

Indentation creep study on a Zr-based bulk metallic glass containing nano-quasicrystals

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Abstract

The effect of crystallization on the creep behavior of a Zr-based bulk metallic glass (BMG) with the composition of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ (at.%) was studied by indentation technique. The crystallization process was studied by isothermal annealing in a differential scanning calorimeter at three different temperatures above the glass transition temperature (677, 682 and 687 K). Two exothermic peaks are detected, the first one corresponds to the formation of a quasicrystalline phase. Indentation creep tests were carried out isothermally at the same three temperatures for studying the correlation between the amount of quasicrystalline phase and the creep behavior. A simple relationship between the viscosity and the crystalline phase fraction was found and the activation energy was found to decrease with the progress of crystallization.
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1. Introduction

In recent years the deformation behavior of bulk metallic glasses (BMGs) in the supercooled liquid region has been studied over a wide range of strain rates [1–6]. 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 the creep of different crystalline materials and glasses [7–11]. The most important advantages of this method are the ease of sample preparation and that a small piece of specimen is enough for the measurement. The latter is particularly important feature 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 $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ (at.%) bulk metallic glass during the initial state of crystallization. In a previous work [12], the glass transition and the crystallization temperatures of this alloy were determined by differential scanning calorimetry (DSC) at 5 K/min heating rate as 625 and 725 K,

respectively. Indentation creep experiments showed that in the supercooled liquid state at low strain rates the deformation can be regarded as Newtonian flow in the temperature range 663–683 K and between the strain rate 5×10^{-5} and $5 \times 10^{-4} s^{-1}$, i.e. the viscosity was found to be independent of the strain rate.

In this paper the effect of formation of nanometer size quasicrystalline particles on the creep behavior is studied by indentation test. There are only a few investigations [13,14] on the influence of the preceding crystallization on the creep process and to the knowledge of the authors, detailed characterization of the effect of crystallization on high temperature plastic behavior of this composition is missing in the literature. The viscosity and the activation energy of deformation are determined as a function of the transformed fraction, which is proportional to the crystalline phase content.

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 crystallization behavior of the alloy was studied by DSC measurements. Isothermal heat-treatments were carried out at 677, 682 and 687 K which are slightly above

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$(T_g + T_{x0})/2$ where $T_g = 625$ K is the glass transition temperature and $T_{x0} = 725$ K is the onset temperature of crystallization.

The crystalline phases were identified by X-ray diffraction. The X-ray diffractograms were measured by a Philips Xpert powder diffractometer with Cu K α radiation.

The effect of crystallization on the creep behavior was studied by isothermal indentation test using a Setaram TMA-92 thermo-mechanical analyzer at the temperatures of 677, 682 and 687 K. The indentation measurements were carried out on specimens of 3 mm in height by using a flat end cylindrical punch of 1.2 mm in diameter under constant load of 0.5 N which corresponds to 0.4 MPa pressure.

3. Results and discussion

The heat flow as a function of the measuring time, recorded during isothermal annealing at 677, 682 and 687 K is shown in Fig. 1(a). The heat flow versus time curve contains two exothermic peaks. The X-ray diffractograms taken after the first and the second peaks, respectively, are shown in Fig. 2. The X-ray patterns revealed, that the first exothermic peak corresponds to the formation of a metastable quasicrystalline phase while the second one is related to the crystallization of stable phases, namely Zr₂Ni, Be₂Zr, Zr₂Cu, Cu₂Ni and NiTi. These phases

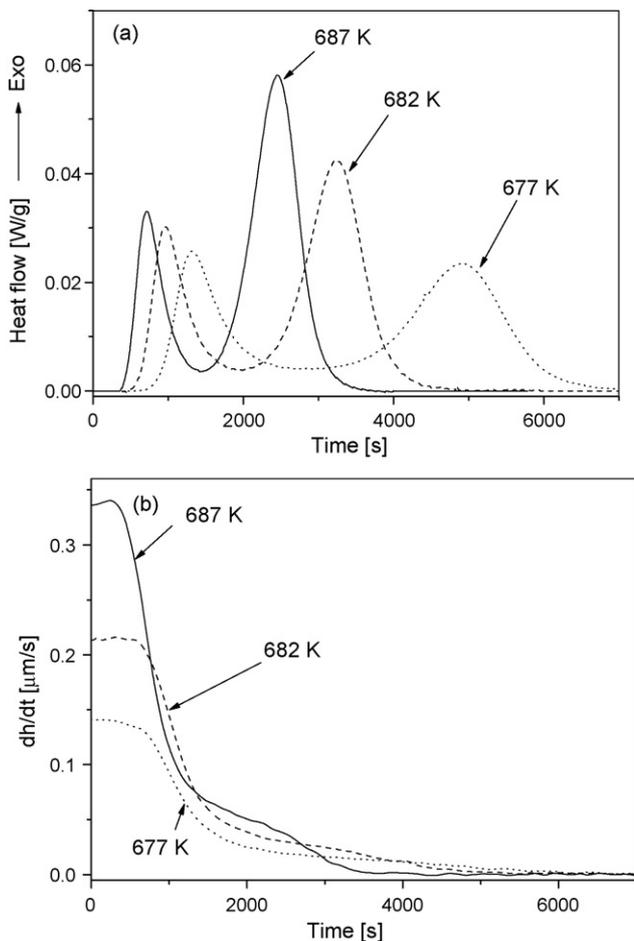


Fig. 1. The heat flow (a) and the indentation rate, dh/dt (b) as a function of time during isothermal annealing at 677, 682 and 687 K.

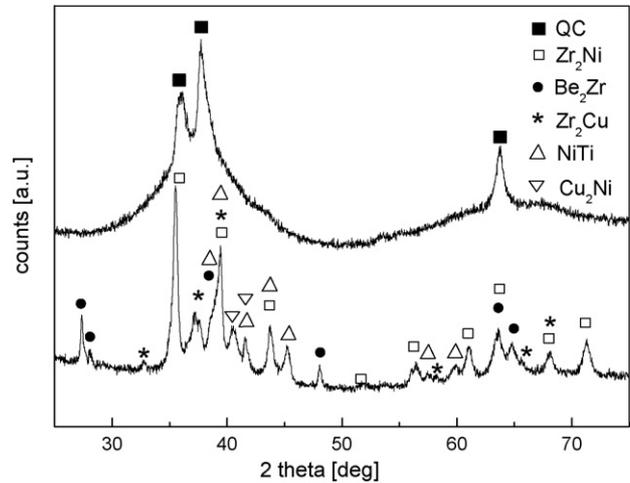


Fig. 2. X-ray diffraction patterns after the first (upper curve) and the second (lower curve) isothermal DSC peak at 687 K. QC: quasicrystalline phase.

have been also observed in other ZrTiCuNiBe bulk metallic glasses with different compositions [15–18]. The average size of the quasicrystalline particles at the end of the first exothermic peak is 12 nm as estimated from the breadth of the X-ray peak profiles using the Scherrer-equation. Integrating the heat flow versus time function, the heat released during crystallization (H) can be calculated at any time of annealing. It is found that the total heat released during crystallization, i.e. the area under the two DSC peaks is the same within the experimental error for all the three temperatures, $H_{total} = 60 \pm 1$ J/g. At the same time the distribution of the total heat between the two peaks is different for the three temperatures. During the first peak 37, 30 and 25% of the total heat are released at 677, 682 and 687 K, respectively. The higher the temperature, the lower the relative fraction of the first peak in the total heat because of the earlier formation of the stable crystalline phases during annealing.

Isothermal indentation creep tests were carried out at temperatures of 677, 682 and 687 K. The indentation rate (dh/dt or \dot{h}) as a function of time is shown in Fig. 1(b). The plateau at the beginning of the indentation rate curve characterizes the steady state creep in the supercooled liquid state where dh/dt is constant in time. As the crystalline phase fraction increases the indentation rate decreases gradually and the dh/dt versus time curve can be divided into two characteristic regimes which coincide with the two exothermic peaks in the DSC trace. The indentation rate decreases faster during the formation of the quasicrystalline phase than during the second step of the crystallization process in which the stable phases are being formed. About 80% of the initial value of dh/dt has been lost during the first crystallization peak, although only 25% of the total crystallization heat was released, indicating that the formation of a relatively small amount of quasicrystalline phase has a considerable effect on the deformation behavior of BMGs at high temperature.

It has been convincingly confirmed by experimental and theoretical investigations for different metals, alloys and ionic crystals that the equivalent stress (σ) and strain rate ($\dot{\epsilon}$) in indentation creep tests can be expressed by the applied pressure (p)

and the indentation rate (\dot{h}), respectively, as [7,10]:

$$\sigma = \frac{p}{3} \quad (1)$$

and

$$\dot{\epsilon} = \frac{\dot{h}}{d}, \quad (2)$$

where d is the diameter of the cylindrical indenter. The viscosity (η) can be determined at any time during the isothermal annealing by the following equation:

$$\eta = \frac{\sigma}{3\dot{\epsilon}} = \frac{pd}{9\dot{h}}. \quad (3)$$

Using the heat flow versus time and the indentation rate versus time data, the viscosity was calculated as a function of the heat released during crystallization normalized by the total heat, H/H_{total} . The latter quantity is called as relative released heat (H_{rel}). The relative released heat can be taken proportional to the crystallized fraction at least for the first crystallization peak. The relative released heat obtained in the first peak (0.25) at 687 K is close to the relative fraction of the integral intensity of the quasicrystalline peaks (0.2) in the X-ray pattern of Fig. 2 which suggests that the proportionality factor between the relative volume fraction of the quasicrystalline phase and the relative released heat is close to one. This is also supported by transmission electron microscopy (TEM) observations on the specimen annealed to the end of the first exothermic peak. As a consequence, the values of H_{rel} can be regarded as a measure of the crystallized fraction. In Fig. 3 the viscosity as a function of the relative released heat is plotted for the first crystallization peak, i.e. the maximum value of H_{rel} is 0.2. As the volume fraction of the crystalline phase increases, the viscosity of the amorphous–nano-quasicrystalline “composite” increases which can be attributed to the much higher viscosity of the crystalline component and the changes in the flow defect structure in the amorphous matrix during annealing. It is noted that Yan et al. [19] have also found that nano-scale crystalline precipitates increase the viscosity of $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$ bulk metallic glass.

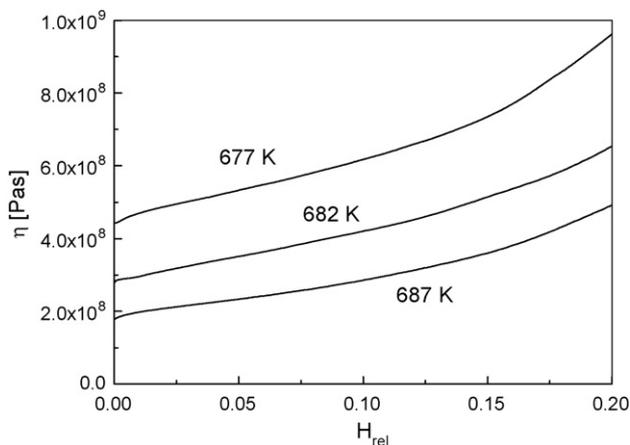


Fig. 3. The viscosity as a function of the relative released heat during formation of the quasicrystalline phase.

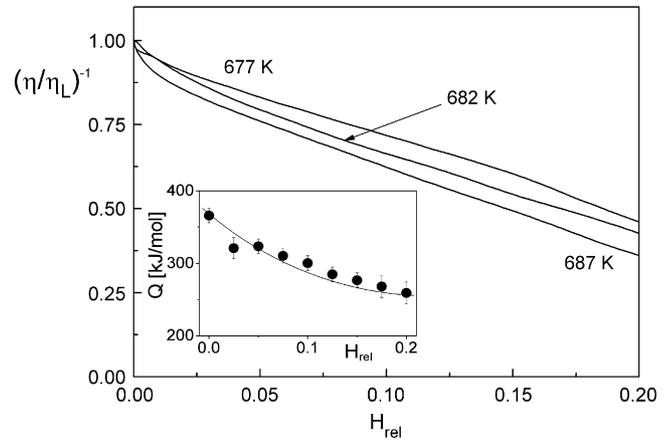


Fig. 4. The reciprocal normalized viscosity as a function of the relative released heat at 677, 682 and 687 K. The inset shows the changes of the activation energy.

The viscosity was normalized by the value characterizing the full amorphous (liquid) state before starting of the crystallization (η_L). The value of η_L was determined from the initial plateau of dh/dt versus time curve (see Fig. 1(b)). The reciprocal of the normalized viscosity as a function of the relative released heat is plotted in Fig. 4. The $(\eta/\eta_L)^{-1}$ versus H_{rel} can be described by a linear function for the relative released heat range of 0.01–0.2, consequently the normalized viscosity can be described by the following simple relationship

$$\frac{\eta}{\eta_L} = \frac{1}{A - BH_{\text{rel}}}, \quad (4)$$

where $A = 0.96, 0.93$ and 0.91 while $B = 2.4, 2.6$ and 2.8 for 677, 682 and 687 K, respectively. Similar relationship for the normalized viscosity as given in Eq. (4) with the values of $A = 1$ and $B = 2.5$ was derived theoretically for dilute suspensions of spherical particles by other authors [20–22]. In these calculations the suspension is treated as a mixture of two fluids, one fluid having an infinitely large viscosity, the other fluid having viscosity η_L . Our results show that the flow behavior of the supercooled liquid-quasicrystal composite can be also described well by this formula up to about 20% volume fraction of quasicrystals.

The temperature dependence of the experimental values of A and B in Eq. (4) can be attributed to the change of the activation energy of deformation with the relative fraction of quasicrystals. The apparent activation energy of creep, Q was calculated from the slope of $\ln \eta$ versus $1/T$ plot for different values of H_{rel} and plotted in the inset of Fig. 4. The activation energy in the supercooled liquid state is $Q = 366$ kJ/mol which decreases to about 259 kJ/mol for $H_{\text{rel}} = 0.2$. 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 [3,23]. $Q = 432, 410$ and 375 kJ/mol have been obtained by compression tests for the compositions of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ [23], $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ [3] and $\text{Zr}_{65}\text{Cu}_{15}\text{Al}_{10}\text{Ni}_{10}$ [3], respectively. At the same time, to the knowledge of the authors, the effect of crystallization on the activation energy for $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ has not been published yet. The decrease of the apparent activation energy during crystallization can be probably attributed to

the changes in the chemical composition of the remaining liquid phase. Wollgarten et al. [24] have shown that the quasicrystals in $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ are largely depleted of Be and enriched in Ti. The increase of the Be/Ti ratio in ZrTiCuNiBe bulk metallic glasses results in the decrease of the activation energy of diffusion [25] which may be the reason of an easier thermal activation of the flow event in the remaining amorphous phase of the partially crystallized samples.

4. Summary

The influence of the formation of nanometer sized quasicrystalline phase particles on the high temperature creep properties of a Zr-based bulk metallic glass was studied by indentation technique. The crystallized fraction was estimated on the basis of isothermal DSC measurements. The viscosity was found to increase with the increase of the crystalline phase content following a simple relationship, where the reciprocal of the viscosity decreases linearly with the crystalline volume fraction. The activation energy of deformation decreased with increasing crystalline phase content probably due to the changes of the chemical composition of the amorphous phase as the quasicrystals are depleted of Be.

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