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Indentation creep behavior of a Zr-based bulk metallic glass

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Abstract

The deformation behavior of a $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ bulk metallic glass (LM-1B) was studied in the supercooled liquid region by indentation creep test. Before indentation the glass transition and the crystallization temperatures were determined by calorimeter as 625 and 725 K, respectively. The phases formed during crystallization were identified by X-ray diffraction. The indentation creep experiments were carried out at different temperatures and loads. It was found that the creep can be regarded as Newtonian flow at strain rates between 5×10^{-5} and $5 \times 10^{-4}\,s^{-1}$. The values of the viscosity and the activation energy of deformation were determined in the temperature range of 667–687 K.

Keywords: Amorphous materials; Strain; High pressure; Calorimetry

1. Introduction

The deformation behavior of bulk metallic glasses in the supercooled liquid region is of great importance from the point of view of formability. In recent years the viscosity between the glass transition temperature (T_g) and the crystallization temperature (T_x) has been studied over a wide range of strain rate [1–6]. At relatively low strain rates bulk metallic glasses behave as Newtonian liquids but when the strain rate increases non-Newtonian flow occurs. This behavior has been successfully described by the free volume model with constant flow defect concentration [3,6]. At the same time, to explain other deformation phenomena (e.g. stress overshoot and stress oscillations) the shear-induced creation and thermal annihilation of flow defects should be taken into account [2,5,6]. The creation of additional free volume due to deformation is responsible for the strain softening.

High temperature creep behavior is traditionally investigated in tension or compression [5,6]. At the same time, indentation testing has been also successfully applied in studying creep of different crystalline materials and glasses [7–11]. The most important advantages of this method are the ease of sample preparation and a small piece of specimen being enough for the measurement. The latter is particularly important in the case of bulk metallic glasses where the dimensions of samples are often limited. Recently, it has been shown that the viscosity and the activation energy of deformation determined by compression and indentation are in good agreement [11].

The aim of the present study is to investigate the deformation behavior of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ bulk metallic glass in the supercooled liquid state at low strain rates by indentation creep tests. To the knowledge of the authors, detailed characterization of high temperature plastic behavior of this composition is missing in the literature. The changes of viscosity as a function of strain rate and the activation energy of creep are determined.

2. Experimental details

Commercial Zr-based bulk metallic glass (LM-1B) with the composition of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ was studied (manufacturer: Liquidmetal Technologies, Inc.). The diameter and the length of the cylindrical specimens were 9 and 85 mm, respectively. The thermal behavior of the alloy was studied by conventional differential scanning calorimetry (DSC) and by temperature modulated DSC (TMDSC) measurements. The heating rate in the DSC varied between 5 and 40 K/min. In the TMDSC the heating rate was 1 K/min modulated by a sine temperature oscillation with 1 K amplitude and 0.01 Hz frequency. Crystalline phases were identified by X-ray diffraction. X-ray diffractograms were measured by a Philips Xpert powder diffractometer (Bragg–Brentano geometry) with Cu Kα radiation ($\lambda = 0.15418$ nm).

Creep behavior was studied by indentation test using a Setaram TMA-92 thermomechanical analyzer between 667 and 687 K. The indentation measurements were carried out on specimens of 2 mm in height using a cylindrical punch of 1.2 mm in diameter under constant load, which could be varied between 0.5 and 1.5 N. The pressure calculated from the load was between 0.4 and 1.4 MPa.

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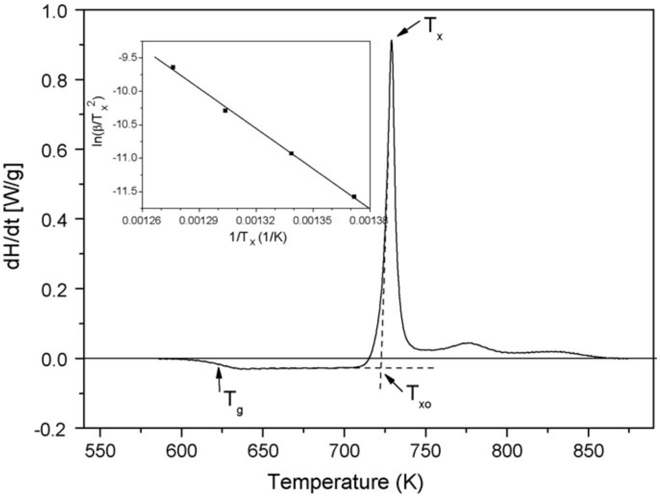

Fig. 1. The DSC curve obtained at 5 K/min heating rate. The inset shows the Kissinger-plot for the temperature of the first crystallization peak.

3. Results and discussion

Fig. 1 shows a DSC curve recorded at 5 K/min. The glass transition temperature was determined as the inflection point of the DSC curve during the glass transition, e.g. at 5 K/min heating rate $T_g = 625 \pm 3$ K.

The change of the specific-heat (Δc_p) in glass state was calculated as a function of temperature by derivating the heat flow–temperature curve obtained from the TMDSC measurements. The glass transition temperature was obtained to be $T_g = 632 \pm 3$ K. T_g was determined as the inflection point of Δc_p curve (Fig. 2). The difference between the glass transition temperatures obtained from DSC and TMDSC measurements can be explained by the different measuring methods.

The temperature of the onset of crystallization, T_{xo} (determined as the intercept of the rising edge of the crystallization peak and the calorimetric baseline) was 725 ± 3 K at 5 K/min heating rate (Fig. 1). The glass forming ability is characterized by the difference between T_{xo} and T_g determined from the DSC curve: $\Delta T_{xg} = 100$ K. If the crystallization is controlled by thermally activated processes, the activation energy can be determined from the shifting of temperature of the crystallization peak (T_x) with varying heating rate (β) of the linear heating DSC scans on the basis of the Kissinger-equation [12]. The activation energy for the crystallization peak obtained from the Kissinger-plot is 166 ± 6 kJ/mol. For a similar composition, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, 115 kJ/mol was found for the activation energy by Busch et al. [13].

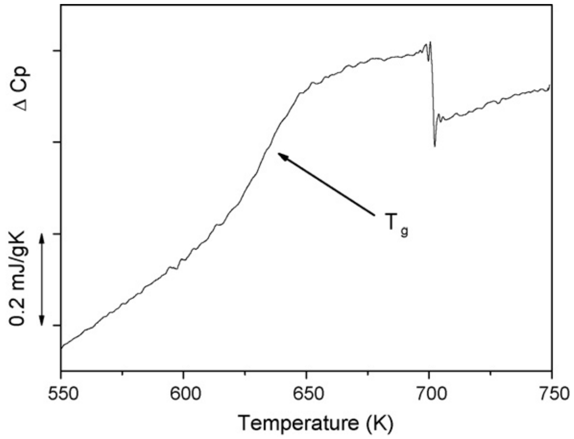

Fig. 2. The change of specific heat vs. temperature obtained from TMDSC measurements.

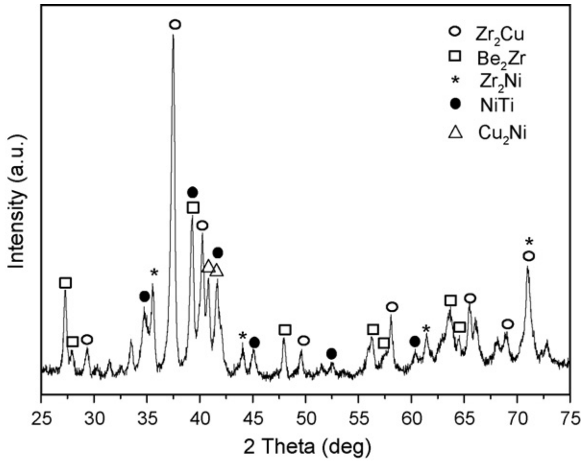

Fig. 3. The X-ray diffraction pattern of the sample heated to 860 K at 5 K/min heating rate.

Fig. 3 shows the X-ray diffractogram obtained after annealing at 5 K/min heating rate up to 860 K. After crystallization, the main phases are Zr_2Cu and Be_2Zr, however Zr_2Ni, Cu_2Ni and NiTi phases are also identified. These phases have been also observed in other ZrTiCuNiBe bulk metallic glasses with different compositions [14–17].

Isothermal indentation creep tests were carried out at temperatures of 667, 672, 677, 682 and 687 K. These temperatures were selected to be well below the onset crystallization temperature (725 K) to avoid the effect of crystalline phases on creep behavior. From the steady state stage of the creep curves the viscosity (η) was determined using the following equation:

$$\eta = \frac{\sigma}{3\dot{\varepsilon}} \tag{1}$$

where σ is the stress and $\dot{\varepsilon}$ is the strain rate. It has been convincingly confirmed by experimental and theoretical investigations for different metals, alloys and ionic crystals that the equivalent stress and strain rate in indentation creep tests can be expressed by the applied pressure (p) and the indentation rate ($\dot{h}$), respectively, as [7,10]

$$\sigma = \frac{p}{3} \tag{2}$$

and

$$\dot{\varepsilon} = \frac{\dot{h}}{d} \tag{3}$$

where d is the diameter of the cylindrical indenter.

The viscosity in high temperature steady state creep of crystalline solids generally depends strongly on the applied stress and the temperature (T) according to the following equation:

$$\eta = \eta_0 \sigma^{1-n} \exp\left(\frac{Q}{RT}\right) \tag{4}$$

where η_0 is a constant, R is the universal gas constant, Q and n are the activation energy and the stress exponent of the deformation process, respectively [10]. In the case of Newtonian viscous flow the value of the stress exponent is exactly 1, i.e. the viscosity depends only on the temperature.

According to the free volume model of Spaepen [18], at relatively low stresses bulk metallic glasses deform by viscous flow and the viscosity can be written as

$$\eta = \frac{kT}{\nu V c_\mathrm{f}} \exp\left(\frac{Q}{RT}\right) \tag{5}$$

where k is the Boltzmann constant, ν is the atomic vibration frequency and c_f is the flow defect concentration. V is the activation volume, which equals a few atomic volumes if several atoms participate in the local flow event. If the temperature of deformation is high and the creep experiments are carried out in a relatively narrow temperature range, the variation of the preexponential term with T can be neglected compared to the exponential term, i.e. Eq. (5) can be approximated by Eq. (4) with $n = 1$. As a consequence of this, in the case of bulk metallic glasses plotting $\ln \eta$ versus $1/T$ the slope gives the activation energy.

The values of viscosity vs. strain-rate are plotted at different temperatures in Fig. 4. It can be seen the viscosity did not change significantly when the strain rate was changed at constant temperature which means that the alloy behaved as a Newtonian liquid between the strain rate 5×10^{-5} to $5 \times 10^{-4}\ \mathrm{s}^{-1}$ and in the temperature range 667–687 K. The viscosity decreased from 1.6×10^9 to 2×10^8 Pa s when the temperature was raised from 667 to 687 K. The value of viscosity measured at 667 K is close to that determined by Waniuk et al. [1] for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ at 663 K (2×10^9 Pa s). The activation energy characterizing the deformation process was determined from the slope of $\ln(\eta)$ to $1/T$ plot as $Q = 366 \pm 15$ kJ/mol (Fig. 5). Other authors have found similar values of activation energy of creep in the supercooled liquid state for other compositions of Zr-based bulk metallic glasses [3,19]. $Q = 432, 410$ and 375 kJ/mol have been obtained by compression tests for the compositions of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [19], $Zr_{55}Cu_{30}Al_{10}Ni_5$ [3] and $Zr_{65}Cu_{15}Al_{10}Ni_{10}$ [3], respectively.

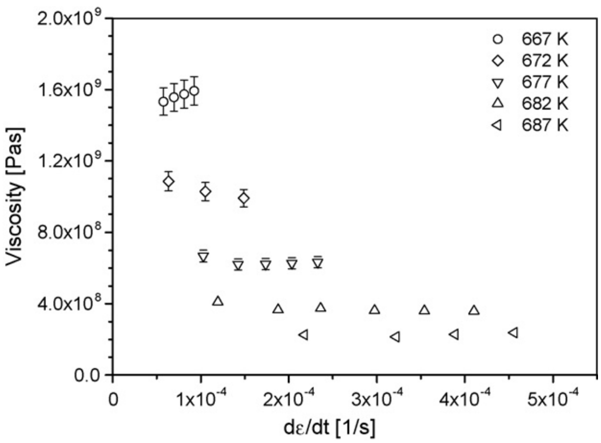

Fig. 4. Viscosity vs. strain-rate at different temperatures.

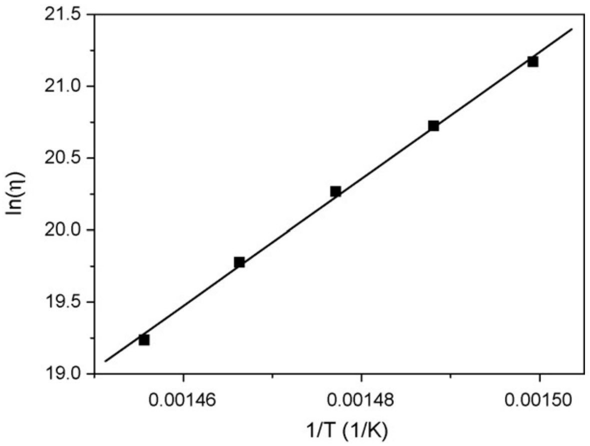

Fig. 5. The $\ln(\eta)$ to $1/T$ plot.

The value of the activation energy of deformation (366 kJ/mol) is much higher than the crystallization activation energy (166 kJ/mol). This phenomena has been also observed for $Zr_{52.5}Al_{10}Cu_{27}Ti_{2.5}Ni_8$ where the activation enegies of crystallization and creep in the supercooled liquid state are 243 and 563 kJ/mol, respectively [11]. The relatively large activation energy of creep is probably consistent with the cooperative nature of atomic movements during plastic deformation and the smaller activation energy of crystallization suggests localized atomic adjustments without collective movements of atoms. The free volume model of plastic deformation of bulk metallic glasses also suggests that the deformation occurs by the rearrangement of localised groups of 10–100 atoms [5].

4. Conclusions

The effectiveness of indentation creep test in studying the deformation behavior of a $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ bulk metallic glass in the supercooled liquid state was demonstrated. For the proper selection of the temperature range of deformation, the glass transition and the crystallization temperatures were determined from DSC curves and their values at 5 K/min heating rate were obtained as 625 and 725 K, respectively. After crystallization the main phases were Zr_2Cu and Be_2Zr. Indentation creep experiments showed that the deformation can be regarded as Newtonian flow in the temperature range 667–687 K and between the strain rate 5×10^{-5} to $5 \times 10^{-4}\ \mathrm{s}^{-1}$, i.e. the viscosity did not change with changing strain rate. The activation energy of deformation was obtained to be 366 kJ/mol, which is more than twice the measured activation energy of crystallization (166 kJ/mol). This difference can be explained by the different mechanisms of atomic transport in the two processes: collective movements of atoms during plastic deformation and localized atomic motions in crystallization.

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