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Crystallization kinetics of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass alloy*

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Abstract. The crystallization reaction of $Zr_{65}Ni_{25}Ti_{10}$ (at. %) metallic glass was studied by using differential scanning calorimetry (DSC) at constant heating rate. Two distinct exothermic peaks were observed from the continuous heating DSC curves, implying the crystallization process undergoes two different stages. The crystallization kinetic parameters, including activation energy (E), Avrami exponent (n) and frequency factor (K_0), were determined with non-isothermal analysis method based on the DSC data. The values of E are 267.353 KJ/mol and 224.293 KJ/mol, n 4.0±0.1 and 6.8±0.1, K_0 4.4±0.05E+20 and 2.0±0.08E+15, for the first and second crystallization stage, respectively. The results suggest that the crystallization mechanism is governed dominantly by interface controlled growth with constant nucleation rate for the first crystallization stage and with increasing nucleation rate for the second stage.

Introduction

Recently, Zr-Ni-Ti ternary alloys have attracted many researchers' attention for their potential application of the hydrogen storage materials. Most works [1,2] were concentrated on the quasicrystals. And investigations on the amorphous were comparatively less conducted. Molokanov et al. [3] have determined the amorphous formation ranges and the glass forming ability (GFA) in the rapidly solidified Zr-Ti-Ni alloys. Yi et al.[4] have studied the nano-crystallization of $Zr_{47}Ni_{30}Ti_{23}$ amorphous ribbons. In previous report [5], the authors have investigated the formation and crystallization of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass and emphasized on the phase transformation during the isothermal annealing process. However, the crystallization mechanism of this glass is not clear, as yet.

In this paper, the crystallization reaction of the $Zr_{65}Ni_{25}Ti_{10}$ (at.%) metallic glass was studied in order to understand the crystallization mechanism by using continuous heating differential scanning calorimetry (DSC) at constant heating rate, and the crystallization kinetic parameters, including activation energy (E), Avrami exponent (n) and frequency factor (K_0), were determined with non-isothermal analysis methods based on the DSC data.

Experimental procedure

The glass forming alloys with a nominal composition of $Zr_{65}Ni_{25}Ti_{10}$ (at.%) were prepared by arc melting mixture of pure Zr (99.9%, wt%), Ti (99.9%, wt%) and high-purity Ni (99.999%, wt%) under a Ti-gettered pure argon atmosphere. The alloy ingots were remelted several times to ensure homogeneity. Amorphous ribbons with a cross-section of ~0.06×5mm^2 were produced by the vacuum single-roller melt spinning technique (the diameter of copper roller and line velocity are 200 mm and 30 m/s, respectively). X-ray diffraction (CuKα Philips APD-10) and transmission electronic microscope (TEM, JEOL 2000FX，operating at 160 KV) were exploited in order to check the amorphicities of ribbons. The continuous heating DSC experiments were performed in Du Pont 2010 differential scanning calorimeter (DSC). The temperature and energy calibration of the instruments were performed using the high-purity In and Zn with an accuracy of ±0.1K for temperature and

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±1μW/cm for the energy measurement. The crystallization thermagrams were recorded as the temperature of the sample was increased at constant rate. Typically, 20 mg of sample were sealed in standard aluminum pans and scanned over a temperature from room temperature to about 823 K in static N_2 air at constant heating rate *B* ranging from10 K/min to 40 K/min.

Results and discussion

The $Zr_{65}Ni_{25}Ti_{10}$(at.%) as-melt spun ribbon was examined by X-ray diffraction (XRD) and transmission electron microscope (TEM), it is shown that the samples are of fully amorphous state [5]. Two distinct exothermic peaks can be seen from the differential scanning calorimetry (DSC) traces at constant heating rate *B* ranging from 10 K/min to 40 K/min as shown in Fig. 1, indicating the crystallization process of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass undergoes two stages. Correspondingly, two main precipitates during the crystallization process of this metallic glass were observed in isothermal annealing experiments, metastable FCC Zr_2Ni phase for the first stage and stable BCT Zr_2Ni phases for the second stage [5]. It is obvious that the exothermic peak shifts towards higher temperatures with the increase of heating rate, which is consistent with the other DSC experiments.

Investigation on the crystallization behavior of metallic glass upon heating can be performed by two basic methods: isothermal and non-isothermal transformation. The former is a classical method and extensively applied because it can be explained by the well-established Johnson-Mehl-Avraim (JMA) equation. However, the JMA equation can also be correctly applied to the non-isothermal conditions when the case obey an additivity rule[7], so the latter is more commonly used in the study of the crystallization of amorphous solids because it possess several advantages [6]. Several methods used for interpreting the non-isothermal transformation were reported by Yinnon et al. [8]. Combining the Kissinger method [9] and the equations proposed by Gao et al. [6, 10], the following relationships are attained:

$$\frac{d[\ln(B/T_P^{\,2})]}{d(1/T_p)} = -\frac{E}{R} \tag{1}$$

$$K_p = \frac{BE}{RT_p^{\,2}} = K_0 \exp(\frac{-E}{RT_p^{\,2}}) \tag{2}$$

$$(\frac{dx}{dt})_p = 0.37nK_p \tag{3}$$

where E is the activation energy, R the gas constant, B the heating rate, T_p the peak temperature, $(dx/dt)_p$ the maximum crystallization rate, n the Avrami exponent, K_0 the frequency factor.

Fig.2 is the Kissinger plots of two exothermic peak temperatures in $Zr_{65}Ni_{25}Ti_{10}$ metallic glass, which can be fitted by a straight line with a slope of $-E/R$. Thus, the activation energy E for two crystallization stages of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass can be achieved. The values of E, listed in Table 1, are 267.353 KJ/mol and 224.293 KJ/mol for the first stage and second stage, respectively.

From the exothermic curves, one obtained the relationship between the crystallized volume fraction and heating temprature of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass as shown in Fig. 3. It is clearly seen that the curves display a sigmoid shape, which is very similar to that between crystallized volume fration and annealing time under isothermal annealing condition. At the same time, one found an intersting phenomenon that the second crystallization stage spans a wider temperature region than the first

crystalliztion stage. This implys that the former reaction takes longer time than the latter, while the temperature of the second stage reaction is higher than that of the first stage reaction.

Fig. 4 shows the the relationship between crystallization rate and temperature of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass can be obtained by differentating Fig. 3. From Fig. 4, the maximum crystallization rate $(dx/dt)_p$ at different heating rate and corresponding peak temperature can be attained. Based on these data, the others two kinetic parameters, Avrami exponent (n) and frequency factor (K_0), can be calculated by using Eq. (2)-(3). The calculated results, listed in Table 1, show that there is greatly

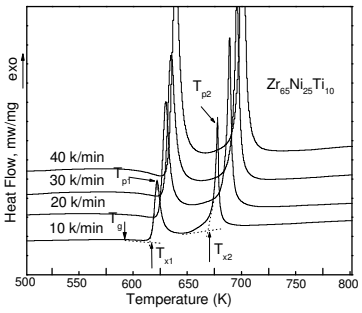

Fig. 1 Typical DSC curves of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass at different heating rates

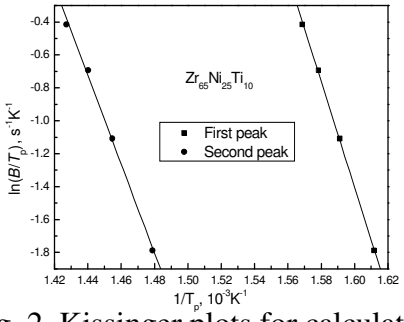

Fig. 2 Kissinger plots for calculation of activation energy by using the peak temperature in the $Zr_{65}Ni_{25}Ti_{10}$ metallic glass

Table1. Kinetic parameters of crystallization in $Zr_{65}Ni_{25}Ti_{10}$ metallic glass

Stage	B (K/min)	T_p (K)	$(dx/dt)_p$ (s^{-1})	E (KJ/mol)	K_0 (s^{-1})	n	<n>
First	10	620.48	0.02312	267.353	4.479E+20	4.4	4.0±0.1
	20	628.47	0.04174		4.465E+20	4.2	
	30	633.04	0.05378		4.410E+20	3.7	
	40	637.49	0.06705		4.208E+20	3.6	
Second	10	676.21	0.02738	224.293	2.084E+15	7.5	6.8±0.1
	20	687.39	0.05133		2.083E+15	7.4	
	30	694.34	0.06708		2.089E+15	6.5	
	40	700.66	0.07907		1.907E+15	5.9	

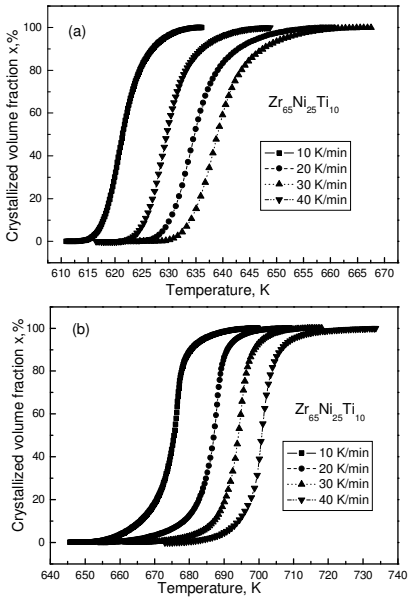

Fig. 3 Relationship between crystallized volume fraction and heating temperature of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass; (a) first exothermic peak, (b) second exothermic peak

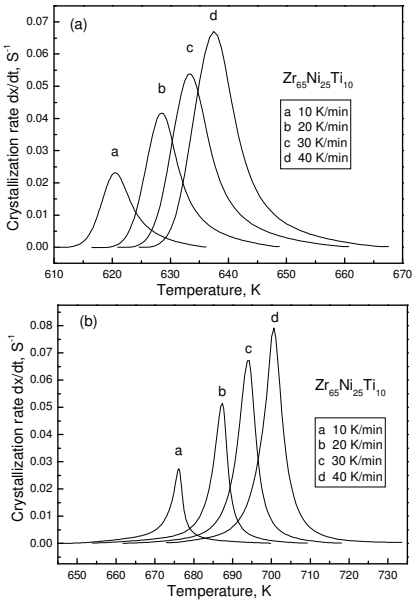

Fig. 4 Relationship between crystallization rate and heating temperature of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass; (a) first exothermic peak, (b) second exothermic peak

difference of kinetic parameters in the first crystallization stage and the second crystallization stage of $Zr_{65}Ni_{25}Ti_{10}$ amorphous alloy. For example, the frequency factor (K_0) of the first stage is five orders larger than that of the second stage and the Avrami exponent (n) of the first stage almost double that of the second stage. Therefore, it is inferred that the crystallization mechanism of the two crystallization stage is different. According to the classic phase transformation theory [11], the phase transformation proceeds with interface controlled growth with constant nucleation rate for n =4 and with interface controlled growth with a nucleation rate which increase with time for n>4. As for the crystallization of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass, one adopts the average value of kinetic parameters allowing for the experimental deviation. The values of <n> are equal to 4.0±0.1 for the first crystallization stage and 6.8±0.1 for the second crystallization stage. Therefore, it is reasonably to believe that the first crystallization stage is governed dominantly by an interface controlled growth with a constant nucleation rate mechanism and the second stage governed by the interface controlled growth with a nucleation rate which increases with time mechanism. The difference of crystallization mechanism for two stages may be due to the interface difference between the crystallized phase and amorphous matrix or the heating temperature.

Summary

Based on the investigation of the crystallization kinetics of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass alloy by using non-isothermal DSC analysis method, the main results are summarized as follow:

1. The crystallization process of $Zr_{65}Ni_{25}Ti_{10}$ metallic glass is double-stages mode, which is correspondent to metastable FCC Zr_2Ni phase precipitate in the first stage and stable BCT Zr_2Ni phase do in the second stage.

2. The activation energy for the crystallization evaluated from the Kissinger equation is 267.353 KJ/mol and 224.293 KJ/mol for the first and second stage, respectively. The frequency factors are 4.4±0.05E+20 and 2.0±0.08E+15 for the first and second stage, respectively.

3. Different crystallization mechanisms were found through analyzing the variation of Avrami exponents, which indicates that the first crystallization stage is governed dominantly by an interface controlled growth with a nucleation rate and the second stage governed by the interface controlled growth with a nucleation rate which increases with time.

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