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An integral fitting method for analyzing the isochronal transformation kinetics: Application to the crystallization of a Ti-based amorphous alloy

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ABSTRACT

An integral fitting method has been developed to determine the phase transformation mechanism and to extract the kinetic parameters during the crystallization of amorphous alloys. The proper kinetic function of the phase transformation was firstly deduced. Theoretical differential scanning calorimetry curves were then calculated. All the kinetic parameters can be extracted by fitting the calculated differential scanning calorimetry curves to experimental data. We applied the integral fitting method to analyze the isochronal crystallization of the $Ti_{50}Cu_{42}Ni_8$ amorphous alloy. Results indicate that a transformation process considering impingement is more suitable to describe the crystallization kinetics of this alloy than using the traditional Johnson–Mehl–Avrami model. Mean values of the obtained kinetic parameters show strong heating rate dependence.

1. Introduction

Amorphous alloys have received wide and intensive attention in the past few decades due to their unique structure, attractive physical or chemical properties and practical applications in various engineering fields [1–5]. However, amorphous alloys may lose or sometimes improve their interesting properties after they are fully or partly crystallized upon thermal annealing. Thus, it is important and necessary to understand their crystallization kinetics and mechanism. Isochronal differential scanning calorimetry (DSC) scans are mostly often used to study the crystallization of amorphous alloys [6–8]. The information of crystallization sequence, temperature, enthalpy, and even the kinetic parameters (for example, the activation energy of a particular process) can be readily obtained from quick scans [7,8].

Using DSC to investigate the crystallization kinetics of different amorphous alloys has been widely discussed [9–12]. Various theoretical models have been developed for the kinetics analysis based on DSC data. Important kinetic parameters can be extracted by comparing the experimental DSC curves to the theoretical ones calculated using an appropriate kinetic model [13,14].

In this work, an integral fitting method was developed to determine the transformation function, $f(\alpha)$, in the crystallization process of amorphous alloys. By direct fitting the theoretical DSC curves to experimental data obtained at various heating rates, kinetic parameters such as the activation energy, kinetic exponent and frequency factor could be obtained. Applying this method to analyze the isochronal crystallization kinetics of the $Ti_{50}Cu_{42}Ni_8$ amorphous alloy, we found that the kinetic model considered impingement was more suitable to describe the transformation processes and provided more accurate kinetic parameters than classical Johnson–Mehl–Avrami (JMA) equation.

2. Theoretical analysis

From the kinetic analysis of a phase transformation, we can determine the important kinetic parameters and the analytical form of the transformation function $f(\alpha)$. The transformed volume fraction, α, according to the JMA model [15–17], can usually be expressed in the following form:

$$\alpha(t) = 1 - \exp\{-[K(T)t]^n\}, \tag{1}$$

where n is the kinetic exponent, and the constant $K(T)$ is usually assumed to have an Arrhenian temperature dependence:

$$K(T) = K_0 \exp\left(-\frac{E_a}{RT}\right), \tag{2}$$

where K_0 is the pre-exponential (frequency) factor, E_a is the activation energy, and R is the ideal gas constant. In most solid-state reactions, the phase transformation rate ($d\alpha/dt$), which is assumed independent on the thermal history under non-isothermal conditions, can be expressed as the product of two separable functions [18]:

$$\frac{d\alpha}{dt} = K(T)f(\alpha). \tag{3}$$

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As an analytical expression describing the kinetic model of the transformation process, the function $f(\alpha)$ involves the mechanism of transformation. According to the JMA model, $f(\alpha)$ can be expressed as

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}. \quad (4)$$

2.1. Deducing the theoretical DSC heat flow function

The specific heat flow (ϕ in W/g) measured from DSC scans can be expressed by the following kinetic equation [18]:

$$\phi = \Delta H_C \frac{d\alpha}{dt}, \quad (5)$$

where ΔH_C is the crystallization enthalpy. Combining Eqs. (2), (3) and (5), the kinetic equation for a theoretical DSC curve can be written as

$$\phi = \Delta H_C K_0 \exp\left(\frac{-E_a}{RT}\right) f(\alpha). \quad (6)$$

Thus, the theoretical DSC heat flow function for the JMA kinetics can be written as

$$\phi = \Delta H_C K_0 \exp(\frac{-E_a}{RT}) n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}. \quad (7)$$

Notwithstanding the apparent wide range of applicability, many cases of deviations from the JMA kinetics have been reported [10,18–22]. These problems could be solved by taking the anisotropic growth into account [18–22]. After considering the impingement effect, we have [22]

$$\frac{d\alpha}{d\alpha_{ext}} = (1-\alpha)^{\lambda}, \quad (8)$$

where α_{ext} (defined as $\alpha_{ext}=[K(T)t]^n$) is the extended crystallization fraction [23], and λ (>1) is the impingement factor. When $\lambda=1$, Eq. (8) can be converted to the JMA equation. When $\lambda>1$, α can be obtained by integrating Eq. (8)[10]:

$$\alpha = 1 - \{1+(\lambda-1)[K_0\exp(-E_a/RT)t]^n\}^{-(1/\lambda-1)}. \quad (9)$$

Calculating the derivative of Eq. (9) with respect to t, we have

$$\frac{d\alpha}{dt} = K_0 \exp(-E_a/RT) n(1-\alpha)^{\lambda}\left[\frac{(1-\alpha)^{-(\lambda-1)}-1}{\lambda-1}\right]^{1-1/n}. \quad (10)$$

The kinetic model of this transformation can then be expressed by the following equation [24]:

$$f(\alpha) = n(1-\alpha)^{\lambda}\left[\frac{(1-\alpha)^{-(\lambda-1)}-1}{\lambda-1}\right]^{1-1/n}. \quad (11)$$

Substituting Eq. (11) into Eq. (6), we can finally express the theoretical DSC heat flow function for the transformation process considering the impingement effect as

$$\phi = \Delta H_C K_0 \exp(-E_a/RT) n(1-\alpha)^{\lambda}\left[\frac{(1-\alpha)^{-(\lambda-1)}-1}{\lambda-1}\right]^{1-1/n}. \quad (12)$$

Eqs. (7) and (12) are suitable for both isothermal and non-isothermal transformation processes. Theoretical DSC curves can be calculated using these two equations with given kinetic parameters. Adjusting the values of trial kinetic parameters until the theoretical DSC curves fit well to the experimental data, we can finally get the exact values of kinetic parameters (E_a, n, K_0 and λ).

2.2. Determining the kinetic function

Before calculating the theoretical DSC curves, we should first determine the proper kinetic function for a particular transformation process. Eq. (7) is valid only when the JMA equation is applicable. The JMA equation was originally developed to analyze isothermal DSC data. Henderson [14] has shown that the validity of the JMA equation can be extended to non-isothermal conditions if the entire nucleation process takes place during the early stage of the transformation and becomes negligible afterwards. A simple but reliable method based on a function, $z(\alpha)$, has been proposed to test the applicability of the JMA equation [18]. Under continuous heating conditions this function is given by

$$z(\alpha) = \phi T^2. \quad (13)$$

This function reaches its maximum when α equals to α_P^M. Values of α_P^M can be used to determine the proper kinetic model and $\alpha_P^M=0.632$ is usually regarded as a characteristic 'fingerprint' of the JMA model [18]. Substituting Eqs. (7) and (12) into Eq. (13), respectively, we can express $z(\alpha)$ as

$$z(\alpha) = \Delta H_C K_0 \exp\left(\frac{-E_a}{RT}\right) n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} T^2, \quad (14)$$

for the JMA kinetics, and

$$z(\alpha) = \Delta H_C K_0 \exp(-E_a/RT) n(1-\alpha)^{\lambda}\left[\frac{(1-\alpha)^{-(\lambda-1)}-1}{\lambda-1}\right]^{1-1/n} T^2, \quad (15)$$

for the transformation kinetics considering the impingement effect.

Fig. 1 shows the normalized $z(\alpha)$ calculated from Eqs. (14) and (15) using trial kinetic parameters as a function of α. The curve corresponding to $\lambda=1$ in Fig. 1(a) was obtained from Eq. (14), while other curves were obtained from Eq. (15). It is obvious that the JMA equation holds only when $\alpha_P^M=0.632$ (position marked by the vertical dash line in figures). α_P^M decreases from its maximum value of 0.632 quickly with increasing λ (shown in Fig. 1(a)). When λ is fixed ($\lambda=4$ in Fig. 1(b)), α_P^M increases with increasing n, but is always less than 0.632 (α_P^M is only about 0.5 even when $n=10$). So, according to the above discussions, the impingement effect should be considered for kinetics analysis when α_P^M is less than 0.632.

2.3. Procedures of integral fitting method and extraction of kinetic parameters

After the appropriate kinetic function is determined, all the kinetic parameters can be extracted by using an integral fitting method. The steps to fit the integral transformation process to the theoretical kinetic function are listed below:

(a) Initial values of the kinetic parameters, E_a, n, K_0 and λ, are firstly chosen by a trial-and-error method. For example, for the crystallization (three-dimensional) of amorphous alloys, reasonable values of E_a are in the range from 100 to 500 kJ/mol, n changes from 1 to 4. (In some special cases, E_a could be a little higher when the crystallized phase is very difficult to form and n could exceed 4 when the nucleation rate is very high). Since the kinetic parameter E_a can usually be obtained with high accuracy by the iso-conversion method [25], the initial value of E_a can be calculated first and adjusted in a narrow range during the next steps.

(b) A Genetic Algorithm [26] method is recommended to perform rigorous fitting process. The initial settings such as the population size and stopping criteria are needed before fitting. Fitting is performed by minimizing the sum of the squares of the residuals, employing a simplex fitting procedure. Values for the kinetic parameters are then obtained.

(c) Change the initially selected values and repeat the above fitting process. If the fitting results keep same (or vary within