

STUDY OF NON-ISOTHERMAL CRYSTALLIZATION OF AMORPHOUS $\text{Cu}_{50}\text{Ti}_{50}$ ALLOY

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Abstract

The crystallization kinetics of amorphous $\text{Cu}_{50}\text{Ti}_{50}$ has been studied using differential scanning calorimetry (DSC) under non-isothermal conditions. The curves at different linear heating rates (2, 4, 8 and 16 K min^{-1}) show sharp crystallization peaks. The crystallization peak shifts to higher temperatures with increasing heating rate. The Kissinger's method of analysis of the shift in the transformation peak is applied to evaluate the activation energy (E_c). The KJMA formalism, which is basically developed for isothermal experiments, is also used to obtain E_c and the Avrami parameter (n).

The DSC data have been analysed in terms of kinetic parameters, viz. activation energy (E_c), Avrami exponent (n) and frequency factor K_0 using three different theoretical models. It is observed that the activation energy values derived from KJMA approach and modified Kissinger equation agree fairly well with each other. The activation energy values obtained from normal Kissinger method, and Gao and Wang expression underestimate the activation energy.

Keywords: Cu-Ti alloys, dimensionality of growth, non-isothermal crystallization

Introduction

Metallic glasses are known to possess superior physical properties compared to the oxide glasses. An important property of most of the metallic glasses is that they combine high strength and hardness with a degree of ductility. These glasses exhibit good corrosion resistance because they lack grain boundaries, dislocations and chemical heterogeneities which act as preferred sites of attack in crystalline solids. Metallic glasses are kinetically metastable and thermodynamically unstable materials. Most of them are stable at temperature close to the room temperature and can be transformed to crystalline state at temperature greater than room temperature. Therefore, the study of crystallization kinetics and the thermal stability of the metallic glasses are important from the application viewpoint.

The thermal analysis technique, namely differential scanning calorimetry (DSC) is most widely used [1–2] for kinetic analysis of crystallization process in amorphous mate-

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rials. The DSC data is generally analysed in Kolmogorov–Johnson–Mehl–Avrami (KJMA) formalism [3–7] to determine the mechanism governing the nucleation-and-growth process. The KJMA method is basically formulated for isothermal crystallization. Though the isothermal thermo-analytical techniques are definitive in most cases, the non-isothermal methods have several advantages over them. For example, non-isothermal experiments can be used to extend the temperature range of measurement beyond those accessible to isothermal experiments [8]. Further, practical processes like industrial synthesis occur under dynamic, non-isothermal conditions. Therefore, attempts have been made to extend the isothermal kinetics analysis methods to non-isothermal experiments [8, 9] and, on the other hand, various non-isothermal methods have been proposed for the analysis of the DSC data [10–12]. Among the non-isothermal methods, Kissinger's method [10] of analysis of the shift of transformation peak with the heating rate is the most widely used. Henderson [8] has described the necessary conditions for the validity of the Kissinger analysis in non-isothermal conditions.

Recently, many thermal studies of crystallization kinetics in Fe-based binary amorphous alloys [2] and multicomponent systems [13] have been reported. These Fe-based systems are useful material due to their soft magnetic properties. Cu–Ti alloy, which is of interest in the present study, belongs to the binary transition metal alloy that can be obtained in amorphous phase over a wide concentration range by rapid solidification. The understanding of thermally-induced crystallization process in such systems is important to determine their thermal stability. Crystallization of Cu₅₀Ti₅₀ glasses and undercooled melts has been reported by Koster *et al.* [14]. In the present work, we have investigated the non-isothermal crystallization of Cu₅₀Ti₅₀ alloy using DSC technique. The kinetics of crystallization is studied using two non-isothermal thermo-analytical methods proposed independently by Kissinger [10] and Gao–Wang [12]. The DSC data have been analysed in terms of kinetic parameters, viz. activation energy (E_c), Avrami exponent (n) and frequency factor K_0 . Further, the experimental data have been fitted to obtain kinetic parameters in KJMA formalism. It is observed that the activation energy values derived from KJMA approach and modified Kissinger equation agree fairly well with each other. The activation energy values obtained from normal Kissinger method, and Gao and Wang expression underestimate the activation energy.

Experimental

Specimens of amorphous Cu₅₀Ti₅₀ ribbons were prepared by a single roller melt-spinning technique in an argon atmosphere at the Institute of Materials Research, Tohoku University, Sendai, Japan. The amorphicity of the ribbons was confirmed by XRD and TEM. The as-quenched samples of Cu₅₀Ti₅₀ ribbons were heated in DSC (DSC-50, Shimadzu, Japan) at four linear heating rates (2, 4, 8 and 16 K min⁻¹) from room temperature to 720 K in air. The DSC scans were recorded by a thermal analyzer (TA-50 WSI, Shimadzu, Japan) interfaced to a computer. The detection sensitivity of the instrument is ~10 μW.

Results and discussion

The DSC curves of as-quenched samples at four heating rates (2, 4, 8 and 16 K min⁻¹) give a single stage crystallization event. The crystallization peaks for heating rates 2, 4, 8 and 16 K min⁻¹ are found to be at 618, 631, 638 and 651 K, respectively. For the crystallization curve at a particular heating rate (α), the crystallized volume fraction (x) can be obtained as a function of the temperature (T). Figure 1 shows the plot of x vs. T at 4 K min⁻¹. The sigmoidal plot exhibits the bulk crystallization and excludes the chance of surface crystallization. At stage 'a' nucleation occurs at various points in the bulk sample, at 'b' growth of nuclei with increased rate reaction as the surface area of nucleation increases. The slowing down stage 'c' shows decrease in surface area as a result of nuclei coalescing. The same nature of graph is confirmed for the other heating rates.

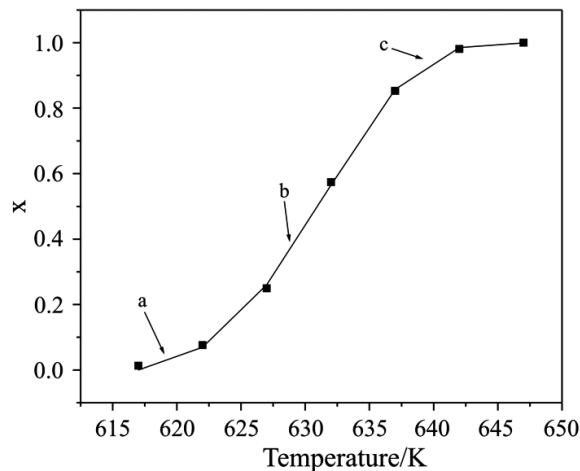


Fig. 1 Plot of volume fraction (x) of crystallized sample as a function of temperature at the heating rate of 4 K min⁻¹

The shift in the crystallization peak temperature (T_p) with increasing heating rate (α) can be used to obtain the activation energy (E_c) from the Kissinger plot of $\ln\alpha/T_p^2$ vs. $1000/T_p$. The plot is shown in Fig. 2. The activation energy is found to be equal to (207.36 ± 32.65) kJ mol⁻¹. The value is quite consistent with the value of $E_c = 261.2$ kJ mol⁻¹ reported by Miao *et al.* [15] for Cu₄₀Ti₆₀.

Gao and Wang [12] has shown that for $E \gg RT$ the following relations are true in linear heating experiments.

$$\alpha \frac{E_c}{K_p R T_p^2} = 1 \quad (1)$$

$$\left(\frac{dx}{dt} \right)_p = 0.37 n K_p \quad (2)$$

$$\frac{d\left(\ln \frac{dx}{dt}\right)_p}{d\frac{1}{T_p}} = -\frac{E_c}{R} \quad (3)$$

where α is the heating rate, E_c is the activation energy, R is the gas constant, n is the Avrami exponent, K_p is the rate constant at peak and $(dx/dt)_p$ is the crystallization rate at the peak. Equation (3) quantifies the slope of the plot of $\ln[(dx/dt)_p]$ vs. $1000/T_p$ shown in Fig. 3. The values of E_c obtained using Eq. (3) is $(166.21 \pm 34.96) \text{ kJ mol}^{-1}$. Avrami exponent n at the four heating rates are given in Table 1.

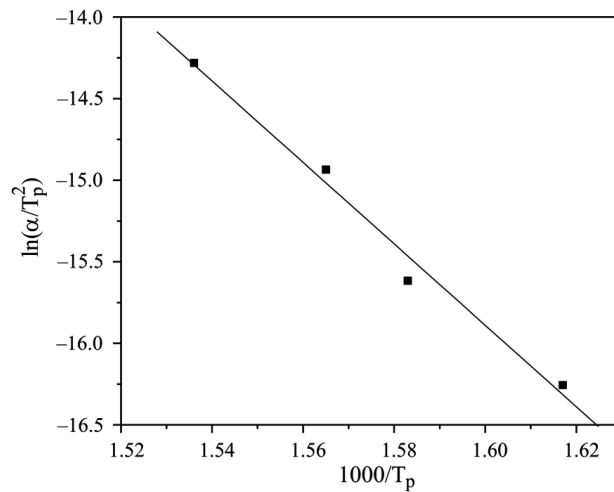


Fig. 2 Kissinger plot of $\ln(\alpha/T_p^2)$ vs. $1000/T_p$

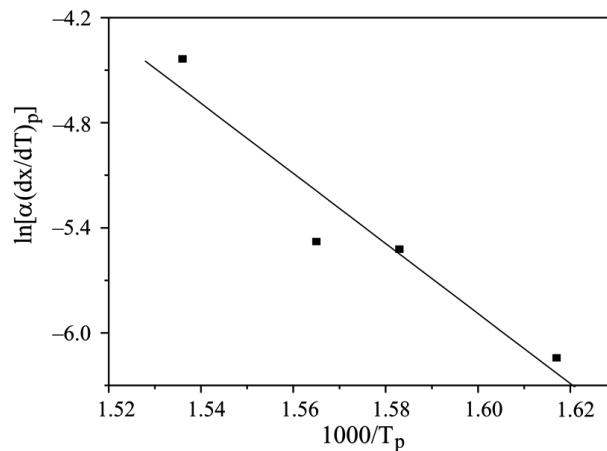


Fig. 3 Gao and Wang plot of $\ln[(dx/dt)_p]$ vs. $1000/T_p$

Table 1 Avrami exponent values at different heating rates for three models

Heating rate/K min ⁻¹	Avrami exponent		
	KJMA	Gao–Wang	MS (16)
2	1.67	3.366	3.14
4	1.5	3.270	2.88
8	1.6	1.658	3.09
16	1.3	2.551	2.84

The fractional crystallization (x) data from the DSC can be fitted to KJMA equation to derive the parameters n , E_c and K_0 . The main assumptions involved in KJMA approach are:

1. The crystallization data follow the iso-kinetic model:

$$\frac{dx}{dt} = K(T)f(x) \quad (4)$$

2. The rate constant is assumed to show Arrhenius temperature dependence:

$$K(T) = K_0 \exp\left(-\frac{E_c}{RT}\right) \quad (5)$$

3. KJMA simplest case equation is

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

The overall assumptions lead to

$$[- \ln(1-x)]^{1/n} = K_0 \int_0^t \exp\left(-\frac{E_c}{RT}\right) dt \quad (7)$$

where n is the Avrami exponent and E_c is the activation energy. Equation (7) can be written as

$$x = 1 - \exp\left[-\frac{K_0}{\alpha} \int_{T_0}^T \exp\left(-\frac{E_c}{RT}\right) dT\right]^n \quad (8)$$

where T_0 is onset crystallization temperature.

Computational fitting of the experimental data to Eq. (8) gives the parameters n , E_c and K_0 . The activation energy is found to be equal to 295 ± 13 kJ mol⁻¹. It is higher than the values obtained by the other two methods. However, it should be noticed that the isothermal model gives activation energy values nearer to those obtained by a non-isothermal model. The comparison of values of n , obtained using KJMA model and the Gao–Wang method along with the earlier results [16] obtained using Matusita and Sakka (MS) [11] method, is shown in the Table 1. The value of K_0 that gives best fitting parameters is found to be $3.0 \cdot 10^{-22}$ s⁻¹.

Conclusions

It is observed that the activation energy values derived from KJMA approach and modified Kissinger equation agree fairly well with each other. The activation energy values obtained from normal Kissinger method and Gao and Wang expression, on the other hand, underestimate the activation energy. However, the values of the Avrami exponent derived from Matusita and Sakka approach and even using Gao and Wang equation seem to provide an idea about the dimensionality of growth, whereas the exponent's value obtained from KJMA method, appears to be merely a fitting parameter.

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