

Effect of nano-quasicrystals on viscosity of a Zr-based bulk metallic glass

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The effect of formation of nano-quasicrystals on the creep behavior of a $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ bulk metallic glass was studied by the indentation technique above the glass transition temperature. The apparent viscosity of the supercooled liquid–quasicrystal composite increases with increasing volume fraction of the quasicrystalline phase following a simple relationship derived previously for dilute suspensions. The formation of quasicrystalline particles is accompanied by the decrease of activation energy of creep. This was related to the increase of the Be/Ti ratio in the supercooled liquid phase.

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The deformation behavior of bulk metallic glasses (BMGs) in the supercooled liquid region has been studied in numerous papers [1–7]. In these experiments the viscosity, as an important material parameter characterizing the deformation behavior, was determined at different strain rates [1,7]. During long-time deformation in the supercooled liquid state, crystalline phases are formed. Although the hard crystalline particles have considerable effect on the viscosity, there are only a few investigations [8–10] on the influence of the proceeding crystallization on the creep process.

The aim of the present study is to investigate the effect of crystallization on the viscosity in the supercooled liquid region for a commercial Zr-based bulk metallic glass (LM-1B) with the composition of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ (manufacturer: Liquidmetal Technologies, Inc). The diameter and the length of the as-produced cylindrical specimens were 9 and 85 mm, respectively. In a previous work [11], the glass transition temperature and the onset temperature of crystallization of this alloy were determined by differential scanning calorimetry (DSC) at 5 K min^{-1} heating rate as $T_g = 625\text{ K}$ and $T_{xo} = 725\text{ K}$, respectively. In another paper [12], the crystallization behavior of this alloy has been studied

by isothermal heat-treatments at 677, 682 and 687 K, which are slightly above $(T_g + T_{xo})/2$. It has been shown that the heat flow versus time curve contains two exothermic peaks as it is shown for 687 K in Figure 1. X-ray diffraction revealed that the first exothermic peak corresponds to the formation of a metastable quasicrystalline (QC) phase while the second one is related to the crystallization of stable phases, namely Zr_2Ni , Be_2Zr , Zr_2Cu , Cu_2Ni and $NiTi$. The X-ray diffraction pattern measured at the end of the first exothermic peak by $Cu\ K\alpha$ radiation is shown in the inset of Figure 1. This pattern contains an amorphous halo and the peaks of the QC phase, consequently up to the end of the first exothermic peak the material can be regarded as a composite of supercooled liquid and QC particles. Integrating the heat flow versus time function, the heat released during crystallization (H) can be calculated at any time of annealing. It was found that the total heat released during crystallization, i.e. the area under the two DSC peaks, was the same within the experimental error for all the three temperatures, $H_{total} = 60 \pm 1\text{ J g}^{-1}$. The crystallization state can be characterized by the relative released heat (H_{rel}). At any time of annealing, H_{rel} can be calculated as the heat released up to this time divided by the total heat, $H_{rel} = H/H_{total}$. It was found that the distribution of the total heat between the two crystallization peaks was different for the three temperatures. At the end of the first peak $H_{rel} = 0.37, 0.30$ and 0.25 were

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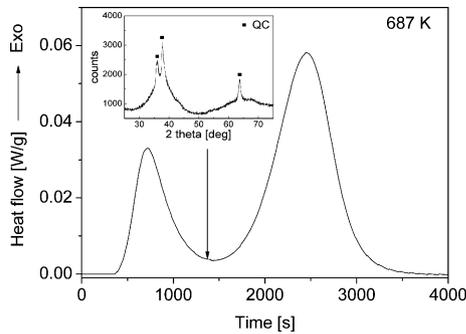


Figure 1. The heat flow as a function of time during isothermal annealing at 687 K. The inset shows the X-ray diffraction pattern taken at the end of the first exothermic peak. QC: quasicrystalline phase.

determined 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 enhanced formation of the stable crystalline phases during annealing.

Previous study revealed that the viscosity increased and the activation energy of creep decreased with increasing time of isothermal annealing [12]. To provide reasonable explanation of these phenomena, detailed investigations of the microstructure and the chemical composition of the QC phase are needed. In this paper the correlation between the viscosity and the microstructure of QC-supercooled liquid composite in $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ BMG is studied. 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 microstructure of the samples annealed isothermally at 677, 682 and 687 K was investigated by a Philips CM-20 transmission electron microscope (TEM) operating at 200 kV. Figure 2a shows the microstructure for the sample annealed up to $H_{rel} = 0.25$ at 677 K. The microstructure can be described as a composite consisting of an amorphous matrix and spherical QC nanoparticles. The distribution of particle diameters is shown in Figure 2b. The average size of the QC particles is 51 nm. It should be noted, however, that the size distribution of QC particles is relatively broad, containing particles of 10 as well as 130 nm size. The average size of the QC particles for $H_{rel} = 0.25$ is found to be between 51 and 58 nm for all the three temperatures, indicating that the difference between the annealing temperatures results only in slight difference in the particle size of QC phase. Figure 2a shows that the nano-QC particles contain grains or subgrains 15–20 nm size. This value is in good agreement with the coherently scattering domain size (12 nm) estimated from the breadth of the X-ray peak profiles in Figure 1 using the Scherrer equation. The correlation between the relative released heat and the volume fraction of the QC phase was investigated by TEM for $H_{rel} = 0.25$ at 677, 682 and 687 K. It was found that the two quantities agreed within the experimental error, therefore in this paper H_{rel} is taken to be equal to the volume fraction of QC particles up to the end of the first crystallization peak. The chemical composition of the QC particles was investigated by

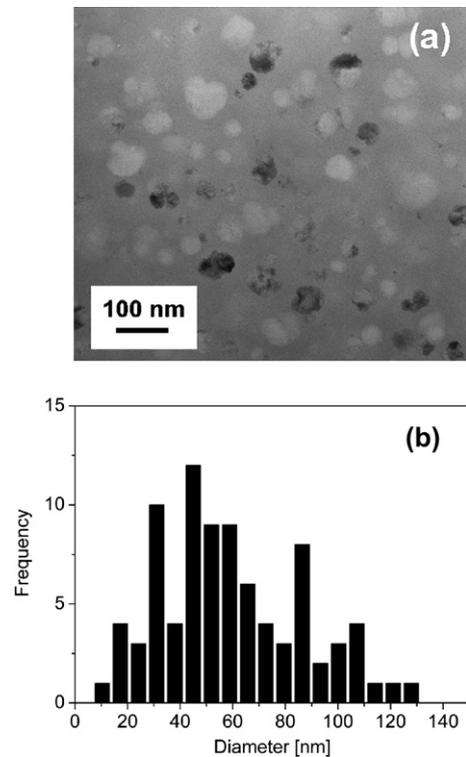


Figure 2. (a) The microstructure of the sample annealed up to $H_{rel} = 0.25$ at 677 K. (b) The distribution of particle diameters determined from TEM.

electron energy loss spectroscopy (EELS). In Figure 3 bright-field TEM image of the microstructure as well as the element maps for Cu, Be and Ti are shown for the sample annealed for $H_{rel} = 0.25$ at 682 K. In Figure 3b–d the lighter the gray, the higher the concentration of elements. The element maps reveal that the QC particles are enriched in Ti and depleted from Be and Cu. It is noted that the area shown in Figure 3a and b is different from that recorded in Figure 3c and d but this fact has no effect on the conclusions drawn from the figures.

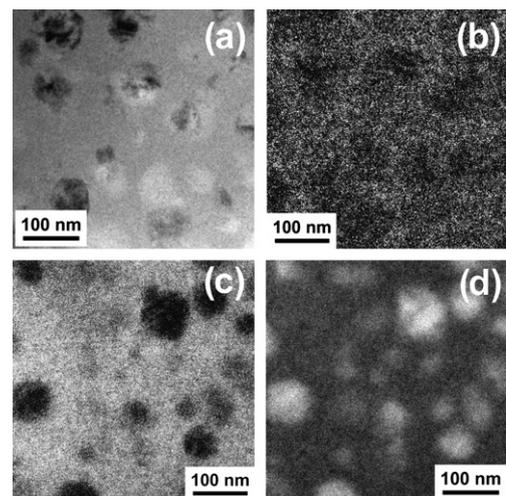


Figure 3. TEM image of the sample annealed up to the end of the first crystallization peak at 682 K. The element maps obtained by electron energy loss spectroscopy (EELS) for Cu (b), Be (c) and Ti (d).

Similar compositional differences between the amorphous and the QC phases were observed by Wollgarten and coworkers [13] for $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$.

The viscosity was measured by isothermal indentation tests using a Setaram TMA-92 thermomechanical analyzer at the temperatures of 677, 682 and 687 K. It has been shown previously that the viscosity and the activation energy of deformation determined by compression and indentation are in good agreement for BMGs [14]. The most important advantages of the indentation method are the ease of sample preparation and the small specimen size needed for the measurement. The latter is a particularly important feature in the case of bulk metallic glasses where the dimensions of samples are often limited. 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 a constant load of 0.5 N which corresponds to 0.4 MPa pressure. The pressure used here is about three orders of magnitude smaller than that applied in a usual compression test [15]; consequently the stress-induced crystallization may be neglected in our experiments.

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 as one-third of the applied pressure and the indentation rate normalized by the diameter of the cylindrical punch, respectively [16,17].

The viscosity (η) can be determined at any time during the isothermal annealing as one-third of the ratio of the equivalent stress and strain rate [16]. Using the heat flow versus time and the indentation rate versus time data, the viscosity was calculated as a function of H_{rel} for the first crystallization peak. This function is regarded as the relation between the viscosity and the volume fraction of QC phase.

The partially crystallized sample can be considered as a dilute suspension of undeformable spherical QC particles in a viscous liquid phase. A general relationship between the viscosity and the volume fraction of the undeformable spherical particles (V) in dilute suspensions was derived theoretically by other authors [18–20]:

$$\frac{\eta}{\eta_L} = \frac{1}{1 - 2.5V}, \tag{1}$$

where η_L is the viscosity of the liquid phase. In these calculations the suspension is treated as a mixture of two fluids, one fluid having an infinitely large viscosity (hard particles) and the other fluid having viscosity η_L (liquid). Beenakker [20] has shown that if all the hydrodynamic interactions between the spheres are taken into account, the ratio of η/η_L differs from Eq. (2) by a maximum of 6% up to $V = 0.2$. In order to study the validity of this relationship for our QC-supercooled liquid composite, the apparent viscosity was normalized by the viscosity of the liquid phase measured before starting the crystallization (η_{L0}). In Figure 4 the reciprocal of the normalized viscosity, η_{L0}/η is plotted as a function of H_{rel} which is taken to be equal to V . Figure 4 shows that the η_{L0}/η versus H_{rel} function can be approximated by

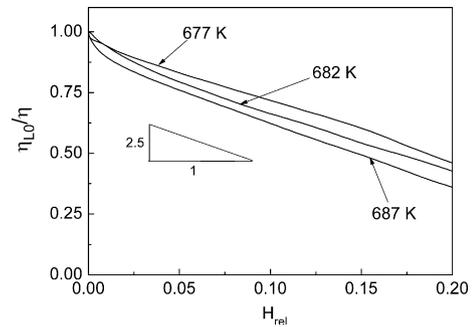


Figure 4. The reciprocal normalized viscosity η_{L0}/η as a function of the relative released heat (H_{rel}) during formation of the QC phase.

a linear function with the slope equal to -2.5 for the relative released heat range of 0.01–0.2. Consequently η/η_L is described well by the formula given in Eq. (1). Our results show that at high-temperature the QC-supercooled liquid composite deforms as a dilute suspension at least up to about 20% volume fraction of QC. The temperature-dependence of η_{L0}/η versus H_{rel} function (see Fig. 4) can be explained by the change of the activation energy of creep of the liquid phase with increasing the volume fraction of QC, which results in the variation of η_L with H_{rel} . Consequently, η can be given by the following formula:

$$\eta = \eta_L(H_{rel}) \cdot f(H_{rel}), \tag{2}$$

where

$$f(H_{rel}) = \frac{1}{1 - 2.5H_{rel}}. \tag{3}$$

The viscosity of the liquid phase, η_L , was determined as the ratio of the experimentally determined viscosity, η , and $f(H_{rel})$ given in Eq. (3) and plotted as a function of H_{rel} at 677, 682 and 687 K in Figure 5. Assuming an Arrhenius-type dependence of viscosity on the temperature, the apparent activation energy of creep of the liquid phase, Q was calculated from the slope of $\ln \eta_L$ vs $1/T$ plot for different values of H_{rel} and plotted in the inset of Figure 5. The activation energy in the supercooled liquid state is $Q = 366 \text{ kJ mol}^{-1}$, which decreases to about 259 kJ mol^{-1} for $H_{rel} = 0.2$. The decrease of the activation energy during the formation of the QC phase can be probably attributed to the changes in the chemical composition of the remaining liquid phase.

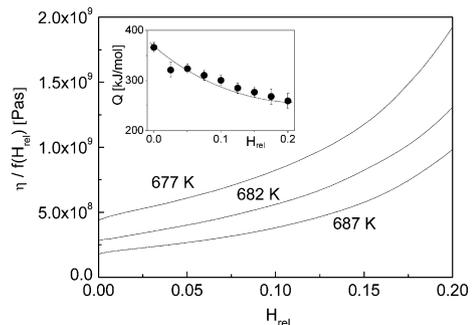


Figure 5. The viscosity of the liquid phase as a function of the relative released heat (H_{rel}) at 677, 682 and 687 K. The inset shows the changes of the activation energy.

Figure 3 shows that the liquid phase is largely depleted in Ti and enriched in Be. The increase of the Be/Ti ratio in ZrTiCuNiBe bulk metallic glasses results in the decrease of the activation energy of diffusion [21], which may be the reason for an easier thermal activation of the flow event in the remaining amorphous phase of the partially crystallized samples.

In this paper, the influence of the formation of nanometer sized QC particles on the viscosity of a Zr-based bulk metallic glass was studied by the indentation technique. The viscosity was found to increase with the increase of the QC phase content following a simple relationship, where the reciprocal of the viscosity decreases linearly with the crystalline volume fraction. The activation energy of creep decreases with increasing QC phase content, probably due to the increase of the Be/Ti ratio in the supercooled liquid phase. It should be noted that for a crystalline volume fraction higher than 0.3, Eq. (3) was found to be not valid and the viscosity increases much faster as a function of crystalline fraction than with a volume fraction below 0.3. This can be attributed to the interaction of crystalline particles and percolation effects as suggested in Refs. [15,22]. The theoretical description of viscosity in this state is difficult as the increase of the crystalline fraction is superimposed by the transformation of the QC phase to stable crystalline phases.

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