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ARTICLE

Kinetic Analysis of Crystallization Behaviors in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ Bulk Metallic Glass

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Abstract: The kinetics of crystallization of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass was studied by differential scanning calorimetry (DSC) in both non-isothermal and isothermal (at different heating rates) modes. Under isochronal process, theoretical models were adopted to analyze the apparent activation energies for characteristic temperatures. The results indicate that the apparent activation energies for characteristic temperatures in the $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass by Kissinger model, Flynn-Wall-Ozawa (FWO) model and Augis-Bennett (AB) model are in good agreement with each other. Furthermore, crystallization transformation kinetics during isothermal process was analyzed by the Johnson-Mehl-Avrami (JMA) model. The Avrami exponent *n* ranges from 3.25 to 4.12 in the isothermal mode. It is noted that the activation energy corresponding to isothermal conditions calculated using Arrhenius equation is larger than the value calculated by the Kissinger method in isochronal conditions, because the energy barrier in isothermal annealing mode is higher than that of isochronal conditions.

Key words: metallic glass; differential scanning calorimetry; crystallization kinetics; Johnson-Mehl-Avrami (JMA) model; Avrami exponent

Bulk metallic glasses has received much attention in scientific and engineering areas due to their excellent mechanical properties (higher strength and hardness)[1-10].Therefore, they are potential materials in various engineering and scientific fields.

However, metallic glass tends to transfer from amorphous state to crystalline state by thermal treatment. In addition, thermal stability always links the mechanical properties in amorphous alloys. Thus, it is essential to investigate the thermal stability and crystallization behavior in bulk metallic glasses. Differential scanning calorimetry (DSC) or differential thermal analysis (DTA) is widely used to study thermal stability and crystallization behavior in amorphous materials[11-15]. The parameters of thermal properties for amorphous materials, such as glass transition temperature (T_g) corresponding to the onset of crystallization (T_x), crystallization peak temperature (T_p) and enthalpy could be obtained from the DSC curves. Besides, apparent activation energy could be calculated by relevant models from the DSC data. Thermal stability and crystallization restrict the applications of bulk metallic glasses.

It is well known that the kinetics of crystallization for amorphous materials are sensitive to the kinetic parameters, which includes the activation energy of crystallization, crystalline phase, crystallization time, temperature, mechanisms of nucleation and growth process for bulk metallic glasses[16]. Investigations on thermal properties and crystallization behaviors of bulk metallic glasses were performed in recent years[9,17-20].

Compared with the conventional metallic glasses, Zn-based bulk metallic glass presents higher corrosion resistance, lower glass transition temperature T_g and density[2].

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It can be a potential material for micro-devices. However, applications of the bulk metallic glasses are associated with the thermal properties, in particular, crystallization properties. In order to clarify crystallization behaviors in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass, the aim of the present work is to analyze the thermal stability and relevant thermal parameters by various models: Kissinger model, Flynn-Wall-Ozawa model and Augis-Bennett model in non-isothermal mode. Meanwhile, the kinetic parameters in isothermal mode were discussed.

1 Experiment

In the current work, $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass with diameter of 2 mm was fabricated in a quartz crucible in purified argon atmosphere, and then mechanically cut to prepare DSC samples. Prior to experiments, the samples were polished carefully using diamond paste to remove surface oxide. Then the samples were washed by ethanol in an ultrasonic cleaning machine.

X-ray diffraction experiments in the bulk metallic glasses were conducted at room temperature to examine their amorphous character using Cu Kα radiation (D8, Bruker AXS Gmbh, Germany)[21]. DSC experiments were performed (Pekin Elmer, DSC-7) under high purity dry nitrogen. In non-isothermal mode, the crystallization kinetics of the samples was characterized by DSC at different constant heating rates: 10, 20, 30 and 40 K/min. In parallel, isothermal crystallization of the samples were measured in the super-cooled liquid region (SLR), both above the T_g and below the T_x. The samples were heated up to the annealing temperature at a heating rate of 40 K/min and then held at this temperature to achieve crystallization until completion.

2 Results and discussion

2.1 Non-isothermal crystallization behavior

The corresponding glass transition temperature (T_g), onset temperature of crystallization (T_x), crystallization peak temperature (T_p), the melting temperature for amorphous metals (T_m) and the liquids temperature (T_l) are defined in Fig.1.

X-ray diffraction experiments confirm the occurrence of crystallization (Fig.2a). Since the heating was conducted with a low heating rate (about 1.5 K/min), phase transformation occurs at a lower temperature. This phenomenon is very rapid, as indicated by the drastic increase in the main crystalline peak area (Fig.2b). Compared to Zr-based and Co-based metallic glasses, the Zn-based metallic glass exhibits lower $\Delta T_x (=T_x - T_g)$, suggesting lower glass forming ability[22, 23].

Typical DSC curves of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass were obtained at different heating rates of 10, 20, 30 and 40 K/min. The values of T_g, T_x and T_p were shifted to higher temperature by increasing the heating rate. The phenomenon was observed in other metallic glasses[16,24-28], suggesting that the characteristic temperatures during the crystallization process are sensitive to heating rates.

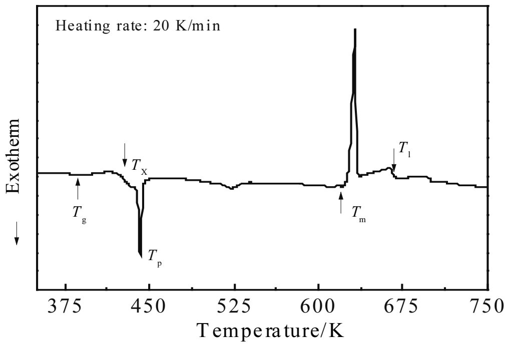

Fig.1 DSC curve in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass at a heating rate of 20 K/min

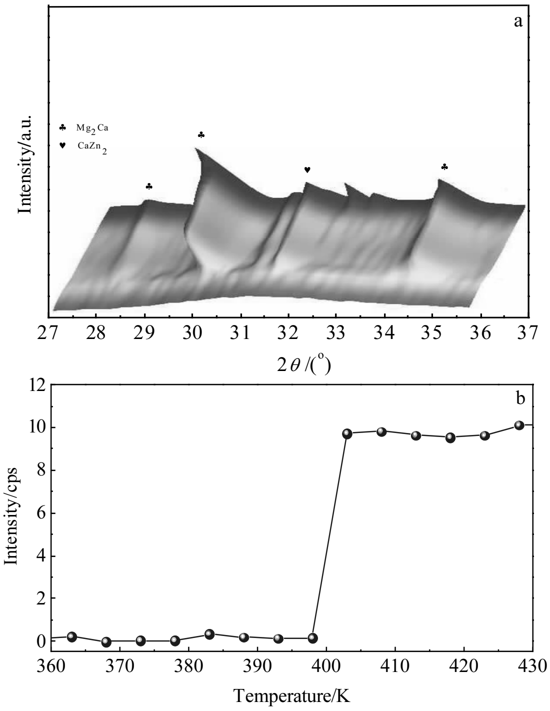

Fig.2 X-ray diffraction patterns (3D representation) during continuous heating at 1.5 K/min, from 303 K to 423 K in Zn-based metallic glass (a), diffraction peak area against time during continuous heating at 1.5 K/min in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ metallic glass (b)

2.1.1 Kissinger model

According to the Kissinger model, the activation energy E_a of phase transformation occurring in bulk metallic glass is usually determined by DSC experiments with different heating rates, and then calculated using the Kissinger's equation[17, 27, 29]. The relevant equation is written as:

$$\ln\left(\frac{R_h}{T_\theta^2}\right) = -\frac{E_a}{RT_\theta} + C_1 \qquad (1)$$

where R_h is the heating rate, T_θ is the characteristic temperature at a fixed stage of the relaxation in glass materials during the crystallization process, such as T_g, T_x and T_p, and C_1 is a constant. The values of apparent activation energies for T_g, T_x and T_p in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass are 328, 223 and 104 kJ/mol, respectively.

2.1.2 Flynn-Wall-Ozawa model

The Flynn-Wall-Ozawa method is another widely adopted method to calculate the apparent activation energy for bulk metallic glasses during the non-isothermal crystallization process[27, 30, 31]. The apparent activation energy is evaluated by the following equation:

$$\ln(R_h) = -1.052\frac{E_a}{RT_\theta} + C_2 \qquad (2)$$

Where, C_2 is a constant. The values of apparent activation energies for T_g, T_x and T_p by Flynn-Wall-Ozawa equation are 335, 230 and 111 kJ/mol, respectively.

2.1.3 Augis-Bennett model

The activation energy of crystallization process for the samples could be determined by the Augis-Bennett method[27, 31, 32], which is given by:

$$\ln\left(\frac{R_h}{T_\theta - T_o}\right) = -\frac{E_a}{RT_\theta} + C_3 \qquad (3)$$

where T_o is the absolute temperature and C_3 is a constant.

The values of apparent activation energy T_g, T_x and T_p are 321, 218 and 100 kJ/mol, respectively. Compared with other metallic glasses[16, 24-28], the Zn-based metallic glass presents lower activation energy for crystallization. According to Tao et al.'s work[33], Zn-based metallic glass presents lower jump energy potential barriers during the crystalline grain nucleation and growth.

2.1.4 Johnson-Mehl-Avrami model

It is noted that the predicted activation energies for characteristic temperatures in Zn-based metallic glass show a good agreement with each other. All these methods are based on the Johnson-Mehl-Avrami (JMA) theory with respect to the change crystallization fraction in relation to time. Thus, different models are more or less exact depending on the assumptions and level of approximation. In general, differences between these models are not pronounced, because the obtained activation energies of bulk metallic glass have relatively similar values by different models. The major reasons is that the same classical theory is adopted.

Meanwhile, for the Kissinger's model,

$$\ln R_h - 2\ln T_\theta - C = -\frac{E_a}{RT_\theta} \qquad (1a)$$

$$\ln R_h = -\frac{E_a}{RT_\theta} + \left(2\ln T_\theta + C\right) \qquad (1b)$$

For the Flynn-Wall-Ozawa model,

$$\ln R_h - C = -1.052\frac{E_a}{RT_\theta} \qquad (2a)$$

$$\ln R_h = -1.052\frac{E_a}{RT_\theta} + C \qquad (2b)$$

For the the Augis-Bennett model,

$$\ln R_h - \ln\left(T_\theta - T_o\right) - C = -\frac{E_a}{RT_\theta} \qquad (3a)$$

$$\ln R_h = -\frac{E_a}{RT_\theta} + \left(\ln\left(T_\theta - T_o\right) + C\right) \qquad (3b)$$

Compared with $\ln T_\theta$, the variation of $\ln R_h$ is much larger, in other words, the $\ln T_\theta$ reaches a constant at different $\ln R_h$ values, as shown in Fig.3. Hence, Eqs.(1b), (2b) and (3b) could be expressed as follows:

$$\ln R_h = -\frac{E_a}{RT_\theta} + k \qquad (1c)$$

$$\ln R_h = -1.052\frac{E_a}{RT_\theta} + k' \qquad (2c)$$

$$\ln R_h = -\frac{E_a}{RT_\theta} + k'' \qquad (3c)$$

where k, k' and k'' are constants. It can be found that Eqs. (1c), (2c) and (3c) express the same physical meaning and present similar type of construction. Thus, the activation energies for characteristic temperatures (T_θ) in bulk metallic glasses are consistent with each other at different heating rates (R_h).

The Kissinger model, FWO model and AB models could be rewritten in the following form:

$$\ln R_h = -\frac{E_a}{RT_\theta} + C \qquad (4)$$

From Eq.4,

$$\frac{E_a}{RT_\theta} = -\ln R_h + C \qquad (4a)$$

$$T_\theta = \frac{E_a}{R\left(-\ln R_h + C\right)} = \frac{E_a}{RC\left(\frac{-\ln R_h}{C} + 1\right)} \qquad (4b)$$

Generally, $\frac{-\ln R_h}{C} \approx 0$.

Therefore, $\frac{-\ln R_h}{C} + 1 \approx 1 + \frac{\ln R_h}{C}$.

Then,

$$T_\theta = \frac{E_a}{RC}\left(1 + \frac{\ln R_h}{C}\right) = \frac{E_a}{RC} + \frac{E_a}{RC^2}\ln R_h \qquad (4c)$$

It is well known that the thermal properties of bulk metallic glasses are sensitive to heating rate; the relation could be expressed by the Lasocka equation[27, 34]:

$$T_\theta = \lambda + \beta\ln(R_h) \qquad (5)$$

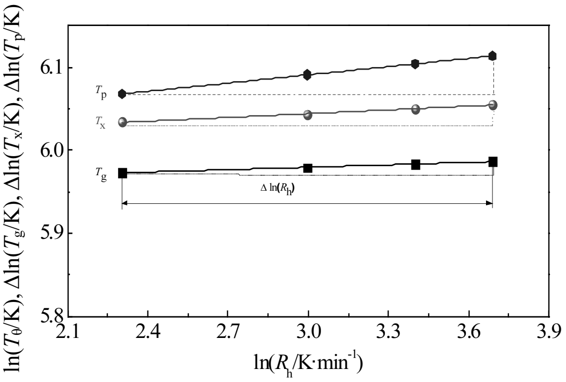

Fig.3 Variation of $\ln T_θ$, $\Delta\ln(T_g)$, $\Delta\ln(T_x)$, $\Delta\ln(T_p)$ with $\ln R_h$ in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass (as-cast)

It should be noted that for Eq.4c and Eq.5, if $E_a/RC=\lambda$ and $E_a/RC^2=\beta$, the Kissinger model, Flynn-Wall-Ozawa model and Augis-Bennett model could be described by the Lasocka equation.

2.2 Isothermal crystallization behavior

The DSC curves at different annealing temperatures are shown in Fig.4. For the analysis of transformation kinetics from the amorphous state to crystalline state, the phase transformation depends on the crystallized volume fraction, which can be described by the Johnson-Mehl-Avrami (JMA) model as follows[18, 26, 35-38]:

$$\alpha(t) = 1 - \exp\left(-(Kt)^n\right) \tag{6}$$

where n is the kinetic exponent, and reflects both the crystallization mechanism and dimensionality of the crystallization process, and t is the time.

The relationship between the crystallization volume fraction and temperature for Zn-based metallic glass is shown in Fig.5. All the curves present a sigmoid dependence on temperature. The phenomena were observed in different glassy materials during the isothermal crystallization processes. K is the reaction rate constant (a function of annealing temperature), which could be defined by the Arrhenius temperature dependence:

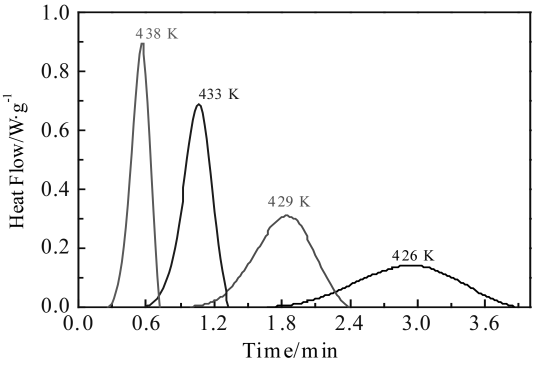

Fig.4 Isothermal DSC curves at different annealing temperatures in Zn-based metallic glass

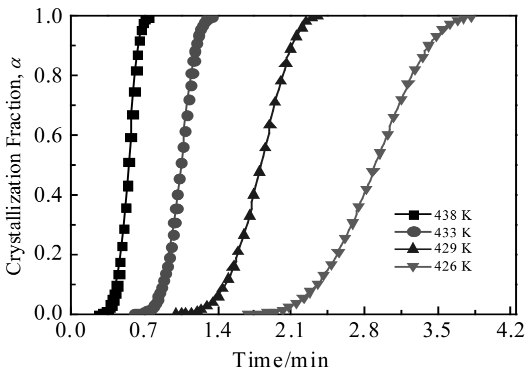

Fig.5 Crystallization volume fraction α as a function of annealing time at various annealing temperatures in Zn-based metallic glass

$$K = K_0 \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

where K_0 is the frequency factor, E_a is the effective activation energy during the overall crystallization process, R is the ideal gas constant, and T is the absolute temperature. During the isochronal phase transaction process, the phase transaction rate $d\alpha/dt$ is calculated by[26, 37, 38]:

$$\frac{d\alpha}{dt} = Kf(\alpha) \tag{8}$$

where $f(\alpha)$ is a transformation function of the crystallized volume fraction α. Based on the discussion in the previous literatures[26, 38, 39], the $f(\alpha)$ could be defined as follows:

$$f(\alpha) = n(1-\alpha)\left[-\ln(1-\alpha)\right]^{1-1/n} \tag{9}$$

There are several methods to calculate the activation energy of phase transformation. Transformation kinetics can be described by the Johnson-Mehl-Avrami (JMA) equation[13, 40-42]:

$$\alpha(t) = 1 - \exp\left[-K(t-\tau)^n\right] \tag{10}$$

where τ is the incubation time, which is a fitting parameter. Taking the double logarithm of the Eq. (4), the following expression is deduced[13, 41]:

$$\ln\left[-\ln(1-\alpha(t))\right] = n\ln K + n\ln(t-\tau) \tag{11}$$

By plotting $\ln\left[-\ln(1-\alpha)\right]$ versus $\ln(t-\tau)$ at various annealing temperatures with $0.2 \leqslant \alpha \leqslant 0.8$, the kinetic exponents n at various isothermal temperatures are shown in Fig.6.

As far as diffusion-controlled growth theory is concerned[14], n =1.5 means that growth of particles with a nucleation rate is close to zero; $1.5<n<2.5$ indicates growth of particles with decreasing nucleation rate, n =2.5 reflects growth of particles with a constant nucleation rate, and n >2.5 pertains to the growth of small particles with an increasing nucleation rate[14, 43]. The average kinetic exponents n for Zn-based metallic glass are above 3, which implies that crystallization mechanisms in the glass is the growth of small particles with an increasing nucleation rate[44, 45].

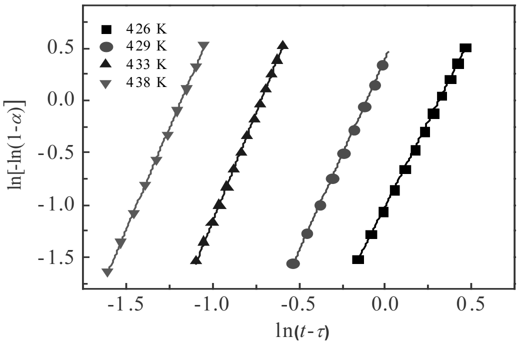

Fig.6 Avrami plots at various annealing temperatures in Zn-based metallic glass with $0.2 \leqslant \alpha \leqslant 0.8$

3 Conclusions

1) In non-isothermal crystallization mode, the apparent activation energies for characteristic temperatures (T_g, T_x and T_p) are calculated by the Kissinger model, Flynn-Wall-Ozawa (FWO) model and Augis-Bennett (AB) model. The theoretical predictions agree with each other.

2) Crystallization transformation kinetics in isothermal is analyzed by the Johnson-Mehl-Avrami (JMA) model. The Avrami exponent n fluctuates from 3.25 to 4.12 in isothermal mode, which suggests that the growth of small particles associate with an increasing nucleation rate. Compared with isochronal crystallization behavior, the isothermal crystallization presents higher apparent activation energy because the energy barrier in isothermal annealing mode is higher than that of isochronal conditions.

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$Zn_{38}Mg_{12}Ca_{32}Yb_{18}$大块金属玻璃的晶化动力学行为

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摘 要：采用差示扫描量热分析仪，研究了 $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ 大块金属玻璃的在等时和等温状态下的晶化动力学行为。在等时条件下，不同的理论模型来分析特征温度的名义激活能。结果表明，采用 Kissinger 模型，Flynn-Wall-Ozawa 模型和 Augis-Bennett 模型计算的名义激活能相互吻合。再者，采用 Johnson-Mehl-Avrami 模型分析了等温过程中晶化转变动力学机。Avrami 指数 n 的分布区间介于 3.25 到 4.12。分析发现，在等温晶化过程中采用 Arrhenius 方程计算得到的激活能比在等时晶化过中采用 Kissinger 方程的激活能要大，这可能是由于等温退火过程中能垒比等时晶化过程中的要高所引起的。

关键词: 金属玻璃；差示扫描量热分析仪；晶化动力学；Johnson-Mehl-Avrami 模型；Avrami 指数

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