

Applicability of Johnson-Mehl-Avrami model to crystallization kinetics of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy

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Abstract: The applicability of Johnson-Mehl-Avrami(JMA) model to the crystallization kinetics of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy is investigated by differential scanning calorimetry(DSC) under isochronal and isothermal conditions. A criterion x_m , at which a defined function $z(x)$ exhibits the maximum value, is introduced to check the validity of JMA model to the kinetics analysis. The value of x_m has a constant of 0.632 for JMA model. It is found that the values of x_m at different isothermal annealing temperatures (743, 748, 753 and 758 K) are almost near 0.632, which indicates that the isothermal crystallization kinetics can be modeled by JMA equation. However, the values of x_m at different heating rates (10, 20, 30 and 40 K/min) are about 0.52, implying that JMA model is not valid to the isochronal crystallization kinetics. The reason why the JMA model is not valid to the isochronal crystallization kinetics is discussed.

Key words: amorphous alloys; phase transition; thermal analysis; crystallization kinetics; JMA model

1 Introduction

Amorphous alloys are synthesized when liquid alloys are solidified sufficiently rapidly so that the atomic configuration of liquids is frozen into solids. Overcoming the tendency of conventional liquids to crystallization usually requires extremely high cooling rates only attainable by rapid quenching such as melt-spinning. Since 1989, a new class of amorphous alloys, which can be produced at much lower cooling rates, has emerged[1–7]. These are the so-called bulk amorphous alloys. One of the attractions of the bulk amorphous alloys is that they exhibit a large supercooled liquid region ΔT_x (defined as the temperature region between the glass transition temperature T_g and the onset temperature of crystallization T_x), which provides a large experimentally accessible time and temperature window to investigate the crystallization kinetics at the supercooled liquid region[8–9].

Thermal analysis(TA) methods such as DTA or DSC are quite popular for crystallization kinetics analysis of amorphous alloys. An aspect of considerable

importance to kinetic analysis is the determination of the kinetics parameters that reflect the crystallization behaviors. The crystallization kinetics based on the TA data is usually modeled by Johnson-Mehl-Avrami(JMA) equation[10–12]:

$$x(t)=1-\exp\{-[k(t-\tau)]^n\} \quad (1)$$

where x is the crystallized volume fraction, t the annealing time, τ the incubation time, n (called as Avrami exponent) a constant related to the behaviors of nucleation and growth, and k a reaction rate constant.

The JMA equation was first derived for transformations under isothermal annealing condition based on the following assumptions[13–15]: 1) homogeneous nucleation or heterogeneous nucleation at randomly dispersed second-phase particles; 2) growth rate of new phase controlled by temperature and independent on time; and 3) low anisotropy of growing crystals. HENDERSON has pointed out that the validity of the JMA equation can be extended under isochronal condition if the entire nucleation behavior completes at the early stage of the transformation, and it becomes negligible afterward[13–14]. Thus, the crystallization

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rate is defined only by temperature and does not depend on the previous thermal history. Nevertheless, the assumptions above should be carefully considered before JMA model is used for crystallization kinetics analysis. The most popular testing method for isothermal TA data is an inspection of the linearity of JMA plot $\ln[-\ln(1-x)]$ vs $\ln(t-\tau)$. In some cases, the JMA plots show straight lines, but the crystallization kinetics cannot be modeled by JMA equation[16]. Thus, a more practical and reliable test method is needed. Based on a function $z(x)$ (seen in the appendix), which can be easily obtained by a simple transformation of DSC data, a simple and practical method to verify the validity of JMA equation is derived to check the value of crystallized volume fraction x_m corresponding to the peak of function $z(x)$. For crystallization kinetics that can be modeled by JMA equation, it has been calculated that the value of x_m is a constant of 0.632[16]. The detail can be seen in the appendix. In this paper, within the frame of criterion of x_m , the applicability of JMA model to the crystallization kinetics of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy is discussed under isothermal and isochronal conditions.

2 Experimental

An ingot with nominal composition of $Zr_{60}Al_{15}Ni_{25}$ was prepared by arc melting a mixture of metals Zr (99.9%, mass fraction), Al (99.99%) and Ni (99.99%) in a water-cooled copper crucible under titanium-gettered argon atmosphere. A plate-like specimen with a cross-section of 1 mm \times 10 mm and length of 50 mm was produced by suction casting in a copper mold, and its amorphous nature was identified by X-ray diffractometry(XRD) using monochromatic $Cu K_{\alpha}$ radiation. The crystallization kinetics of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy was investigated under isothermal and isochronal conditions using a differential scanning calorimeter (NETZCH, DSC 404) under flowing high purity argon. For the isothermal analysis, the amorphous samples were firstly heated to the annealing temperature (743, 748, 753 and 758 K) at a rate of 50 K/min, and then held for a certain period of time until the completion of crystallization. The isochronal DSC plots were recorded at the heating rates of 10, 20, 30 and 40 K/min. Al_2O_3 and Al pans were utilized for the isochronal and isothermal annealing, respectively. The crystallization products were identified by XRD.

3 Results and discussion

The $Zr_{60}Al_{15}Ni_{25}$ specimen produced by suction casting in a copper mold is verified to be a single amorphous phase by XRD (not shown here). The isothermal crystallization kinetics of $Zr_{60}Al_{15}Ni_{25}$ bulk

amorphous alloy is investigated by DSC in the supercooled liquid region at 743, 748, 753 and 758 K. All the isothermal DSC traces exhibit a single exothermic peak after a certain incubation period (Fig.1). The detailed isothermal DSC data are listed in Table 1.

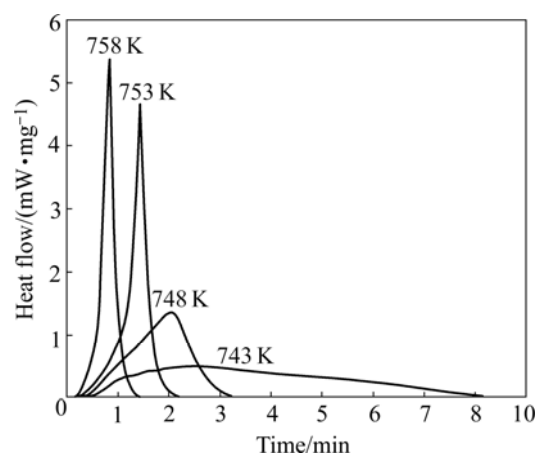


Fig.1 Isothermal DSC plots of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy at different annealing temperatures

Table 1 Isothermal kinetic parameters of crystallization of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy at different annealing temperatures

Annealing temperature/ K	Incubation time, τ /min	Avrami exponent, n	Reaction constant, k/min^{-1}	Peak width, $(t_{95\%}-t_{1\%})/\text{min}$
743	0.52	1.51	0.24	7.73
748	0.41	2.32	0.60	2.75
753	0.39	3.80	0.93	1.42
758	0.31	4.15	1.79	0.82

The exothermic reaction corresponds to the simultaneous precipitation of Al_2NiZr_6 and $AlNi_4Zr_5$ phases (Fig.2(a)). From Table 1, it can be seen that the incubation time τ (defined as the time scale between the time t_0 and $t_{1\%}$, t_0 is the time to reach the annealing temperature and $t_{1\%}$ the time to reach 1% crystallized volume fraction) is relatively short for different annealing temperatures, which is maybe attributed to relatively high annealing temperatures. The value of τ increases slightly when the annealing temperature decreases, however, the exothermic peak width (referred to the time scale between 1% and 95% of transformation into the crystalline state) broadens significantly, indicating a more sluggish crystallization behavior.

The crystallized volume fraction in a given time during crystallization is determined by measuring the partial area of the exothermic peak, and the results are shown in Fig.3. Plotting $\ln[-\ln(1-x)]$ vs $\ln(t-\tau)$ using the data $x=15\%-85\%$, the isothermal JMA plots at different annealing temperatures are obtained (Fig.4). These plots are nearly straight lines, indicating that the isothermal

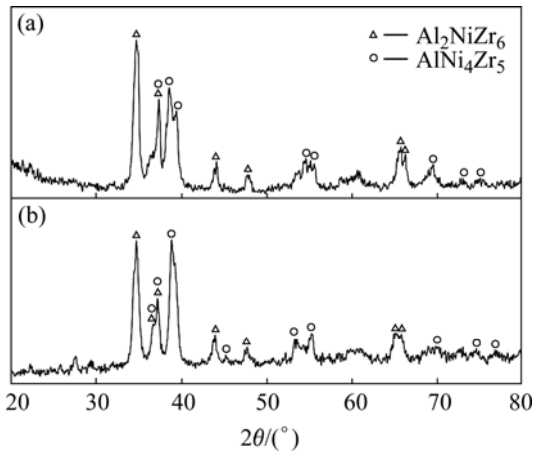


Fig.2 XRD patterns of crystallization products of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy isothermally annealed at 758 K for 30 min (a) and linearly heated to 1 000 K at heating rate of 40 K/min (b)

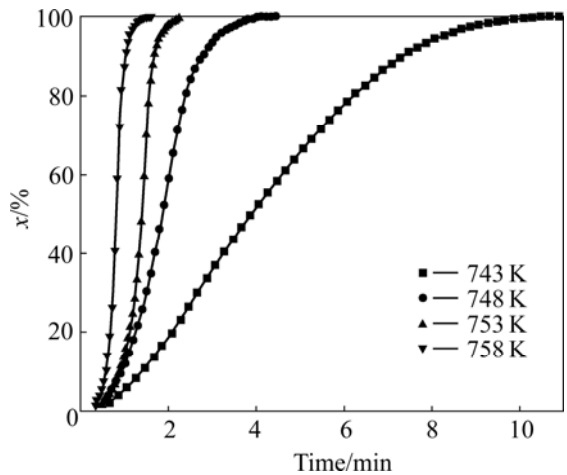


Fig.3 Crystallized volume fraction x as function of annealing time t for $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy at different annealing temperatures

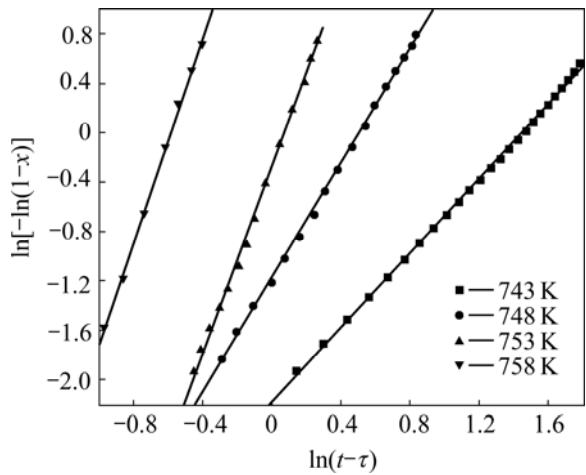


Fig.4 Isothermal JMA plots of crystallization of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy at different annealing temperatures

crystallization kinetics may be modeled by JMA equation. The Avrami exponents n and the reaction rate constants k are calculated by the slopes and intercepts of these JMA lines (Table 1).

Fig.5 shows the isochronal DSC curves of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy at the heating rates of 10, 20, 30 and 40 K/min and the detailed results are listed in Table 2. All the DSC curves show a single exothermic peak, during which Al_2NiZr_6 and $AlNi_4Zr_5$ phases precipitate (Fig.2(b)). The precipitation of complicated compounds Al_2NiZr_6 and $AlNi_4Zr_5$ indicates that substantial redistribution of elements occurs during the crystallization under isothermal and isochronal conditions. The Kissinger plot $\ln(\beta/T_p^2)$ vs $1/T_p$ is shown in Fig.6. Based on the slope of the Kissinger plot, the effective activation energy E_c is calculated to be 345 kJ/mol. The crystallized volume fraction x in a given time during isochronal crystallization is also determined by measuring the corresponding partial area of the exothermic peak. Plotting $\ln[-\ln(1-x)]$ vs $\ln(1/T)$ using the data $x=15\%-85\%$, the isochronal JMA plots at different heating rates are obtained (Fig.7). These plots are obviously non-linear, suggesting that the JMA model is not valid to the isochronal crystallization kinetics. The Avrami exponents obtained by the slopes of these plots are found to be approximately 3.59.

Table 2 Isochronal DSC data of $Zr_{60}Al_{15}Ni_{25}$ bulk glassy alloy at different heating rates

Heating rate, $\beta/(K \cdot min^{-1})$	Onset temperature of crystallization, T_x/K	Temperature of exothermic peak, T_p/K
10	758.6	763.0
20	767.8	770.2
30	773.5	777.2
40	777.7	781.9

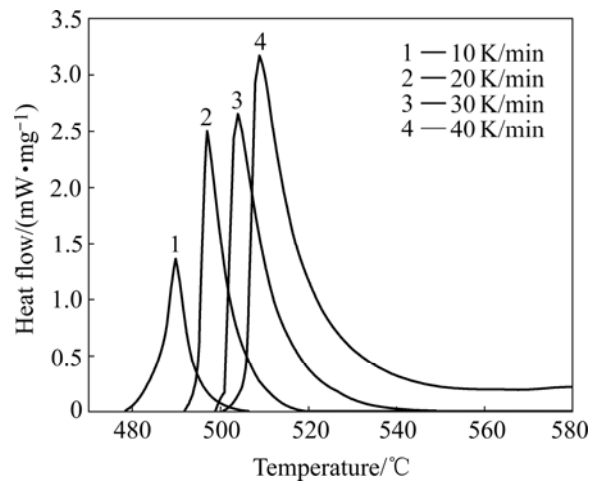


Fig.5 Isochronal DSC plots of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy at different heating rates

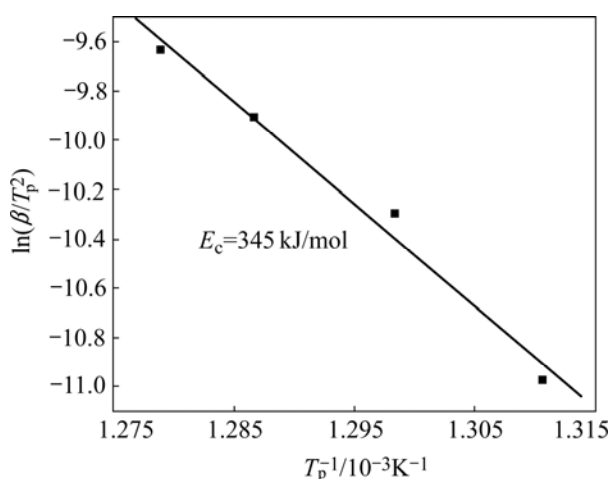


Fig.6 Kissinger plot of crystallization of $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ bulk amorphous alloy

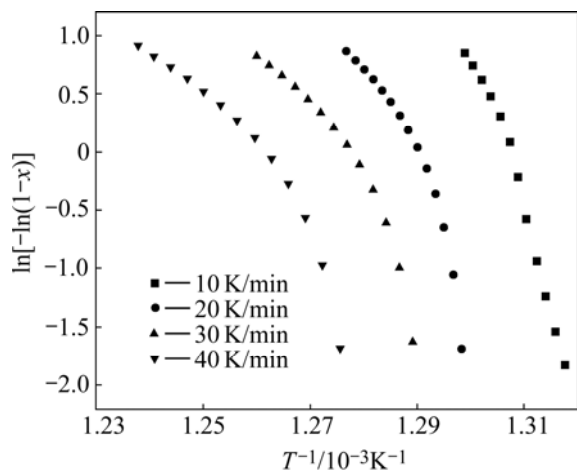


Fig.7 Isochronal JMA plots for crystallization of $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ bulk amorphous alloy at different heating rates

The normalized isothermal functions $z(x)$ with respect to the crystallized volume fraction x for the crystallization of $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ bulk amorphous alloy at different annealing temperatures are shown in Fig.8. It can be seen that the values of x_m corresponding to the maximum value of isothermal function $z(x)$ locate at the range of 0.61–0.65, which further demonstrates that the JMA model is valid to the isothermal crystallization kinetics. The normalized isochronal functions $z(x)$ with respect to the crystallized volume fraction x at different heating rates are shown in Fig.9. It can be seen that the values of x_m of the isochronal function $z(x)$ locate at the range of 0.51–0.55, which further verifies that the isochronal crystallization kinetics can not be modeled by JMA equation.

During the crystallization of an amorphous alloy, the ordered regions in the amorphous phase, as the so-called quenched-in nuclei, maybe provide the nucleation

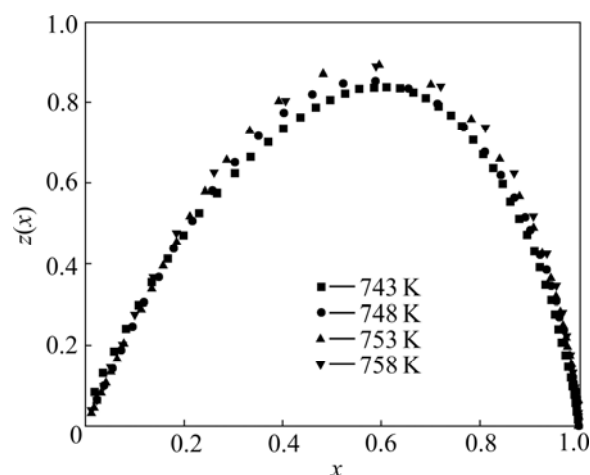


Fig.8 Normalized function $z(x)$ obtained by transformation of isothermal DSC data of crystallization of $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ bulk amorphous alloy

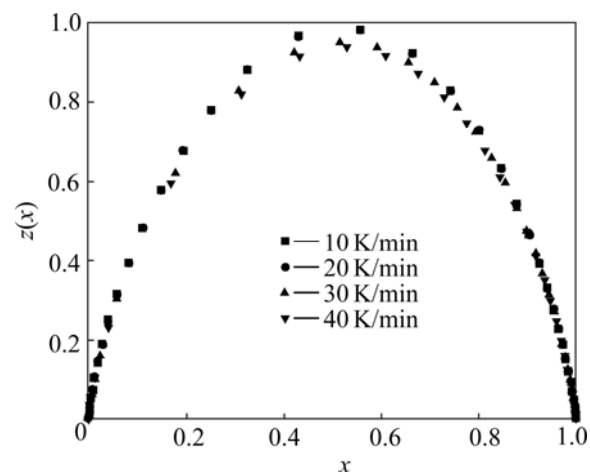


Fig.9 Normalized function $z(x)$ obtained by transformation of isochronal DSC data of crystallization of $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ bulk amorphous alloy

sites for the precipitation of the primary phase[17–18]. When the active size of the quenched-in nuclei is larger than the critical cluster radius at a given temperature, these nuclei may directly grow with time. There exist numerous orders (nanocrystallites) in the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ amorphous alloys and their average size is about 7 nm [19]. Within the frame of transient nucleation theory, the critical radius of the nucleus during the crystallization of an amorphous alloy is estimated to be about 1 nm[20]. Then, it can be concluded that the size of orders in the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ bulk amorphous alloy is overcritical. As a result, it is reasonable that the crystallization reaction is activated by the growth of these pre-existing short-range orders.

Under the isothermal condition, the Avrami

exponents varying from 1.51 to 4.15 (Fig.4) suggest a diffusion-controlled three-dimensional growth during the crystallization of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy. At lower annealing temperatures (743 and 748 K), the Avrami exponents (1.51 and 2.32 respectively) are smaller than 2.5, which indicates that the crystallization is governed by three-dimensional growth with a decreasing nucleation rate[21]. The amorphous state of a multi-component system with significant atomic size difference forms dense random packed atomic configuration[22]. Mobility of atoms in such atomic configuration is obviously difficult. The large effective activation energy for crystallization E_c demonstrates that the atomic diffusion in Zr-Al-Ni system is difficult, especially at low temperature. At the initial crystallization stage, the overcritical orders grow with the nucleation rate of zero. The growth of the overcritical cluster nuclei and formation of new nuclei need the atomic rearrangement. The difficult atomic diffusion at low temperature retards the nucleation and growth, resulting in a decreased nucleation rate and broad exothermic peak width (Fig.2). However, the Avrami exponents at 753 K and 758 K are larger than 2.5, which implies an increased nucleation rate[21]. At higher temperatures, such as 753 K and 758 K, the growth of the overcritical nuclei changes the composition in their neighborhood and results in an enhancement of the nucleation rate adjacent to the growing nuclei because of the easy mobility of atoms, which causes a chain reaction-like process, leading to an increased nucleation rate.

The JMA model can be valid in isochronal crystallization kinetics provided that a new crystalline phase grows from a constant number of nuclei and all nucleation is completed before the crystallization reaction starts. This is the so-called isokinetic crystallization, where the crystallization rate only depends on temperature but not on the previous thermal history[12]. As it is known that the crystallization process of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy starts from the growth of pre-existing overcritical orders and is governed by three-dimensional growth with an increased nucleation rate when being annealed at 753 K. In the case of isochronal crystallization, the onset temperatures of crystallization T_x are higher than 753 K (Table 2). Thus, it can be concluded that the nucleation rate during isochronal crystallization process increases with time, since the higher the temperature is, the easier the mobility of atoms is. The nucleation and growth during the isochronal crystallization of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy are overlapped. Therefore, the isochronal crystallization kinetics does not fulfill the

isokinetic premise, which is the reason why it cannot be modeled by JMA equation.

4 Conclusions

The normalized functions $z(x)$ obtained by transformation of isothermal and isochronal DSC data demonstrate that the JMA model is valid to isothermal crystallization kinetics of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy but not to the isochronal crystallization kinetics. From the isothermal kinetics parameters at different annealing temperatures, it is concluded that isothermal crystallization reaction starts from the three-dimensional growth of pre-existing overcritical ordered regions (nanocrystallites), with a decreased nucleation rate at 743 K and 748 K but an increased nucleation rate at 753 K and 758 K. The difference of the nucleation behavior at different annealing temperatures is attributed to the change of the mobility of atoms at different temperatures. During the isochronal crystallization of $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy, the nucleation and growth overlap, which does not fulfill the isokinetic crystallization that is the premise of the validity for JMA model to the isochronal condition. As a result, the isochronal crystallization kinetics cannot be modeled by JMA equation.

Appendix

1 Basic assumptions of JMA model

There are three basic assumptions inherent in any kinetics analysis of isothermal and isochronal TA data. These assumptions are formulated as follows[16]:

1) The crystallization rate dx/dt is proportional to the measured specific heat flow φ , normalized per sample mass (W/g):

$$\frac{dx}{dt} = \frac{\varphi}{\Delta H_c} \quad (2)$$

where ΔH_c is the total enthalpy change associated with the crystallization reaction. It is assumed that the crystallized volume fraction x , up to any time t , is proportional to the corresponding partial area of the exothermic peak. Thus the crystallized volume fraction in a given time during crystallization can be calculated by measuring the partial area of the exothermic peak.

2) The crystallization rate can be expressed as a product of temperature dependent reaction rate constant $k(T)$ and x dependent kinetic model function $f(x)$:

$$\frac{dx}{dt} = k(T)f(x) \quad (3)$$

3) The rate constant $k(T)$ in Eqn.(3) follows Arrhenius form:

$$k(T) = k_0 \exp\left(\frac{-E_c}{RT}\right) \quad (4)$$

where k_0 is a pre-exponential factor, E_c the effective activation energy and R the gas constant.

Taking into account the three assumptions above, the kinetic equation for the JMA model can be expressed as:

$$\varphi = \Delta H_c k_0 \exp\left(\frac{-E_c}{RT}\right) f(x) \quad (5)$$

in which the kinetic model function $f(x)$ is an algebraic expression of JMA model as:

$$f(x) = n(1-x)[- \ln(1-x)]^{(n-1)/n} \quad (6)$$

The function $f(x)$ should be invariable with respect to procedural parameters, such as sample mass and heating rate (isochronal) or temperature (isothermal).

The validity of the three assumptions above (Eqn.(2)–(4)) should be verified before kinetics analysis of TA data using JMA model.

2 Test criterion x_m for JMA model

From the logarithmic form of Eqn.(1), the Avrami exponent n can be obtained from the slope of a JMA plot:

$$\frac{d \ln[- \ln(1-x)]}{d \ln(t-\tau)} = n \quad (7)$$

A similar testing method has also been developed for isochronal TA data. The slope of plot $\ln[- \ln(1-x)]$ vs $\ln(1/T)$ can be expressed as[16]

$$\frac{d \ln[- \ln(1-x)]}{d \ln(1/T)} \cong -\frac{nE_c}{R} \quad (8)$$

The value of Avrami exponent n can be calculated if the effective activation energy E_c is known. E_c can be evaluated by Kissinger equation[23]:

$$\ln \frac{\beta}{T_p^2} = -\frac{E_c}{RT_p} + C \quad (9)$$

where β is the heating rate and T_p the temperature of exothermic peak where φ has the maximum value. A Kissinger plot $\ln(\beta/T_p^2)$ vs $1/T_p$ should be a straight line with a slope of $-E_c/R$. Then the effective activation energy E_c can be calculated.

The DSC curves $\varphi(t)$ (isothermal) and $\varphi(T)$ (isochronal) corresponding to the same kinetic model may be quite different. Moreover, the DSC curves $\varphi(t)$ and $\varphi(T)$ depend on the annealing temperature T and

heating rate β respectively. However, the function $f(x)$ should be independent on these procedural variables. The function $f(x)$ is proportional to a function $z(x)$, which is defined under isothermal condition as[24]:

$$z(x) = \varphi(t) \quad (10)$$

And under isochronal condition, $z(x)$ is expressed as

$$z(x) = \varphi T^2 \quad (11)$$

For practical reasons, the function $z(x)$ is usually normalized within the (0 1) range, which exhibits the maximum value at x_m . It has been verified that the value of x_m is a constant of 0.632 for the JMA model [16]. Then, the applicability of JMA model to a crystallization kinetics can be tested by checking the value of x_m .

The criterion of x_m has been verified as a simple and practical method to test the applicability of kinetics analysis to JMA model[25]. The error limit of x_m by typical TA data is about ± 0.02 . Thus, the validity of the JMA model to a certain crystallization kinetics can easily be tested by checking the value of x_m of the function $z(x)$. If the value of x_m locates into the range (0.61 0.65), the crystallization kinetics can be modeled by JMA equation. Reversely, JMA model does not work.

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