

Isochronal and isothermal crystallization in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass

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Abstract: Non-isothermal crystallization transformation kinetics and isothermal crystallization kinetics in super-cooled liquid region (SLR) in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glasses were studied by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). In isochronal mode, the average values of activation energy in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass determined by different models (Kissinger method, Flynn-Wall-Ozawa method and Augis-Bennett method) are in good agreement with each other. In addition, the isothermal transformation kinetics in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glasses was described by the Johnson-Mehl-Avrami (JMA) model. For $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass, the Avrami exponent n ranges from 2.2 to 2.9, indicating that crystallization mechanism in the bulk metallic glass was mainly diffusion-controlled; crystal growth is controlled by long range ordering diffusion in three-dimensional growth during isothermal crystallization process. The average value of activation energy in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass is 469 kJ/mol in isothermal transformation process.

Key words: $Zr_{55}Cu_{30}Ni_5Al_{10}$; metallic glass; thermal analysis; crystallization kinetics; Avrami exponent

1 Introduction

Unlike the crystallized counterparts, bulk metallic glasses lack of long-range order in the atomic assembly. Therefore, metallic glasses possess unique combination of structural and functional properties, such as high strength, large elasticity, low elastic modulus and excellent corrosion resistance [1–11]. Thus, bulk metallic glasses are potential materials as applications in various engineering fields. However, amorphous alloys, which are in a metastable state, can change to crystalline state in the super-cooled liquid region. The crystallization kinetics for bulk metallic glasses is an important property, which is always linked with physical properties and mechanical properties.

There are many publications concerning the crystallization kinetics either in isochronal or isothermal modes in amorphous materials (polymer, metallic glass and glass). In bulk metallic glasses, many researchers performed differential scanning calorimetry (DSC) or differential thermal analysis (DTA) and used Johnson–Mehl–Avrami (JMA) model to analyze their

results, especially the kinetics of this evolution. It is well known that the kinetics of crystallization in amorphous materials is sensitive to the kinetic parameters, which mainly include the activation energy of crystallization, mechanisms of nucleation and growth process for bulk metallic glasses, nature of crystalline phases, crystallization time and temperature. ROY and RAGHUVANSHI [12] analyzed the isothermal and non-isothermal crystallization kinetics in $Al_{65}Cu_{20}Ti_{15}$ bulk metallic glass. In fact, the Avrami exponent indicated that crystallization was governed by three-dimensional diffusion-controlled growth in isothermal mode. In our previous investigation [13], the crystallization transformation kinetics in $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass in isothermal and non-isothermal modes were analyzed by Kissinger model and JMA model. It is interesting to note that the activation energy corresponding to isothermal conditions calculated by Arrhenius equation is larger than the value calculated by the Kissinger method under isochronal conditions. The reason lies in an energy barrier higher in isothermal annealing mode than in isochronal mode. More recently, KONG et al [14] have investigated the non-isothermal

kinetics in $\text{Fe}_{78}\text{Zr}_7\text{B}_{15}$ amorphous alloy with JMA model, and they have shown that the crystallization mechanisms are different in two crystallization stages. In particular, ABU EL-OYOUN [15–19] reported the crystallization kinetic parameters in different amorphous glasses by isoconversional methods: Kissinger–Akahira–Sunose (KAS) method, Tang method, Starink method, Flynn–Wall–Ozawa (FWO) and Vyazokin method. A new analysis method (various heating rates, VHR) was also used to discuss the crystallization kinetic parameters (apparent activation energy E_a and kinetic exponent n) in amorphous materials in continuous heating mode [20,21]. AL-HENITI [22] reported that under non-isothermal crystallization conditions in $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ metallic glass, the Avrami exponent (n) for the two stages of crystallization were $n_1=4$ and $n_2=5$. Based on the JMA model, PRASHANTH et al [23] demonstrated that the crystallization process in $\text{Zr}_{65}\text{Ag}_5\text{Cu}_{12.5}\text{Ni}_{10}\text{Al}_{7.5}$ glassy powder was diffusion-controlled with a three-dimensional growth. OKAI et al [24] investigated the $\text{Ca}_{50}\text{Mg}_{22.5}\text{Cu}_{27.5}$ bulk metallic glass in super-cooled liquid region (isothermal annealing), and showed that the crystal growth was determined by a long-range diffusion processes. Finally, crystallization kinetics in metallic glass-matrix composites (TiC/Ti-based metallic glass matrix composite) was also in agreement with JMA model [25].

However, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glasses have received considerable attention because of their possible application as structural and functional materials. For instance, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ [26–28] bulk metallic glasses show excellent glass forming ability, wide super-cooled liquid region and high mechanical properties. In the $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass, many features have been investigated, such as crystallization [26, 29–32], structural relaxation [33–35], glass forming ability [36]. However, there is only little work on the non-isothermal crystallization properties and some discrepancies exist between the different reported results and some questions are open: 1) $\text{Cu}_{46}\text{Zr}_{45}\text{Al}_7\text{Y}_2$ [37–39] and $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ [26–28] bulk metallic glasses show excellent glass forming ability, wide super-cooled liquid region and high mechanical properties. The thermal properties of the two bulk metallic glasses: glass transition temperature (T_g), temperature of the onset of crystallization (T_x) and crystallization peak temperature (T_p), are very similar in the two alloys. These two alloys have similar characteristic temperature (T_g , T_x). Do they exhibit similar crystallization features? 2) Experiments could be performed under isothermal or non-isothermal conditions. Does this difference lead to different behavior? Therefore, the aim of the present work is to give answers to these questions and to try to describe the kinetics

using theoretical models.

2 Theoretical background

2.1 Isothermal annealing

During an isothermal annealing, transformation kinetics from the amorphous state to the crystalline state can occur, and the phase transformation is characterized by the crystallized volume fraction, α . This evolution can be described by the JMA model and the following equation [30, 36, 40–42]:

$$\alpha(t) = 1 - \exp[-(Kt)^n] \quad (1)$$

where n is the kinetics exponent (Avrami exponent), which reflects both the crystallization mechanism and the dimensionality of the crystallization process; t is the annealing time; K is the reaction rate constant (K depends on the annealing temperature), with an Arrhenius temperature dependence:

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

where K_0 is the frequency factor; E_a is the effective activation energy during the overall crystallization process; R is the mole gas constant; T is the thermodynamic temperature.

2.2 Non-isothermal annealing

During the isochronal phase transaction process, the phase transaction rate $d\alpha/dt$ [36, 42] is usually written as:

$$\frac{d\alpha}{dt} = Kf(\alpha) \quad (3)$$

where $f(\alpha)$ is a transformation function of the crystallized volume fraction α [36, 42]. This function $f(\alpha)$ is usually defined as:

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

During the crystallization process in amorphous materials, the activation energy of the phase transformation can be evaluated using various methods: Kissinger method [43–45], Flynn–Wall–Ozawa method [43,45] or Augis–Bennett method [46]. The Kissinger method is the most common one.

2.2.1 Kissinger method

According to this model, the activation energy E_a of phase transformation occurring in bulk metallic glass can be determined using DSC experiments carried out with various heating rates [43–45] and using the following equation:

$$\ln\left(\frac{R_h}{T_a^2}\right) = -\frac{E_a}{RT_a} + C \quad (5)$$

where R_h is the heating rate; T_a is the temperature at a fixed stage of the relaxation in amorphous materials,

such as T_g , T_x and T_p in this investigation; C is a constant. It can be found that E_a could be obtained from a plot of $\ln(R_h/T_a^2)$ vs $1000/T_a$.

2.2.2 Flynn–Wall–Ozawa method

During the non-isothermal crystallization process, the Flynn–Wall–Ozawa method is another effective method to calculate the activation energy for bulk metallic glasses [43,45]. The formula could be expressed as:

$$\ln R_h = -1.052 \frac{E_a}{RT_a} + C \quad (6)$$

In a similar way, a plot of $\ln R_h$ vs $1000/T_a$ gives a value of the activation energy E_a .

2.2.3 Augis–Bennett method

The activation energy of crystallization process for the samples could also be calculated by Augis–Bennett method [46]. In this model,

$$\ln\left(\frac{R_h}{T_a - T_0}\right) = -\frac{E_a}{RT_a} + C \quad (7)$$

where T_0 is a characteristic (and adjustable) temperature.

Let us mention that these three methods are very similar and require similar plots.

3 Experimental

In the present work, master ingots of alloys with composition of $Zr_{55}Cu_{30}Ni_5Al_{10}$ were kindly provided by Prof. Y. Yokoyama, Institute of Materials Research, Tohoku University, Sendai, Japan. Plate samples were mechanically cut to prepare DSC samples. In order to remove surface oxidation prior to experiments, these samples were carefully polished using diamond paste and finally washed in ethanol in an ultrasonic cleaning machine. Structure of the specimens in the bulk metallic glasses was examined by X-ray diffraction using Cu K_α radiation produced by a commercial device (D8, Bruker AXS GmbH, Germany), either at room temperature or during continuous heating up to 873 K. The working conditions were 40 kV and 40 mA for the X-ray tube and a scanning rate of 0.025 ($^\circ$)/step.

The thermal properties and phase transformations were investigated by a standard commercial instrument (Pekin Elmer, DSC-7) under high purity dry nitrogen at a flow rate of 20 mL/min. Aluminium pans were used as sample holders. In order to ensure the reliability of experimental data, temperature and enthalpy were calibrated by indium standard specimen ($T_m=429.7$ K, $\Delta H_c=28.48$ J/g) and zinc standard with 3.283 mg ($T_m=692.6$ K, $\Delta H_c=108.37$ J/g), with an accuracy of ± 0.2 K and ± 0.02 mW, respectively.

The crystallization kinetics of the samples was characterized by DSC, at different constant heating rate

ranges. In the case of isothermal crystallization investigation, isothermal crystallization of the samples in super-cooled liquid region (SLR) was tested at temperature above T_g and below T_x . The samples were heated to the isothermal tested temperature at a heating rate of 20 K/min. The temperature was held for various periods to induce the crystallization behaviour until completion. Finally, the samples were cooled down to room temperature.

4 Results and discussion

4.1 Non-isothermal crystallization

Figure 1 displays the XRD pattern of the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass. A typical broad diffraction peak appears, and the diffraction peak corresponding to a crystalline phase is not observed. Therefore, $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass exhibits typical characteristics of an amorphous structure.

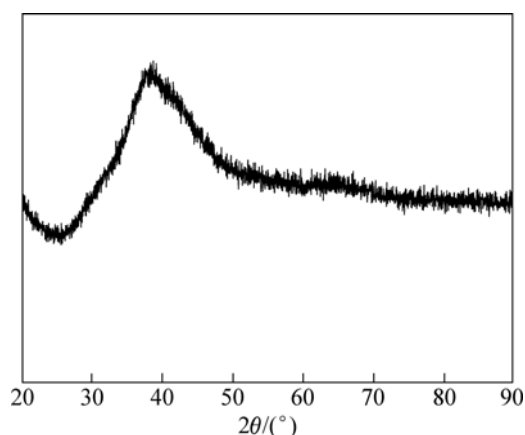


Fig. 1 XRD pattern of as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass

The DSC curves of $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass obtained using continuous heating with different heating rates are shown in Fig. 2. The crystallization peak temperature (T_p) shifts to higher temperature as heating rate is increased. This result is similar to what is classically observed. In the $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass, the peak is a little more complicated, since a kind of double peak is observed. However, the question is: Are these two phases due to same phase or not? When the heating rate is 20 K/min, peaks occur at 761 K (the first peak) and 765 K (the second peak), respectively. Therefore, two apparent peaks during the course of heating with 20 K/min up to 761 K (the first peak) and 765 K (the second peak) occur and then XRD patterns indicate that the corresponding crystalline phases are identical (Fig. 3).

In the literature, the crystallization behaviour in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass was investigated by

in-situ synchrotron radiation. YAVARI et al [47,48] found that crystallization in $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass occurs via initial nucleation and growth of a metastable phase that transforms to equilibrium tetragonal Zr_2Cu . To confirm this mechanism, X-ray diffraction experiments were performed during a continuous heating, the average heating rate was 1.5 K/min and diffractograms were recorded each 5 K (Fig. 4).

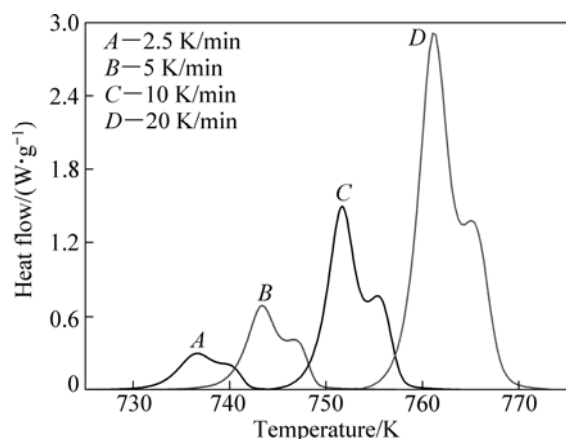


Fig. 2 DSC curves of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glasses with different heating rates

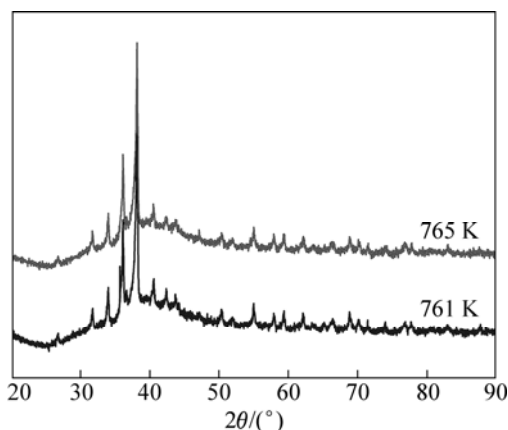


Fig. 3 XRD patterns after heating at 761 K or 765 K with heating rate of 20 K/min for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass

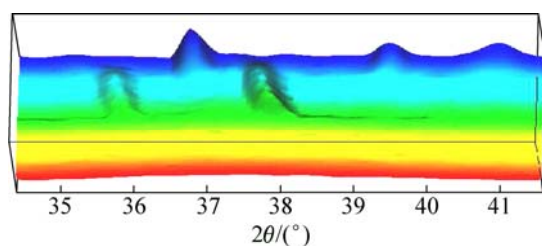


Fig. 4 XRD spectrum (3D representation) during continuous heating at 1.5 K/min from 573 K to 873 K for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass

The formation of crystalline particles is clearly revealed by the apparition of diffraction peaks. The nature of the crystalline phases change when the temperature increases. For instance, the peak in the range 37.5° – 38.0° disappears and a new peak appears close to 37° . This new peak can be attributed to a body-centered tetragonal phase similar to Zr_2Cu . Figure 5 illustrates this evolution. But it is not possible on this figure to detect a two-steps evolution in the low temperature crystallization process (in the range of 700–750 K). TEM observation should also give precious information. However, since the present work is focused mainly on the kinetics aspects rather than on the nature of the crystalline phases, and no detailed investigation of the phenomenon was conducted.

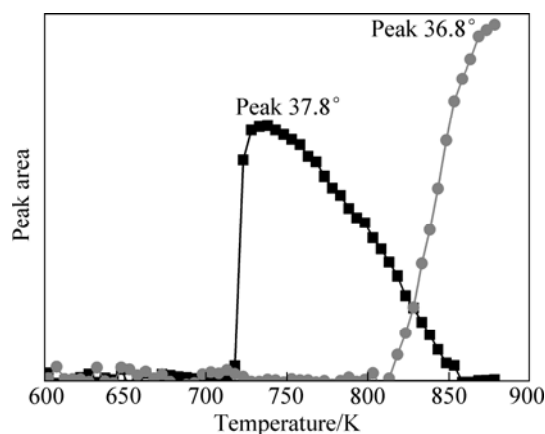


Fig. 5 Diffraction peak area versus time during continuous heating at 1.5 K/min for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass

The relationship between the crystallization volume fraction α and temperature during non-isothermal crystallization process of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass is shown in Fig. 6. All the curves present a sigmoid dependence with temperature. The same evolution is

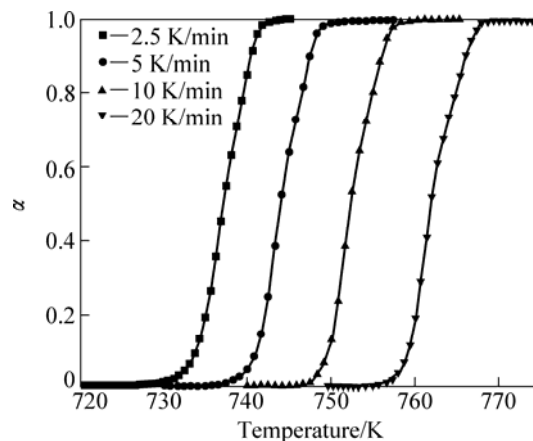


Fig. 6 Plots of crystallization volume fraction α of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass as function of temperature at different heating rates

observed in all the amorphous materials (bulk metallic glasses and polymers) in the non-isothermal crystallization mode.

The activation energy E_a can be determined by Kissinger's method, Flynn–Wall–Ozawa (FWO) method and Augis–Bennett (AB) method. The relevant fitting results by FWO method at different crystalline volume fraction α (ranging from 0.1 to 0.9) are shown in Fig. 7. The results are in good agreement with the Kissinger's equation, FWO equation and AB equation since straight lines are clearly observed.

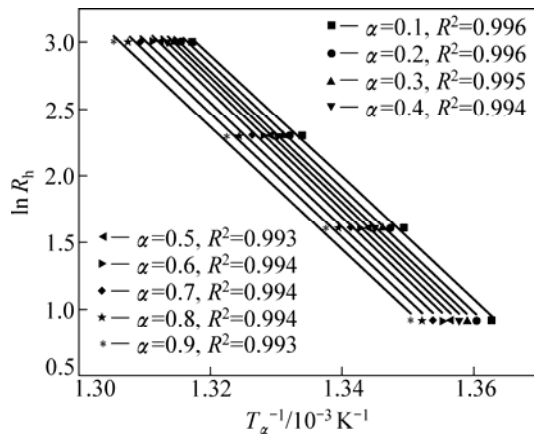


Fig. 7 FWO plots of $Zr_{55}Cu_{30}Ni_5Al_{10}$ in non-isothermal heating mode at any fixed crystallization volume fraction α (range from 0.1 to 0.9)

Figure 8 presents the calculated results of activation energy for $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass. The activation energy for crystallization in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass is not constant, fluctuating slightly with crystallization volume fraction α in non-isothermal heating mode. The average values of activation energy for $Cu_{46}Zr_{45}Al_7Y_2$ and $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glasses in non-isothermal heating mode are very similar [13]. Meanwhile, the average values of

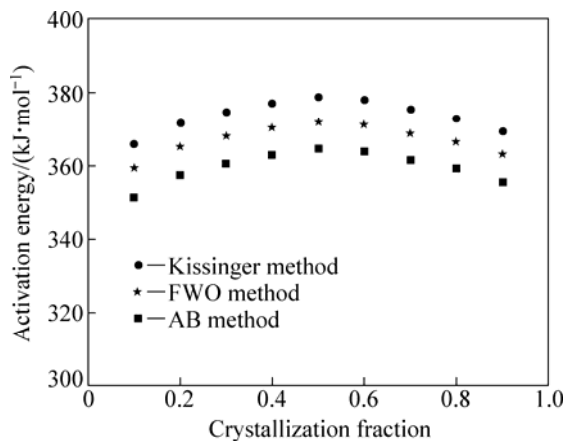


Fig. 8 Activation energy E_a as a function of crystallization volume fraction α in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glasses (α range from 0.1 to 0.9) in non-isothermal heating process

activation energy for $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass determined by different models (Kissinger method, FWO method and AB method) are in good agreement with each other.

4.2 Isothermal behaviours

In order to well understand the crystallization kinetics of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass, the crystallization kinetic of the samples was investigated in isothermal situation at different annealing temperatures. The DSC curves obtained for $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass at different annealing temperatures are shown in Fig. 9. They look like those recorded under non-isothermal conditions. It can be found that every DSC curve exhibits a single exothermic peak after a certain incubation time (τ). Additionally, by increasing annealing temperature, it is obvious that the incubation time slumps. The reason is that atoms in the samples have a higher mobility at higher annealing temperature, which leads to concentration fluctuations necessary for large-scale crystallization to set in [49]. From these curves, the evolution of crystalline volume fraction versus the annealing time during isothermal annealing is shown in Fig. 10. The higher the annealing temperature is, the steeper the curves are. Meanwhile, all the curves exhibit a typical sigmoid evolution.

As mentioned above, the transformation kinetics can be described using the JMA equation [36, 50]:

$$\alpha(t) = 1 - \exp[-K(t - \tau)^n] \quad (8)$$

where τ is the incubation time, which in fact is a fitting parameter. Taking the double logarithm of Eq. (8), the following expression is deduced [36]:

$$\ln[-\ln(1 - \alpha(t))] = n \ln K + n \ln(t - \tau) \quad (9)$$

By plotting $\ln[-\ln(1 - \alpha)]$ versus $\ln(t - \tau)$ at various annealing temperatures with $0.2 \leq \alpha \leq 0.8$ (Fig. 11), the kinetic exponent n and the reaction rate constant K can be calculated and the values are given in Table 1.

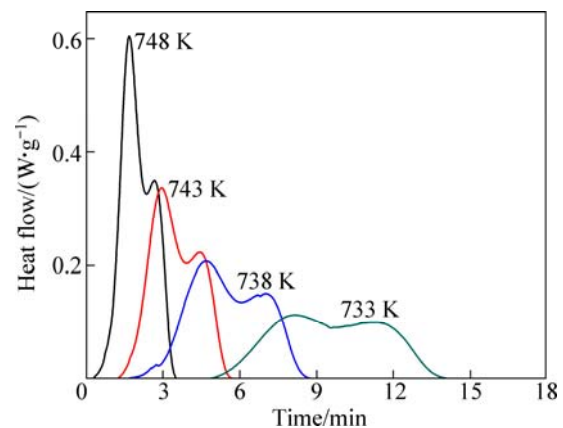


Fig. 9 Isothermal DSC curves of $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass at various annealing temperatures

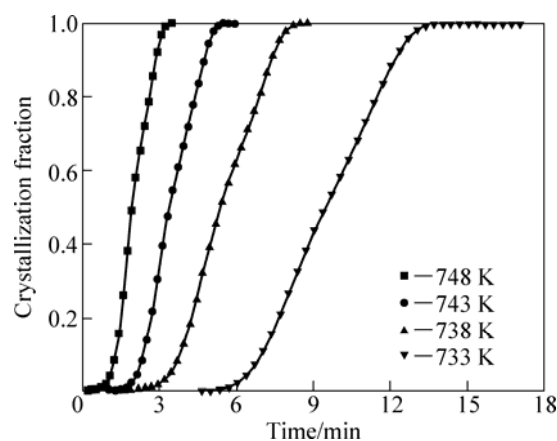


Fig. 10 Plots of crystallization volume fraction α of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass as function of time at different annealing temperatures

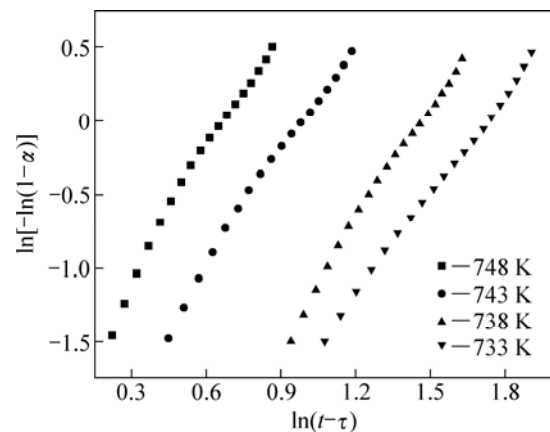


Fig. 11 Avrami plots of $\ln[-\ln(1-\alpha)]$ vs $\ln(t-\tau)$ at various annealing temperature with $0.2 \leq \alpha \leq 0.8$ from isothermal DSC curves for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass

Table 1 Kinetic exponent n , reaction rate constant K and incubation time τ at different annealing temperatures with $0.2 \leq \alpha \leq 0.8$ in $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glasses

Annealing temperature/K	n	τ/min	K
748	2.9	0.27	0.51
743	2.5	1.13	0.37
738	2.6	1.70	0.23
733	2.2	4.72	0.17

The kinetic exponent n varies with annealing temperatures from 2.2 to 2.9 in the $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass. Diffusion-controlled growth theory [25,51,52] predicts that: $1 < n < 1.5$ implies growth of particles of appreciable initial volume; $n=1.5$ means a growth of particles with a nucleation rate close to zero; $1.5 < n < 2.5$ indicates growth of particles with decreasing nucleation rate; $n > 2.5$ corresponds to the growth of small particles with an increase in nucleation rate.

The average kinetic exponent n for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass is about 2.5, which implies that crystallization mechanism in the $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass is mainly diffusion-controlled [30], and crystal growth is controlled by long range ordering (LRO) diffusion in three-dimensional growth during isothermal crystallization process [53].

Let us now turn to the influence of the nucleation and growth behaviour during crystallization on the activation energy. The activation energy for the crystallization process in isothermal mode can be determined using the Arrhenius equation [30]:

$$t(\alpha) = t_0 \exp\left(\frac{E_a}{RT}\right) \quad (10)$$

where t_0 is a constant. The plots of $\ln t(\alpha)$ vs $1/T_a$ in $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass during isothermal process are shown in Fig. 12. All the fitting lines are almost straight lines. The average value of activation energy for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass is 469 kJ/mol. However, this activation energy decreases when the crystalline fraction increases (Fig. 13). This decrease

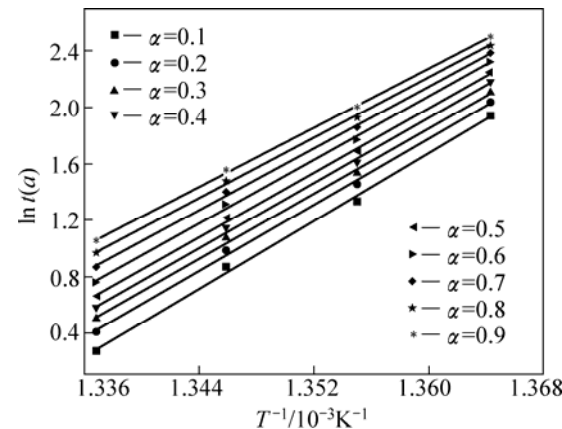


Fig. 12 Plots for calculation of activation energy in $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ bulk metallic glass

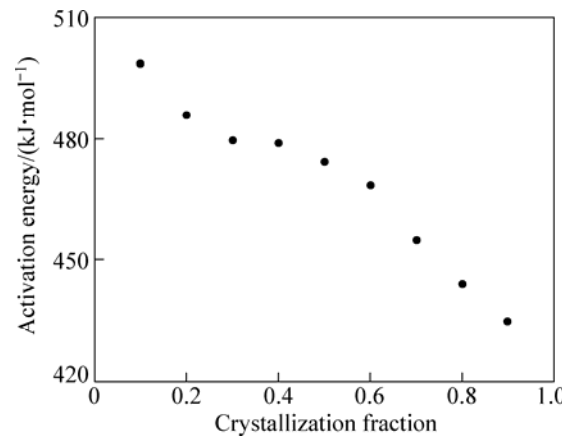


Fig. 13 Activation energy E_a as function of crystallization volume fraction α in $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ (α ranging from 0.1 to 0.9) in isothermal mode

could be due to the fact that this energy is the sum of two components: one term corresponding to the nucleation and the other to the growth (connected to the diffusion). When crystallization progresses, the energy required for nucleation can progressively disappear and then E_a can decrease.

5 Conclusions

1) In non-isothermal mode, the average values of activation energy for $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass determined by different models (Kissinger method, Flynn–Wall–Ozawa method and Augis–Bennett method) are good agreement with each other.

2) Under isothermal annealing conditions, the Avrami exponent n ranges from 2.2 to 2.9 in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass. These values, close to 2.5, indicate that the crystallization mechanism is mainly diffusion-controlled. Crystal growth occurs by a three-dimensional long range ordering.

3) In isothermal transformation process, the average value of activation energy for $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass is 469 kJ/mol. The classical models developed in the literature are really appropriated to describe the crystallization process in $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass.

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Zr₅₅Cu₃₀Ni₅Al₁₀ 大块金属玻璃的等时和等温晶化

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摘 要: 采用差示扫描量热仪 (DSC) 和 X 射线衍射仪 (XRD) 研究 $Zr_{55}Cu_{30}Ni_5Al_{10}$ 大块金属玻璃的非等温晶化转变动力学和在过冷液相区的等温晶化动力学行为。在非等温过程中, 采用不同方法 (Kissinger, Flynn-Wall-Ozawa 和 Augis-Bennett) 得到的 $Zr_{55}Cu_{30}Ni_5Al_{10}$ 大块金属玻璃平均激活能彼此之间吻合很好。此外, 采用 Johnson-Mehl-Avrami (JMA) 模型描述 $Zr_{55}Cu_{30}Ni_5Al_{10}$ 大块金属玻璃的等温转变动力学。研究结果表明: $Zr_{55}Cu_{30}Ni_5Al_{10}$ 大块金属玻璃的 Avrami 指数 n 介于 2.2 和 2.9 之间, 表明其晶化机制主要是扩散控制过程。在等温晶化的过程中, 晶核长大主要是三维的长程有序扩散控制的过程, 平均激活能为 469 kJ/mol。

关键词: $Zr_{55}Cu_{30}Ni_5Al_{10}$; 金属玻璃; 热分析; 晶化动力学; Avrami 指数

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