and anisotropy of growing crystals should be low [8]. These conditions must be carefully considered before the JMA equation is used for the interpretation of isothermal TA data and any conclusions concerning the growth morphology are made. Henderson [6, 7] has shown that the validity of the JMA equation can be extended in non-isothermal conditions if the entire nucleation process takes place during early stages of the transformation and becomes negligible afterwards. The crystallization rate is defined only by the temperature and does not depend on the previous thermal history. Nevertheless, even in this case the applicability of the JMA model should be critically examined, in particular the meaning of the kinetic exponent *m*.

Although the limits of applicability of the JMA equation are well known, in practice it is not so easy to verify whether they are fulfilled or not. The aim of this paper is to develop a simple and reliable testing method for kinetic analysis of isothermal and non-isothermal data.

Theory

In kinetic interpretation of thermal analysis (TA) data it is assumed that the measured heat flow ϕ is proportional to the rate of the kinetic process $\mathrm{d}\alpha/\mathrm{d}t$ [9]:

$$\phi = \Delta H_{\mathrm{c}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) \tag{3}$$

where ΔH_{c} is the crystallization enthalpy. The rate constant in Eq. (2) follows Arrhenius form: $K(T) = A\exp(-E_{\mathrm{a}}/RT)$ where the pre-exponential factor A and activation energy E_{a} are kinetic parameters that should not depend on the temperature T and the fractional conversion α. Taking into account these assumptions the kinetic equation for the JMA model can be written as

$$\phi = \Delta H_{\mathrm{c}}A\exp(-E_{\mathrm{a}}/RT)m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m} \tag{4}$$

It is convenient to define two functions $y(\alpha)$ and $z(\alpha)$ that can easily be obtained by a simple transformation of experimental data. For practical reasons the $y(\alpha)$ and $z(\alpha)$ functions are normalized within (0, 1) interval. In non-isothermal conditions these functions are defined as [10–12]:

$$y(\alpha) = \phi\exp(E_{\mathrm{a}}/RT) \tag{5}$$

$$z(\alpha) = \phi T^2 \tag{6}$$

In isothermal conditions these functions are defined as

$$y(\alpha) = \varphi \tag{7}$$

$$z(\alpha) = \phi t \tag{8}$$

The $y(\alpha)$ and $z(\alpha)$ plots should be independent with respect to procedural variables such as heating rate (non-isothermal conditions) and temperature (isothermal conditions) and their shape also should be identical for isothermal and non-isothermal data. If there is pronounced influence of the procedural parameters affecting the shape of the $y(\alpha)$ and $z(\alpha)$ functions then probably some of the assumptions formulated above are not fulfilled. Such behavior can be caused by many factors. One possibility is that the baseline was not drawn correctly due to substantial change of sample heat capacity during the measurement. Another possible explanation is that the measured data correspond to a more complicated process due to complex reaction scheme. Thermal inertia effects caused by lower thermal contact between the sample and temperature sensor or low thermal conductivity of amorphous material can also play an important role.

The $y(\alpha)$ and $z(\alpha)$ functions exhibit maxima at α_M and α_p^∞ respectively. It can easily be shown that $\alpha_M < \alpha_p^\infty$. The maximum of the $y(\alpha)$ function for the JMA model depends on the value of the kinetic exponent. It is equal to $\alpha_M=0$ for $m \leq 1$ and $\alpha_M=1-\exp(m^{-1}-1)$ for $m>1$. On the other hand the maximum of the $z(\alpha)$ function for the JMA model is a constant being $\alpha_p^\infty = 0.632$. This value is a characteristic 'fingerprint' of the JMA model and according to our experience it can be used as a simple test of the applicability of this model. The value of the kinetic exponent then can be estimated from the position of the maximum of the $y(\alpha)$ function. It should be pointed out, however, that typical error limit of α_M and α_p^∞ determined from TA data is about ±0.02.

Experimental

DSC experiments presented in this paper were performed by using a Perkin-Elmer DSC-7 instrument on samples of approximate 10 mg encapsulated in conventional aluminum sample pans in an atmosphere of dry nitrogen. The instrument was calibrated with In, Pb and Zn standards. Non-isothermal DSC curves were obtained with selected heating rates 2–20 K min^{-1} in the range 30–600°C. The $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass was prepared by synthesis from pure elements (5N purity) in an evacuated silica ampoule by melting and homogenization at 950°C for a period of 12 h. The amorphous nature and purity of prepared material was checked by X-ray diffraction and energy dispersive microanalysis.

Results and discussion

The crystallization kinetics of chalcogenide glass of $Ge_{0.3}Sb_{1.4}S_{2.7}$ composition has been described previously [13–17]. In this case an orthorhombic Sb_2S_3 phase is formed and due to its relatively high entropy of fusion one can expect spherulitic crystal growth habit [18]. If the crystals grow from a constant number of preexisting nuclei then the JMA model is valid in non-isothermal conditions and the kinetic exponent m should be close to 3. This prediction seems to be confirmed for the bulk sample as evident from the shape of the $y(\alpha)$ and $z(\alpha)$ functions shown in Fig. 1. The maximum of the $z(\alpha)$ function falls in the range predicted for the JMA model. The maximum of the $y(\alpha)$ function well corresponds to the value of the kinetic exponent m=3 anticipated above. There are small but noticeable differences among curves for

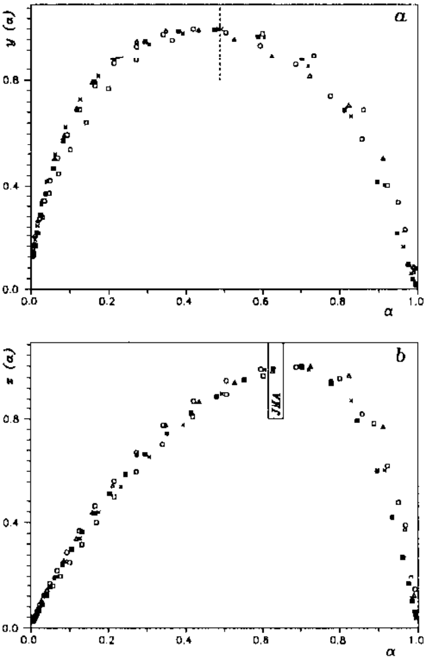

Fig. 1 Transformed DSC data for the crystallization of bulk $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass: a –Normalized $y(\alpha)$ function. b – Normalized $z(\alpha)$ function. The heating rates are shown by points: □– 2 K min^{-1}; ○ – 5 K min^{-1}; △ – 10 K min^{-1}; × – 15 K min^{-1}; ■– 20 K min^{-1}. Solid lines show typical interval of α_p^{∞} values for the JMA model. The dotted line corresponds to theoretical α_M value for the JMA model (m = 3)

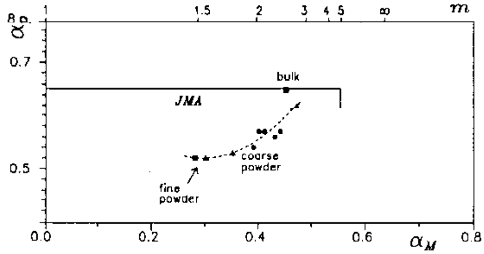

Fig. 2 Generalized representation of the crystallization behavior of $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass. Full lines corresponds to the limits of applicability of the JMA model. Points correspond to experimental data: ● – [16]; ▲ [17]; ■– [this work]. The dotted line is drawn as guide to eye

Table 1 The kinetic exponents M, N of autocatalytic model corresponding to the JMA kinetic exponent m

m	M	N
1	0	1
1.5	0.35	0.88
2	0.54	0.83
3	0.72	0.76

different heating rates. These differences probably can be attributed to lower thermal contact between the bulk sample and the temperature sensor. Nevertheless, the assumptions formulated above seem to be fulfilled.

A comparison of the crystallization behavior of powder and bulk sample of $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass is shown in Fig. 2 in the generalized diagram based on the maxima of the $y(\alpha)$ and $z(\alpha)$ functions. The present results are combined with some previously published data [16, 17]. The value of α_p^∞ for fine powder (<1 μm) sample is lower than corresponds to the JMA model indicating more complex mechanism. The coarse powder (<100 μm) sample exhibit slightly higher value of α_p^∞ but it is still below the value typical for the JMA model. However, the values of α_M and α_p^∞ for the bulk sample well correspond to the crystallization of spherulitic crystals.

As mentioned above the JMA model is valid in non-isothermal conditions provided that a new crystalline phase grows from a constant number of nuclei and all nucleation is completed before the macroscopic crystal growth started. This so called site saturation is important condition for the isokinetic crystallization process where the crystallization rate is defined only by temperature and it does not depend on the previous thermal history. In the light of these facts it seems that the nucleation and growth processes are probably overlapped for fine powder sample. Therefore the overall crystallization cannot be described by the JMA model. Mutual overlapping of the nucleation and growth phases is obviously lower for coarse powder sample but still the JMA model is not valid in this case. It seems that in the bulk sample the nucleation is completed before the growth phase is started and, therefore, the condition of the validity of the JMA model in non-isothermal conditions is fulfilled. Fine powder sample exhibit lower value of α_M than corresponds to the bulk sample which reveals lower influence of the crystallized phase due to dominant surface nucleation. These conclusions were confirmed by direct microscopic observations.

Generally speaking, the shift of the maximum of the $z(\alpha)$ function to lower values of fractional conversion (α_p^∞<0.6) indicates increasing complexity of the crystallization process. Such complex behavior observed for many crystallization processes can be conveniently described by means of the autocatalytic model [19–21]:

$$\phi = \Delta H_c A \exp(-E_a/RT)\alpha^M(1-\alpha)^N \tag{9}$$

where the parameters M and N define relative contributions of acceleratory and decay regions of the kinetic process. It was shown [22] that the autocatalytic model is physically meaningful only for M<1. The maxima of the $y(\alpha)$ and $z(\alpha)$ functions for this model depend on the value of the kinetic exponents M and N. The maximum of the $y(\alpha)$ function can be expressed as $\alpha_M = M/(M+N)$. The JMA model is a special case of the autocatalytic model as shown in Table 1. Therefore, the autocatalytic model is a plausible mathematical description for the nucleation and growth processes in amorphous solids. Increasing value of the kinetic exponent M indicates more important role of the crystallized phase on the overall kinetics. Similarly, it seems that a higher value of the kinetic exponent $N>1$ means increasing complexity. However, more experimental data are needed to get detailed insight into real physical meaning of these kinetic exponents.

Conclusions

Presented results clearly indicate that the JMA model has limited validity in non-isothermal conditions and it is strongly recommended to test always its applicability for particular crystallization process. In addition to this validity test there are several basic assumptions implicitly involved in kinetic treatment of isothermal and non-isothermal TA data which should be also checked before any kinetic analysis is made. An unified approach based on two functions $y(\alpha)$ and $z(\alpha)$ obtained by a simple transformation of experimental data is proposed allowing to test the validity of the JMA model as well as the basic assumptions in kinetic analysis. The $y(\alpha)$ and $z(\alpha)$ functions exhibit maxima at α_M and α_p^∞, respectively ($\alpha_M<\alpha_p^\infty$). Their position and shape should be invariant with respect to procedural variables such as heating rate (non-isothermal conditions) and temperature (isothermal conditions). The shape of these plots should also be identical for isothermal and non-isothermal data. The validity of the JMA can easily be verified checking the maximum α_p^∞ of the $z(\alpha)$ function. If the maximum falls into $0.61\leq\alpha_p^\infty\leq0.65$ range then experimental data probably correspond to the JMA model.

It is convenient to describe the crystallization kinetics in terms of generalized diagram, i.e. α_p^∞ *vs.* α_M plot. This diagram helps to visualize the complexity of the crystallization process as well as to verify the applicability of the JMA model. The autocatalytic model includes the JMA model and, therefore, it is a plausible mathematical description for the nucleation and growth processes in amorphous solids. The main advantage of the autocatalytic model is the possibility to describe quantitatively complex crystallization processes.

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