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Limitation of the Johnson-Mehl-Avrami equation for the kinetic analysis of crystallization in a Ti-based amorphous alloy

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Abstract: The primary crystallization of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy was studied by isochronal differential scanning calorimetry (DSC). The activation energy was determined by the Kissinger-Akahira-Sunose method. Trying to analyze the crystallization kinetics of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy by two different methods, it was found that the crystallization kinetics did not obey the Johnson-Mehl-Avrami equation. A modified method in consideration of the impingement effect was proposed to perform kinetic analysis of the isochronal crystallization of this alloy. The kinetic parameters were then obtained by the linear fitting method based on the modified kinetic equation. The results show that the isochronal crystallization kinetics of the amorphous $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ alloy is heating rate dependent, and the discrepancy between the Johnson-Mehl-Avrami method and the modified method increases with the increase of heating rate.

Keywords: amorphous alloys; crystallization; kinetics; Johnson-Mehl-Avrami equation; impingement

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1. Introduction

Crystallization investigations of amorphous alloys are very important to understand the mechanism of phase transformations, evaluate the glass-forming ability (GFA), and produce well-controlled microstructures [1-2]. For example, the quantitative analysis of crystallization kinetics provides useful information about the origin of GFA and the key parameters of controlling the nanocrystallization of amorphous alloys. The Johnson-Mehl-Avrami (JMA) model [3-5] is most widely used to analyze the phase transformation kinetics. In the JMA model, the time dependence of the transformed volume fraction (α) can usually be written as

$$\alpha(t) = 1 - \exp\left\{-[K(T)t]^n\right\} \quad (1)$$

where n is the kinetic exponent, t and T are the time and temperature, respectively, and $K(T)$ is the temperature-dependent constant. $K(T)$ is defined as $K(T)= K_0\exp(-E/RT)$, where E is the activation energy, K_0 a pre-exponential frequency factor, and R the ideal gas constant.

Eq. (1) is commonly used in many isothermal kinetic analyses [4-5] and can be extended to non-isothermal (isochronal) phase transformations [6-7]. However, significant deviations from the JMA kinetics have been found in various amorphous alloys [8-11]. The reason of deviation has been considered as the breakdown of assumptions in the JMA theory [12]. Thus, the applicability of the JMA model should be carefully examined before kinetic analysis.

In this paper, the non-isothermal crystallization kinetics of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy was analyzed. The linearity of Avrami plots [13] and the Malek's method [14] were used to examine the applicability of the JMA model. Finally, the isochronal kinetics of this amorphous

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alloy was analyzed by a modified JMA method with considering the impingement effect.

2. Experimental

Uniform ingots with the nominal composition of $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ were prepared with arc-melting mixtures of pure elements (>99.9%) in a water-cooled copper crucible under a Ti-gettered Ar atmosphere. Ribbons about 40 μm thick and 3 mm wide were produced by single-roller melt spinning. The crystallization kinetics was studied by heating the ribbons isochronally in differential scanning calorimetry (DSC, NETZSCH 404C) under a flowing high-purity Ar gas. The typical constants of heating rate are in the range of 2.5-40 K/min.

3. Theoretical analysis

3.1. Applicability of the JMA model

The most widely used method for testing the applicability of the JMA model for non-isothermal DSC experiments is to inspect the linearity of the Avrami plot (the plot of $\ln[-\ln(1-\alpha)]$ as a function of $1/T$) [15]. According to Eq. (1), the slope of the Avrami plot can be expressed as

$$\frac{\mathrm{d}\ln[-\ln(1-\alpha)]}{\mathrm{d}(1/T)} \cong \frac{nE}{R} \tag{2}$$

The kinetic exponent (n) can be calculated if E is known. However, a double logarithmic function is not very sensitive to subtle changes of the variables. Therefore, the plot of $\ln[-\ln(1-\alpha)]$ *vs.* $1/T$ may appear quite linear even when the JMA model is actually not completely fulfilled [14]. Thus, a more practical and reliable testing method proposed by Malek *et al.* [14] was widely used [9-10, 13]. By introducing a new function $z(\alpha)$ (defined as $z(\alpha)=\phi T^2$, where ϕ is the specific heat flow measured from DSC), a practical method can be developed to verify the validity of the JMA equation. According to its definition, $z(\alpha)$ can be easily obtained from one simple DSC scan. Detailed calculation indicates that, for the crystallization whose kinetics can be analyzed by the JMA equation, the value of α_P^M should be a constant of 0.632 [14], here α_P^M represents the transformed volume fraction where $z(\alpha)$ reaches a peak value.

3.2. Modified method for extracting the kinetic parameters

When the JMA model was not suitable for kinetic analysis in some cases, many researchers tended to make explanations by using complicated transformation mechanisms, and finally concluded with a changeable n [16-18]. However, it was also proposed that the deviation from the linear Avrami plot might result from the impingement effect, which was due to the capillarity effect, the vacancy annihilation, or the blocking caused by anisotropic growth [19-20]. A modified kinetic equation considering the impingement effect has been deduced as follows [20]:

$$\alpha = 1-\left\{1+(\lambda-1)\left[K_0\exp\left(-\frac{E}{RT}\right)t\right]^n\right\}^{-\frac{1}{\lambda-1}} \tag{3}$$

where λ is the impingement factor ($\lambda>1$). In isochronal experiments, t can be expressed as $t=(T-T_0)/\beta$, where T_0 and β are the starting temperature and the constant of heating rate, respectively. Taking the logarithms of both sides of Eq. (3) twice, we can obtain

$$\ln\left[\frac{1}{\lambda-1}\left(\frac{1}{(1-\alpha)^{\lambda-1}}-1\right)\right] = -\frac{nE}{RT}+n\left[\ln\frac{K_0(T-T_0)}{\beta}\right] \tag{4}$$

Now, n is basically determined by the slope of plotting $\ln\{(\lambda-1)^{-1}\cdot[(1-\alpha)^{-(\lambda-1)}-1]\}$ *vs.* $1/T$. Compared to the first term on the right side of Eq. (4), the effect of the second item on the actual value of the slope can be neglected. Because λ is unknown before the kinetic analysis, a series of λ values is selected in a reasonable range, and the linear relationship of $\ln\{(\lambda-1)^{-1}\cdot[(1-\alpha)^{-(\lambda-1)}-1]\}$ *vs.* $1/T$ is examined by fitting the plotted curve using the least-square method. The proper value of λ should be determined when the plotted line shows the best linearity.

4. Results and discussion

Isochronal DSC curves of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy measured at various heating rates are shown in Fig. 1. Two well-separated crystallization peaks appear in

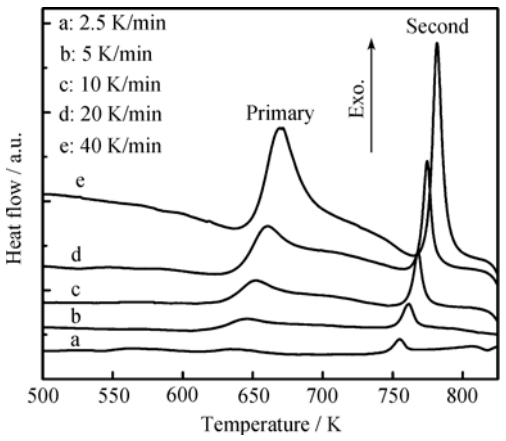

Fig. 1. Isochronal DSC curves of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy measured at various heating rates.

the whole temperature range, which is consistent with previously reported results [21]. In this work, the kinetic analysis of the primary crystallization stage was studied for simplification.

The $\ln[-\ln(1-\alpha)]$ *vs.* $1/T$ curves at all heating rates are plotted to test the applicability of the JMA model for the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy. As shown in Fig. 2(a), these curves show obvious deviation from linearity. In addition, $z(\alpha)$ as a function of the transformed volume fraction curve is plotted, as presented in Fig. 2(b). The values of α_P^M are found much smaller than 0.632, indicating that the JMA model is not applicable for kinetics analysis of the first crystallization of this amorphous alloy. Thus, the modified method considering the impingement effect should be used for kinetic investigations.

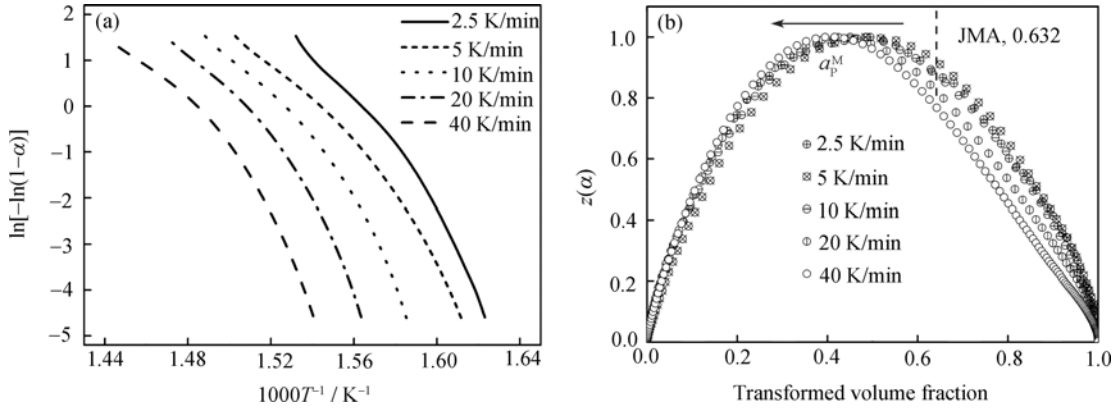

Fig. 2. Plots for the first crystallization of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy: (a) Avrami plots obtained from Eq. (2); (b) $z(\alpha)$ as a function of transformed volume fraction.

Fig. 3 gives the curves plotted according to Eq. (4) with different values of λ using DSC data obtained at a constant heating rate of 40 K/min, as well as the curve calculated according to the JMA model (λ=1). The deviation from linearity changes sensitively with λ. The curves indicate that the deviation decreases with increasing λ, and the deviation gets the smallest at λ=1.79. Then, with the further increase of λ, the deviation from the linearity increases again. Thus, the appropriate impingement factor should be around 1.79 for the first crystallization occurring during the isochronal heating at 40 K/min. From Fig. 3, the slope (S) of the plot corresponding to λ=1.79 is about −71.76. The actual value of n can then be calculated if the activation energy is known.

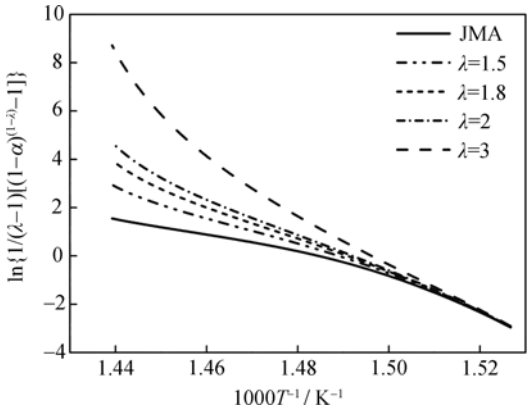

Fig. 3. Plots of $\ln\{(\lambda-1)^{-1}\cdot[(1-\alpha)^{-(\lambda-1)}-1]\}$ *vs.* $1000/T$ with different values of λ for the first crystallization of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy measured at the heating rate of 40 K/min.

The activation energy (E) for the crystallization of amorphous alloys can be determined by many methods, and the model-free iso-conversion methods are the most reliable ones. Among them, the Kissinger-Akahira-Sunose (KAS) method (also known as the generalized Kissinger method) is the most commonly used [22]. For the first crystallization of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy, E is determined by the KAS method in the range of 278±8 kJ/mol.

Thus, by the linear regression of Eq. (4), the impingement factor λ and the slope S can be obtained simultaneously. The data fitting results at different heating rates are listed in Table 1. It is clear that n and λ exhibit strong heating rate dependence. When the modified method is used, λ increases from 1.38 to 1.79, and n increases from 1.92 to 2.15 with the heating rates increasing from 2.5 to 40 K/min. On the other hand, minor changes in E have a limited effect on the value of n. For instance, the a±10 kJ/mol deviation of E can only cause the a±5% deviation of n. Based on the above discussion, it can be seen that kinetic parameters obtained by using the JMA model for kinetic analysis of this amorphous alloy are not valid. Comparing the values of n calculated using the JMA model and the modified model, it

Table 1. Data fitting results of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy based on the JMA model and the modified method at different heating rates

Heating rate / (K·min^{-1})	Method	λ	S	n	Standard deviation
2.5	JMA	—	−54.35	1.62	0.157
	Modified	1.38	−64.08	1.92	0.117
5	JMA	—	−51.55	1.54	0.164
	Modified	1.48	−65.01	1.94	0.081
10	JMA	—	−50.75	1.52	0.178
	Modified	1.54	−65.80	1.97	0.089
20	JMA	—	−52.29	1.56	0.200
	Modified	1.65	−71.42	2.14	0.093
40	JMA	—	−48.08	1.44	0.242
	Modified	1.79	−71.76	2.15	0.105

can be seen that the discrepancy is large, particularly at high heating rates; for example, the discrepancy is about 33% at the heating rate of 40 K/min.

5. Conclusion

The non-linearity of the Avrami plots and the deviation of α_P^M from the typical value of 0.632 for the JMA model suggest that the JMA equation has a limited application in studying the isochronal crystallization kinetics of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy. A modified method considering the impingement effect is found more suitable to determine the kinetic parameters. With the appropriate impingement factor determined by the deviation of modified Avrami plots from linearity and the activation energy calculated by the KAS method, the actual value of the kinetic exponent can be obtained. The results show that the first crystallization of the $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ amorphous alloy is heating rate dependent. The modified method can be used for analyzing the crystallization kinetics of similar amorphous alloys when the JMA model may not be applicable.

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