Non-isothermal Crystallization Kinetics and Isothermal Crystallization Kinetics in Supercooled Liquid Region of Cu–Zr–Al–Y Bulk Metallic Glass

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Abstract The crystallization kinetics of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ bulk metallic glasses in non-isothermal and isothermal conditions was studied by differential scanning calorimetry. In the non-isothermal and isothermal modes, the average activation energy of $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is larger than that of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$, meaning the higher stability against crystallization of $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$. In addition, the average activation energies for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ calculated using Arrhenius equation in isothermal mode are larger than the values calculated by Kissinger–Akahira–Sunose method in non-isothermal mode, indicating that the energy barrier is higher in isothermal mode. The Johnson–Mehl–Avrami model was used to analyze the crystallization kinetics in the non-isothermal and isothermal modes. The Avrami exponent n for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ is above 2.5, indicating that the crystallization is mainly determined by a diffusion-controlled three-dimensional growth with an increasing nucleation rate, while the Avrami exponent n for $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is in the range of 1.5–2.5 in the non-isothermal mode, implying that the crystallization is mainly governed by diffusion-controlled three-dimensional growth with decreasing nucleation rate. Finally, the Avrami exponents n for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ are different in the non-isothermal and isothermal conditions, which imply different nucleation and growth behaviors during the crystallization processes.

KEY WORDS: Bulk metallic glass; Yttrium addition; Crystallization behavior; Activation energy

1 Introduction

Bulk metallic glasses (BMGs) are the potential materials that can be applied on structural and functional fields due to their high yield strength at the room temperature, excellent wear and corrosion resistance [1–5]. Recently, Cu-based BMGs have been widely investigated due to their excellent glass-forming ability (GFA), good thermal stability, wide supercooled liquid region (SLR), high mechanical properties

at room temperature and relatively low-cost elements contained [6]. It is widely accepted that minor yttrium addition can effectively improve the glass-forming ability and mechanical properties of the Cu-based BMGs [7–10]. For example, for the $\text{Cu}_{46}\text{Zr}_{47-x}\text{Al}_7\text{Y}_x$, the critical diameter of the Cu–Zr–Al BMGs can be increased from 5 to 10 mm after adding 2 at.% of yttrium, the yield strength decreased from 1960 to 1750 MPa, and the plastic strain before failure increased from 1.87 to 5% [11].

Since the metallic glasses are metastable materials, they will transform into crystalline state during heating in the SLR. From the technological point of view, the thermal stability of BMGs is of great importance. Therefore, a great attention is paid on the crystallization kinetics of BMGs, which helps us to understand the crystallization process of the metallic glasses. There are numerous reports on the crystallization kinetics of BMGs in either non-isothermal or

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isothermal modes [12–16]. The differential scanning calorimetry (DSC) is used to investigate the crystallization kinetics and related parameters, such as activation energy, incubation time and mechanisms of nucleation and growth. Depending on the heating process, different models have been proposed to describe the crystallization kinetics, such as the Kissinger method [13] and the Johnson–Mehl–Avrami (JMA) method [14, 15]. However, only a few efforts have been made regarding the crystallization kinetics of Cu–Zr–Al BMGs with the addition of yttrium. Therefore, it is necessary to understand in depth the crystallization kinetics of Cu-based BMG with minor yttrium addition.

In this work, the crystallization kinetics of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs was investigated using the DSC in both non-isothermal and isothermal conditions and their kinetic parameters were calculated to explain the details of the nucleation and growth behaviors during the crystallization processes.

2 Experimental

Master alloy ingots with nominal composition of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ were prepared by arc-melting a mixture of Cu (99.9%), Zr (99.9%), Al (99.99%) and Y (99.99%) in a high-purity argon atmosphere. To ensure complete melting and compositional homogeneity, the alloy ingots were re-melted four times. Then, the molten alloys were suction casting into a copper mold to obtain a rod with 3 mm in diameter under negative pressure. The microstructures of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ were investigated by X-ray diffraction (XRD, SHIMADU XRD-6000, CuK_α) and transmission electron microscopy (TEM, JEOL JEM-2010). The thermal characteristic parameters of the samples were determined by differential scanning calorimeter (DSC, METTLER-TOLEDO TGA/DSC1) under a high-purity argon atmosphere at the heating rate of 20 K/min.

Non-isothermal and isothermal crystallization kinetics was determined by DSC. The non-isothermal heating process was performed at different heating rates of 10, 20, 30 and 40 K/min. Then, isothermal crystallization of the alloys was investigated in the SLR. The samples were heated up to the isothermal annealing temperature at a heating rate of 20 K/min, and then held for 60 min. Baseline corrections during the experiments were conducted for all the DSC curves.

3 Results and Discussion

3.1 XRD and TEM Analysis

The XRD patterns of the as-cast $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs are shown in Fig. 1a, exhibiting

a broad amorphous peak in the 2θ range of 30° – 48° , which is the characteristic of amorphous structure. Figure 1b shows TEM image of the as-cast $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ sample, displaying a bright-field image, confirming a uniform microstructure with no diffraction contrast. Furthermore, the corresponding selected area electron diffraction (SAED) pattern shows an amorphous ring (the inset of Fig. 1b), indicating its nearly fully amorphous structure.

3.2 Non-isothermal Behaviors

Figure 2 shows the DSC curves of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs at the heating rate of 20 K/min. The glass transition temperature (T_g) and crystallization onset temperature (T_x) were obtained, and thus the SLR, i.e., above T_g and below T_x , was in between 693 and 763 K for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and in between 696 and 770 K for $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$.

Figure 3 shows the DSC curves of the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs under heating rates of 10, 20, 30 and 40 K/min. All the DSC curves exhibit a broad region of exothermic relaxation, an endothermic glass transition and one exothermic peak corresponding to successive transformation from a metastable supercooled liquid state to the equilibrium crystalline intermetallic phases. It can be seen that T_g , T_x and crystallization peak temperature (T_p) are shifted to higher temperatures with increasing heating rate, indicating that both the glass transition and crystallization depend on the heating rate during the continuous heating.

Regarding the relationship between the crystallization volume fraction (α) and the temperature during the non-isothermal crystallization process, it has been suggested that the fractional area of the exothermic peak on a DSC curve is proportional to the crystallization volume fraction. Therefore, the crystallization volume fraction can be accurately derived by measuring the partial area of the exothermic peak, and the crystallization volume fraction as a function of temperature is shown in Fig. 4. All the curves display a sigmoid dependence with the temperature, and the phenomena were observed in all BMGs during the non-isothermal process. It is found that the crystallization volume fraction slightly increases within the ranges of $\alpha > 0.2$ and $\alpha < 0.8$, implying that the crystallization reaction proceeds slowly at the beginning and end of the crystallization process. The crystallization volume fraction increases sharply in the middle stage, i.e., $0.2 \leq \alpha \leq 0.8$, indicating that the crystallization reaction occurs quickly. Therefore, the crystallization process mainly occurs in this region.

Typically, it is important to investigate the local activation energy E_a during the non-isothermal crystallization process for the amorphous materials and the Kissinger–

Fig. 1 XRD patterns of as-cast $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs **a**, TEM image of as-cast $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ BMG **b** (The inset shows the corresponding SAED pattern)

Fig. 2 DSC curves of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs at heating rate of 20 K/min

Akahira–Sunose (KAS) method [17] is an effective method to calculate the E_a of the phase transformation in non-isothermal mode. The KAS method is slightly different from the Kissinger method because the Kissinger method is the maximum rate method (peak temperature), and the nucleation and growth are not considered during the crystallization [18]. However, the KAS method is based on nucleation and growth processes [19]. As such, the E_a can be determined by the KAS equation:

$$\ln\left(\frac{T_a^2}{\beta}\right) = \frac{E_a}{RT_a} + C, \quad (1)$$

where T_a is the characteristic temperatures, β is the heating rate and C is a constant. Plots of $\ln(T_a^2/\beta)$ versus $1000/T_a$ during non-isothermal annealing are shown in Fig. 5, and the E_a can be obtained from the fitting line. Figure 6 shows the E_a as a function of the crystallization volume fraction (α ranges from 0.1 to 0.9) in the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$. It is noted that the value of the E_a slightly

Fig. 3 DSC curves of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs at various heating rates

Fig. 4 Plots of crystallization volume fraction α of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs as a function of temperature at various heating rates

fluctuates with the increase in the crystallization volume fraction. The higher E_a at the initial crystallization stage suggests a higher energy barrier of crystallization, making the reaction occurs slowly and the crystallization volume fraction increases slowly. The E_a begins to drop within the entire crystallized range after crystallization occurs [20, 21]. It is well known that the activation energy plays a crucial role in thermal stability for BMGs. The structure is more stable at greater activation energy during the crystallization process. The average activation energies for the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ are 241 and 296.3 kJ/mol, respectively. It is noted that the average activation energy for the $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is larger than that of the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$, indicating that $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is more stable compared to the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$. The average activation energy increases on account of the added yttrium, demonstrating that the yttrium plays an important role in limiting the atomic mobility of the alloys.

Fig. 6 Activation energy E_a in $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs as a function of crystallization volume fraction α in non-isothermal condition

Fig. 5 KAS plots for different crystallization volume fractions α in $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs in non-isothermal condition

The Avrami exponent n is a key parameter to understand the mechanisms of the nucleation and growth during crystallization process. For the non-isothermal condition, the crystallization kinetics of the BMGs can be modeled by the modified JMA equation, and the Avrami exponent n is obtained from the slope of this plot [22]:

$$\frac{\ln[-\ln(1-\alpha)]}{1/T} = -\frac{nE_a}{R}, \quad (2)$$

where T is the temperature and R is gas constant. Figure 7 shows the plots of $\ln[-\ln(1-\alpha)]$ versus $1/T$ at different heating rates. Only the data for $0.2 \leq \alpha \leq 0.8$ are considered to minimize the experimental error existent in the early and late stages. It can be seen that all the fitting curves are almost straight lines. The Avrami exponent n can be calculated from the slope, and the values of the Avrami exponent n are listed in Table 1. It is noted that the Avrami exponent n decreases with the increasing heating rate. The higher heating rate can decrease viscosity of the alloy at a given temperature by decreasing diffusion activation energy, and consequently lead to accelerating the nucleation of the crystalline phase and suppress grain growth.

3.3 Isothermal Behaviors

The isothermal DSC curves of the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs at various annealing temperatures are shown in Fig. 8. It can be observed that the DSC curves display a single exothermic peak after a certain incubation time τ . The incubation time decreases with the increase in isothermal annealing temperature because the atoms in the alloys have higher mobility at a higher annealing temperature, leading to a critical fluctuation to facilitate long-range atomic ordering for large-scale crystallization [23]. In order to better understand the crystallization kinetics of the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$

Table 1 Activation energy E_a and Avrami exponent n in $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs in non-isothermal condition

Sample	Heating rate (K/min)	E_a (kJ/mol)	n
$\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$	10	241.0	3.37
	20	241.0	3.01
	30	241.0	2.66
	40	241.0	2.51
$(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$	10	296.3	3.03
	20	296.3	2.74
	30	296.3	2.16
	40	296.3	1.76

BMGs in the isothermal crystallization condition, the relationship between the crystallization volume fraction and the annealing time is shown in Fig. 9. All the curves exhibit a typical sigmoidal type at various annealing temperatures. It can be found that the curve becomes steeper at the higher annealing temperature, implying that the crystallization process becomes faster with increasing the annealing temperature. Finally, the samples from metastable states transfer to stable states [21].

The local activation energy E_a for the crystallization process in the isothermal model can be determined using the Arrhenius equation [24, 25]:

$$t(\alpha) = t_0 \exp\left(\frac{E_a}{RT}\right), \quad (3)$$

where $t(\alpha)$ is the annealing time when the crystallization volume fraction reaches α , t_0 is a constant. Figure 10 shows the plots of $\ln[t(\alpha)]$ versus $1/T$ for different crystalline volume fractions (α ranges from 0.1 to 0.9) during isothermal annealing. The E_a as a function of crystallization volume fraction in isothermal mode is shown in Fig. 11. The average activation energies for the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ calculated in the isothermal

Fig. 7 Avrami plots of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs at different heating rates

Fig. 8 Isothermal DSC curves of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs at different annealing temperatures

Fig. 9 Crystallization volume fraction as a function of annealing time for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs at various annealing temperatures

Fig. 10 Plots for activation energy determination in $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs

mode are 318.3 and 366.7 kJ/mol, respectively. It can be found that the $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ exhibits larger activation energy than that in the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$, which is consistent

with phenomenon in the non-isothermal mode. It is demonstrated that $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is more stable compared with the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$.

Fig. 11 Activation energy E_a as a function of crystallization volume fraction α for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs in isothermal mode

This average activation energy corresponding to the isothermal condition determined by using the Arrhenius equation is larger than that calculated by the KAS in the non-isothermal mode. It is found that the results are in good agreement with those reported on other BMGs, such as the $\text{Cu}_{52.5}\text{Ti}_{30}\text{Zr}_{11.5}\text{Ni}_6$ BMG [26] and the $\text{Cu}_{46}\text{Zr}_{45}\text{Al}_7\text{Y}_2$ BMG [15]. Wei et al. [27] found that the activation energy measured with the help of either KAS or Arrhenius equation may possess temperature reliance. With further discussion, it will be found that the lower crystallization temperature range leading to higher activation energy is positioned just within the SLR. Moreover, the higher crystallization temperature range is above the T_x , suggesting that the crystallization in the higher temperature range appears to be a transformation from supercooled liquid to crystalline, whereas in the lower temperature region, a transformation is experienced from amorphous state to crystalline one. It is the differences of atomic mobility and the microstructures between the supercooled liquid and the amorphous state. Compared with isothermal crystallization process, the sample subjected to continuous heating condition would crystallize at a relatively higher temperature. Crystallization at higher temperatures above T_x makes transform from the metastable state to crystalline phases easily. This is reason the energy barrier in the isothermal mode is higher than that of the non-isothermal mode.

The isothermal crystallization kinetics of the BMG can be modeled by the JMA equation [27–30]:

$$\alpha(t) = 1 - \exp\{-[K(t - \tau)]^n\}, \quad (4)$$

where K is a temperature-dependent reaction rate constant. Taking the double logarithm of Eq. (4), the following expression can be deduced [18]:

$$\ln[-\ln(1 - \alpha)] = n \ln(t - \tau) + n \ln k. \quad (5)$$

Figure 12 shows the plots of $\ln[-\ln(1 - \alpha)]$ versus $\ln(t - \tau)$ for $0.2 \leq \alpha \leq 0.8$ at various annealing temperatures. The Avrami exponent n and the reaction constant K can be calculated from Fig. 12, and the values are listed in Table 2. As can be observed from Table 2, the Avrami exponent n increases with increasing the annealing temperature. This is predominantly owing to the difficult atomic diffusion at low temperature, hindering the nucleation and growth process and leading to a lower nucleation rate. At higher temperature, the diffusion of the atoms is relatively easy, resulting in an increasing nucleation rate.

A linear relationship between the Avrami exponent (n), the nucleation rate (a) and the growth index (b) and the dimension of the growth (c) can be found. This linear relationship can be presented in the following form [31, 32]:

$$n = a + bc. \quad (6)$$

Four varied values of the nucleation rate (a) can be taken into account: the zero nucleation rate ($a = 0$), the reducing nucleation rate ($0 < a < 1$), the constant nucleation rate ($a = 1$) and the increasing nucleation rate ($a > 1$). Moreover, the growth index has two types: diffusion-controlled growth ($b = 0.5$) and interface-controlled growth ($b = 1$). Three possible directions of growth can also be seen: one dimension ($c = 1$), two dimension ($c = 2$) and three dimension ($c = 3$).

It was accepted that the crystallization of Cu-based BMG was controlled by diffusion [15], that is to say, $b = 0.5$. According to the diffusion-controlled growth theory [33]: $1.5 < n < 2.5$ is a representation of the growth of the particles with a decreasing nucleation rate; $n = 2.5$ implies the growth of small particles having a constant nucleation rate; and $n > 2.5$ suggests the growth of small particles possessing an elevating nucleation rate.

Compared with $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ (the average Avrami exponent $n > 2.5$), the average value of the Avrami exponent n for $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is $1.5 < n < 2.5$ under non-isothermal condition, implying that crystallization is mainly governed by diffusion-controlled three-dimensional growth with a decrease in nucleation rate. In contrast, crystallization of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ is mainly determined by diffusion-controlled three-dimensional growth with an increasing nucleation rate.

In isothermal condition, the Avrami exponent n for the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ varies from 2.67 to 3.75 at different annealing temperatures ranging from 743 to 773 K. The average Avrami exponent n of about 3.25 provides $c = 3$, $b = 0.5$, and $a > 1$, implying diffusion-controlled three-dimensional growth with an increasing nucleation rate. For $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$, the

Fig. 12 Avrami plots of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ **a**, $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ **b** BMGs at various annealing temperatures

Table 2 Avrami exponent n , reaction rate constant K and incubation time τ at different annealing temperatures for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs

Sample	Annealing temperature (K)	n	τ (min)	K
$\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$	743	2.67	10.2	0.1329
	753	2.94	5.7	0.2003
	763	3.66	1.55	0.3770
	773	3.75	0.23	0.5749
$(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$	733	2.13	5.3	0.0442
	743	2.43	3.8	0.0691
	753	2.58	0.867	0.1357
	763	3.04	0.167	0.2489

Avrami exponent n is over 2.5 at 753 and 763 K, respectively, which provides $c = 3$, $b = 0.5$ and $a > 1$, suggesting diffusion-controlled three-dimensional growth with an increasing nucleation rate. At 733 and 743 K, the Avrami exponents n are 2.43 and 2.13, respectively, which provide $c = 3$, $b = 0.5$ and $0 < a < 1$, implying diffusion-controlled three-dimensional growth with a decreasing nucleation rate.

4 Conclusions

The crystallization kinetics of the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ BMGs is investigated using the DSC in both non-isothermal and isothermal conditions. The main conclusions can be drawn as follows:

1. Under non-isothermal condition, the average activation energy of $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ determined by KAS method is larger than that of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$, suggesting that $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ shows higher stability against crystallization. The average Avrami exponent n of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ is above 2.5, implying that crystallization is mainly determined by diffusion-controlled three-

dimensional growth with an increasing nucleation rate, while the average Avrami exponents n of $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ are in the range of 1.5–2.5, indicating that the crystallization is mainly governed by diffusion-controlled three-dimensional growth with a decreasing nucleation rate.

2. In isothermal mode, the average activation energy of the $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ calculated using the Arrhenius equation is larger than that of $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$, which is consistent with the phenomenon in the non-isothermal mode. The Avrami exponent n of the $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ varies from 2.67 to 3.75, which indicates that the crystallization is mainly governed diffusion-controlled three-dimensional growth with an increasing nucleation rate. Whereas the Avrami exponent n of the $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is over 2.5 over 753 K, which suggest that the crystallization is governed by diffusion-controlled three-dimensional growth with an increasing nucleation rate.
3. The average activation energy for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ calculated using Arrhenius equation in the isothermal mode is larger than that calculated by KAS method in the non-isothermal

mode, indicating that the energy barrier is higher in the isothermal mode.

4. The Avrami exponent n for $\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9$ and $(\text{Cu}_{43}\text{Zr}_{48}\text{Al}_9)_{98}\text{Y}_2$ is different in the non-isothermal and isothermal conditions, which indicates different nucleation and growth behaviors during crystallization processes.

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