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Avrami exponent of crystallization in metallic glass $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$

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A non-isothermal method has been developed to measure the Avrami exponent of crystallization in metallic glass based on the Johnson–Mehl–Avrami isothermal equation. An example of metallic glass $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$ was studied with non-isothermal and isothermal kinetic analysis for determining the Avrami exponent, n, which are 3.5 and 3.4, respectively, and are comparable.

1. Introduction

Since Duwez [1] made the first rapidly solidified amorphous Pd–Si alloy, the crystallization of amorphous materials has been widely studied for their thermal stability, and for understanding glass formation. Because the crystallization of amorphous alloy is actually the nucleation and the growth in highly undercooling melts, it is the best system used for investigating the kinetics of transformation. For almost all metallic glasses, the transformed volume fraction, x, for crystallization on annealing can be described by the Johnson–Mehl–Avrami kinetic equation

$$x = 1 - \exp(-Kt^n) \quad (1)$$

where K is temperature-dependent factor, which is generally taken the Arrhenius form

$$K = K_0 \exp(-\Delta E_a/RT) \quad (2)$$

ΔE_a is the average activation energy, n is Avrami exponent. In the literature concerning the crystallization of amorphous alloys, such as [2, 3], the activation energy is determined by isothermal analysis or by non-isothermal annealing. However, the Avrami exponent is determined traditionally by an isothermal method [4] and its value depends strictly on the incubation time which cannot be given exactly. On the other hand, the isothermal heating is more difficult to perform than non-isothermal anneal by differential scanning calorimeter (DSC) or differential temperature analysis (DTA). Here, we are attempting to propose a method of multi-scanning rate for the measurement of Avrami exponent for an amorphous alloy.

We found the metallic glass $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$ presented single perfect DSC exothermal peak when studying the crystallization behaviour of this amorphous brazing filler metal. So we chose it as an example for measuring the Avrami exponent. The description about the manufacture of the sample can be found elsewhere [5].

2. Description of the method

Assuming K in Equation 2 is time-independent, i.e., satisfying the condition given by Henderson [6] that $x(T, t)$ can be separated into two parts dependent on time or temperature, respectively, hence

$$\frac{dx}{dt} = Knt^{n-1}\exp(-Kt^n) = nK^{1/n}(1-x)[\ln(1-x)^{-1}]^{(n-1)/n} \quad (3)$$

If applying to linear heating $T = T_r + \alpha t$ (α is the heating rate and T_r is room temperature), and substituting from $dT = \alpha\, dt$ for dt in Equation 3, we obtain

$$\frac{d(1-x)}{dT} = -(1/\alpha)nK^{1/n}(1-x) \times [\ln(1-x)^{-1}]^{(n-1)/n} \quad (4)$$

i.e.

$$\frac{d[-\ln(1-x)]}{[-\ln(1-x)]} = (1/\alpha)nK^{1/n}\,dT \quad (5)$$

by integrating above equation

$$\int_0^x \frac{d[-\ln(1-x)]}{[-\ln 1-x)]^{(n-1)/n}} = \int_0^{T_0} \frac{1}{\alpha} nK^{1/n}\,dT \quad (6)$$

Hence

$$[-\ln(1-x)]^{1/n} = (1/\alpha)\int_0^{T_0} nK^{1/n}\,dT \quad (7)$$

For the same amorphous alloy, we proposed n is independent of the temperature and the heating rate, thus

$$\ln[-\ln(1-x)] = -n\ln\alpha + A(T_0) \quad (8)$$

For two different heating rates α_1 and α_2, the fractions transformed are taken as $x_1(T_0)$ and $x_2(T_0)$ at the same temperature, T_0, and so

$$\ln[-\ln(1-x_1)] = -n\ln\alpha_1 + A(T_0) \quad (9)$$

$$\ln[-\ln(1-x_2)] = -n\ln\alpha_2 + A(T_0) \quad (10)$$

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combining Equations 9 and 10, we have

$$n = -\frac{\ln[-\ln(1-x_1)] - \ln[-\ln(1-x_2)]}{\ln\alpha_1 - \ln\alpha_2} \quad (11)$$

Therefore, so long as we choose several different heating rates, $\alpha_1, \alpha_2, \ldots$, and measure the crystallization fractions transformed, $x_1, x_2, \ldots$, at the same temperature, the Avrami exponent can be calculated using Equation 11.

3. Results

The sample used here, metallic glass $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$, is an excellent brazing filler metal showing the potential replacement for silver-brazing filler metals. It was taken from the same spot in the ribbon of thickness about 30 μm. The calorimetric measurements were performed with a DSC Dupont 1090.

The DSC curves with various heating rates (2.5, 5.0, 10, 20 K min^{-1}) are presented in Fig. 1. Through careful calibration of the instrument, the actual heating rates were 2.49, 4.97, 9.94, 18.89, respectively. From these DSC curves, we obtained three groups of useful data listed in Table I. The plots of $\ln[-\ln(1-x)]$ against $\ln\alpha$ is shown in Fig. 2. As seen, three straight lines basically parallel to each other. The gradient of the straight lines is the Avrami exponent, n. For the metallic glass $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$, the average of n is about 3.5.

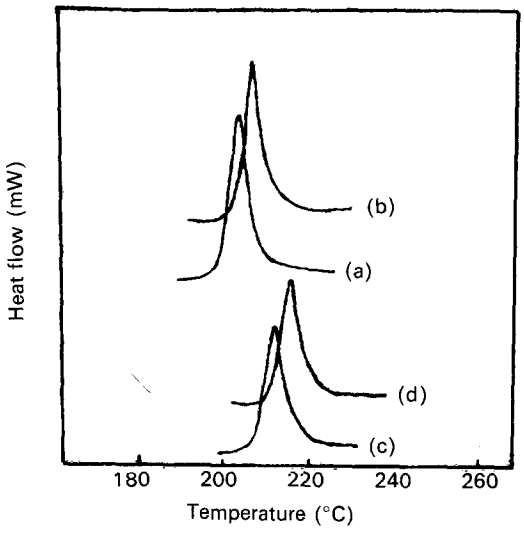

Figure 1 DSC scans of $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$ with a variety of heating rate: (a) 2.49; (b) 4.97; (c) 9.94 and (d) 18.89 K min^{-1}.

TABLE I

Group	α(K min^{-1})	$\ln\alpha$	x	$\ln[-\ln(1-x)]$	n
1	2.49	0.91	0.78	0.41	
	4.97	1.60	0.13	− 1.97	3.40
2	4.97	1.60	0.77	0.39	
	9.94	2.29	0.12	− 2.06	3.50
3	9.94	2.29	0.76	0.36	
	18.89	2.94	0.12	− 2.06	3.48

4. Discussion

In order to illustrate the reliability of the method with multi-scanning rates, the isothermal DSC was made on the same alloy as used for non-isothermal heating, the temperature of which was controlled at 466 K. The isothermal DSC scan is given in Fig. 3. By means of the Johnson–Mehl–Avrami equation for isothermal transformation

$$\ln\ln[1/(1-x)] = \ln K + n\ln(t-\tau)$$

n can be obtained by plotting $\ln\ln[1/(1-x)]$ versus $\ln(t-\tau)$. Fig. 4 shows the result for metallic glass $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$. Here the incubation time, τ, is adjusted to make all points nearly lying in a straight line. From Fig. 4, the Avrami exponent, n is 3.4, which is in good agreement with the value by the non-isothermal method described in the first section.

For the crystallization with constant growth rate, u, taking account of pre-existing nuclei, Greer [7] proposed the expression

$$x = 1 - \exp[(-4\pi/3)u^3(Nt^3 + It^4)]$$

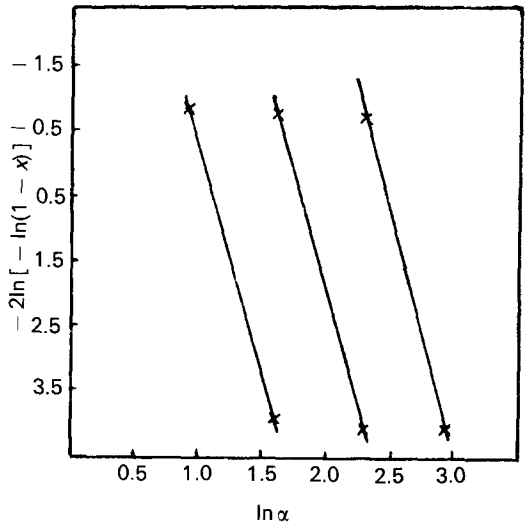

Figure 2 The plots of $\ln[-\ln(1-x)]$ against $\ln\alpha$.

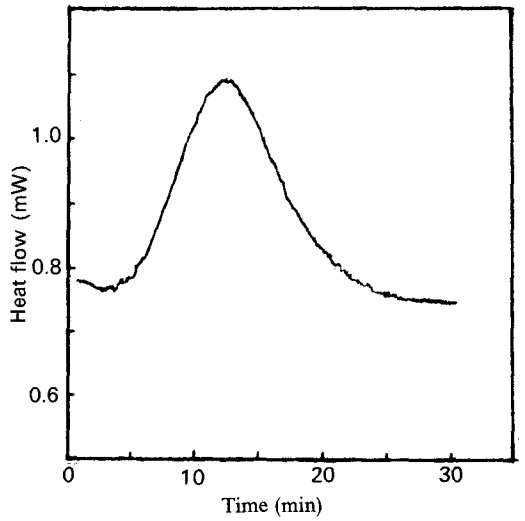

Figure 3 Isothermal DSC curve at temperature 466 K for $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$.

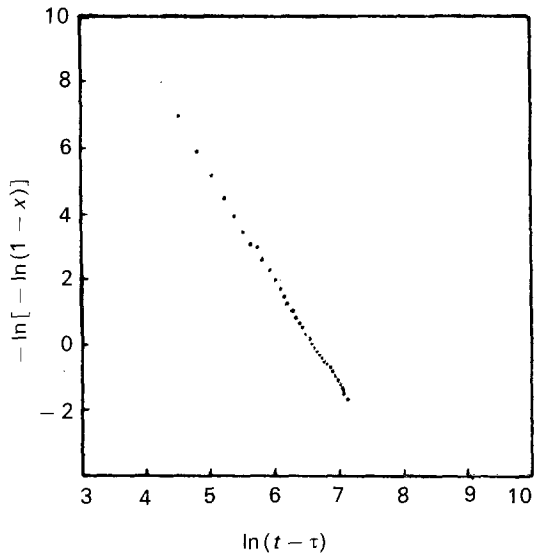

Figure 4 Plots of $\ln[-\ln(1-x)]$ against $\ln(t-\tau)$ of $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$ at the temperature 466 K.

If $N = 0$, Avrami exponent, n is 4, and $I = 0$, n is 3. Then the behaviour of crystallization transition of amorphous alloy $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$ is between these two extremes.

5. Conclusion

1. Based on Johnson–Mehl–Avrami isothermal kinetic equation, a method of non-isothermal analysis has been developed to measure the Avrami exponent of crystallization in metallic glass.

2. An example of amorphous alloy $Cu_{73.8}P_{13.8}Ni_{8.3}Sn_{4.1}$ was investigated by non-isothermal and isothermal analysis. The results of both procedures are in good agreement.

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