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Research Article

THERMAL STABILITY OF $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ METALLIC GLASS

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ABSTRACT

We report a study of kinetics of crystallization of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass ribbon by Differential Scanning Calorimetry (DSC) under non-isothermal condition. The sample was prepared by the standard melt spinning technique, that is, rapid cooling of the melt of the compound on a rotating copper wheel. As prepared sample was confirmed to be amorphous as determined by the X-ray diffraction. DSC results show single exothermic peak in the DSC thermograms for four heating rates used to study crystallization of the sample. Activation energy of the crystallization of the sample is evaluated using Kissinger, Augis-Bennett and Ozawa models.

INTRODUCTION

Metallic glasses, in ribbon or bulk form continue to attract attention of R&D workers due to their possible various applications in diverse areas. Intense work has been done on ferromagnetic glasses for applications as well as scientific points of view while non-ferromagnetic glasses have mainly been investigated to understand metallic disorder systems as well as certain other applications (Luborsky, 1983; Anantharaman, 1984; Moorjani and Coey, 1984; Inoue and Suryanarayana, 2010; Mihai Stoica, 2017). One of important properties of metallic glasses is their thermal stability because, on heating beyond a certain high temperature and/or for an extended time at moderate temperatures, metallic glasses show degradation of most of their properties. In this work, we report studies on thermal stability/kinetics of crystallization of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass which is considered for applications in brazing of certain metals.

MATERIALS AND METHODS

A prealloyed ingot with nominal composition $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ was prepared from the pure elements (purity > 99.9 wt.%) by arc melting in a titanium-gettered argon atmosphere. The ingot was remelted several times in order to achieve homogeneity in composition. *The alloy was then rapidly solidified using a vacuum melt spinner to prepare amorphous ribbons. The X-ray Diffractometer, used to determine structure is a Bruker Model No.*D8 having copper as the target. The thermal behavior and crystallization of the melt spun ribbon was studied using a Differential Scanning Calorimeter (DSC), DSC 821, METTLER-Toledo make. The calibration of the DSC system was done using zinc and indium standards. Commercial Argon gas was used as a purge gas at a rate of 45 SCM using a mass flow controller. DSC scans were performed using constant heating rates of 10, 20, 30 and 40 K/min from room temperature to 920 K, with temperature and power input accuracies of ± 0.1 K (± 0.1 °C) and 0.2 µW, respectively. The crystallization temperatures (T_x) are determined from the onset of the exothermic peak in the DSC curve for the sample. We have also checked crystallization by resistance measurement using four probe method. A constant current source (Keithley Model 227), Nanavoltmeter (Keithley Model 121) and chromel-alumel thermocouple were used to measure current (10 mA), voltage across the voltage leads and temperature, respectively. A more detailed analysis of resistivity behavior of the sample will be published later.

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RESULTS & DISCUSSION

Fig. 1 shows the XRD pattern of the as-spun ribbon of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$. The XRD pattern shows a typical broad maximum, characteristic of amorphous/glassy materials and no distinct crystalline peaks are detected within the sensitivity limits of the diffractometer.

Fig. 2(a) shows the DSC curves for $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass at four different heating rates, i.e. 10, 20, 30, and 40 K/min under non-isothermal conditions. It is observed that the crystallization of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass occurs only in one step. Fig. 2(b) shows that variation of peak temperature (T_p) obtained from the DSC thermograms as a function of heating rate. The peak temperature increases with the heating rate as observed for other metallic glasses. The peak temperatures for 20 to 40 K/min almost vary linearly. Table 1 list values of the on-set crystallization (T_x) and peak crystallization temperature (T_p) of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass sample for the four heating rates. The peaks are very sharp with FWHM of about 3-5 K.

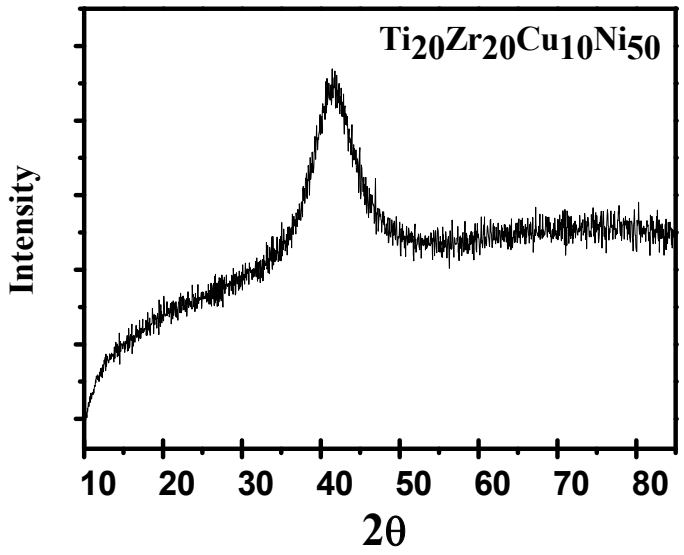

Fig 1 XRD pattern of as-cast metallic glass $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ sample.

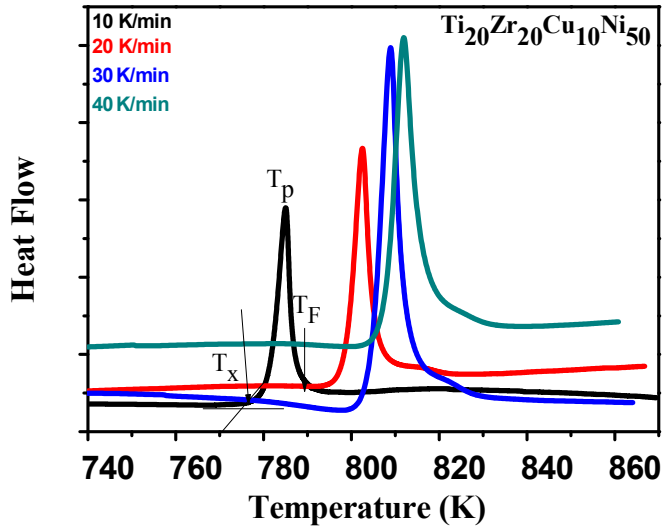

Fig 2(a) DSC thermograms of metallic glass $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ at different heating rates.

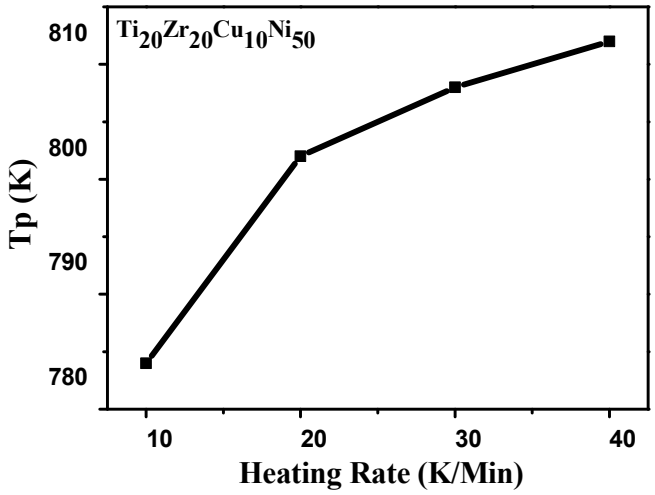

Fig 2(b) Variation of peak temperatures as a function of heating rate.

Table 1 Values of on-set, end-set crystallization temperature (T_x, T_F) and peak crystallization temperature (T_p) of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass sample. T_x, and T_p are in K.

Heating Rate(K/Min)	$Ti_{20}Zr_{20}Cu_{10}Ni_{50}$	
	T_x(K)	T_p(K)
10	781	788
20	795	807
30	798	815
40	805	819

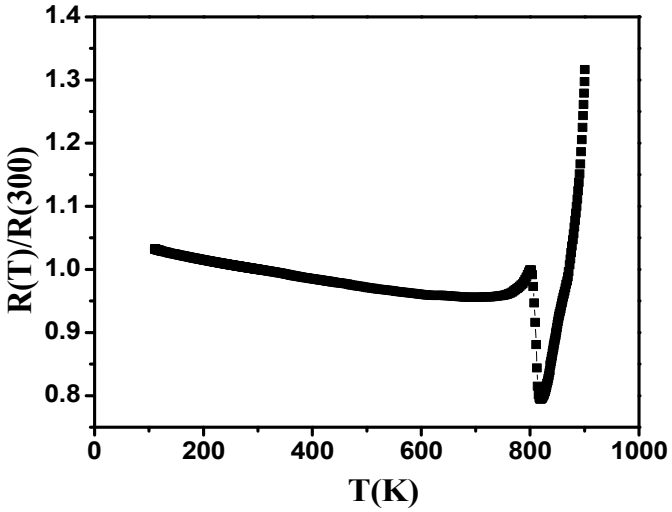

Fig 3 R(T)/R(300) vs. T(K) for $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass

Figure 3 shows the normalized resistance value (R(T)/R(300)), where R(T) is the resistance at a particular temperature, T, and R(300) is the resistance at 300 K as a function of temperature for as spun $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ ribbon. It is observed that just before the crystallization starts, that is when R(T)/R(300) starts dropping, this ratio shows a positive slope. The start of crystallization temperature is approximately 780 K and full crystallization takes place at about 810 K. These values are very similar to the ones observed in the DSC thermograms.

The activation energy of the crystallization, which is basically an effective energy barrier for crystallization can be calculated using various models applied to the non-isothermal DSC

thermograms (Kissinger, 1956 & 1957; Augis and Bennett, 1978; Ozawa, 1965,1970)

Johnson-Mehl-Avrami (Johnson and Mehl, 1939; Avrami, 1939,1940,1941) proposed the following equation for isothermal transformation kinetics in glass-forming liquids:

$$x(t) = 1 - \exp(-\alpha t^n) \quad (1)$$

where x(t) represents the volume fraction of the initial glass material transformed at time t, α is the reaction constant, and n is the Avrami exponent. α is taken to show Arrhenius T dependence given by

$$\alpha = \alpha_o \, e^{(-E_c/kT)} \quad , \quad (2)$$

Where α_o is a constant, E_c is the crystallization or activation energy, k is the Boltzmann constant and T is the isothermal temperature in K (Kelvin). We have used models proposed by Kissinger (Kissinger, 1957), Augis and Bennett (Augis and Bennet, 1978) and Ozawa (Ozawa, 1965 & 1970), who have used the JMA model with the approximation of the highest rate of crystallization at peak maximum in the DSC thermogram. Their theoretical approach led to the following equations.

The Kissinger equation is given by

$$\ln \frac{\Phi}{T_p^2} = -\frac{E_c}{RT_p} + const., \quad \ldots\ldots\ldots\ldots (3)$$

Here, T_p is the peak temperature, Φ is the heating rate, E_c is the activation energy and R is the gas constant. The activation energy for the crystallization is obtained by plotting $(ln\ \Phi/T^2_p)$ *vs* $(1000/T_p)$ as shown in Fig. 3(a). The slope of the straight line, obtained from regression analysis has been used to calculate the activation energy.

The activation energy of the crystallization has also been calculated using an approximation method proposed by Augis and Bennett. Their model resulted in a linear relation between $(ln\ \Phi/T_p)$ and $(1/T_p)$ as given in Eq. 2.

$$\ln \frac{\Phi}{T_p} = -\frac{E_c}{RT_p} + \ln K_0, \quad \ldots\ldots\ldots (4)$$

Where K_0 is a constant. A plot of $\ln(\Phi/T_p)$ vs $1000/T_p$ is shown in Fig. 3(b).

Third model, proposed by Ozawa, gives a linear relation between $(ln\ \Phi)$ and $(1/T_p)$ as expressed below in Eq. 3.

$$\ln \Phi = -\frac{E_c}{RT_p} + const., \quad \ldots\ldots\ldots\ldots (5)$$

The plot of $ln(\Phi)$ versus $(1000/T_p)$ is shown in Fig 3(c).

The activation energies in the last two methods are calculated similarly using the slope of the best fitted straight lines as done for the Kissinger method. The values of activation energies, obtained by these three methods, are listed in Table 2.

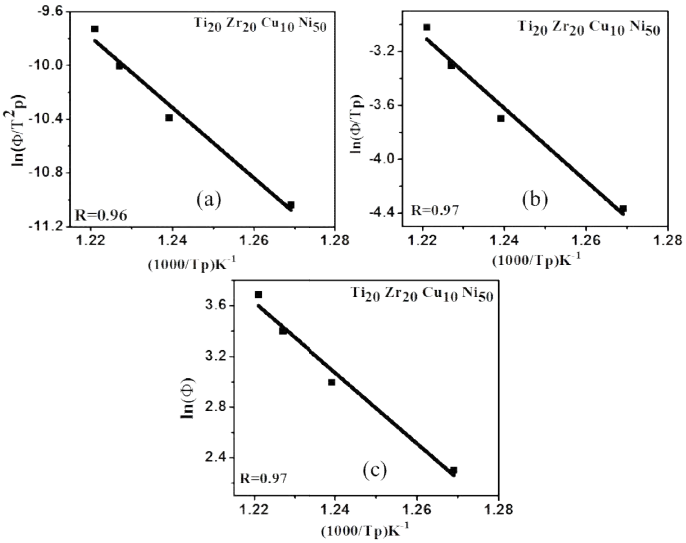

Fig.4 (a) $ln(\Phi/T_p^2)$**vs**$(1000/T_p)$**, (b)** $ln(\Phi/T_p)$vs$(1000/T_p)$ *and* **(c)** $ln(\Phi)$vs$(1000/T_p)$ of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass.

Table 2 Values of activation energy of crystallization of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass as calculated from various models.

Composition	Activation energy for the crystallization process (KJ/mol)		
	Kissinger method	Augis & Bennett method	Ozawa method
$Ti_{20}\ Zr_{20}\ Cu_{10}\ Ni_{50}$	310	302	293

It is to be noted that the activation energies calculated by these three models are almost similar. Kissinger model gives the lowest value while the Ozawa model gives the highest value, differing by ~5% from the value deduced using the Kissinger method. This difference probably lies within the estimated errors (about 5%) in determining the peak temperatures. The Kissinger model is being used mostly to calculate the activation energy of crystallization of metallic glasses. Our results simply show that there is not much difference between three models.

CONCLUSIONS

Crystallization of $Ti_{20}Zr_{20}Cu_{10}Ni_{50}$ metallic glass, produced by a rapid quenching technique, is studied using the Differential Scanning Calorimetry and analyzed using Kissinger, Augis & Bennet and Ozawa methods. It is observed that the activation energies derived using these models are nearly the same within 5% of the value obtained from the Kissinger method which has been extensively used in deriving activation energies of various metallic glasses.

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