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Effect of crystallization on the deformation behavior of a Zr-based bulk metallic glass

The crystallization process in a Zr-based bulk metallic glass with the composition $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ was studied during isothermal annealing above the glass transition temperature at 682 K. Indentation creep tests were applied to study the effect of crystallization on the viscosity. It was found that the increase in viscosity during crystallization is primarily caused by the hard crystalline grains and secondarily by the change of the chemical composition of the remaining liquid phase. The deformation behavior at room temperature is studied by three-point bending tests. The strength of the specimens decreases significantly in the first step of the crystallization process.

Keywords: Metallic glass; Quasicrystal; Indentation creep; Viscosity; Strength

1. Introduction

Due to their unique mechanical properties the deformation behavior of bulk metallic glasses (BMGs) has been intensively studied in recent years [1–4]. BMGs usually have lower elastic modulus, higher strength, and reduced plasticity compared to their crystalline counterparts of the same chemical composition [4]. The application of BMGs at high temperatures often leads to partial or full crystallization. The crystallization results in significant changes in the mechanical properties which depend strongly on the chemical composition and the temperature of annealing [5]. The aim of the present study is to investigate the deformation behavior of a $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ BMG during crystallization. In a previous work [6], the glass transition and the crystallization temperatures of this alloy were determined by differential scanning calorimetry (DSC) at 5 K min^{-1} heating rate as 625 and 725 K, respectively. Indentation creep experiments revealed that in the supercooled liquid state in the temperature range 663–683 K and at low strain rates (between 5×10^{-5} and $5 \times 10^{-4}\text{ s}^{-1}$) the deformation can be regarded as Newtonian flow and the viscosity was found to be independent of the strain rate [6]. In this paper the effect of crystallization on the deformation behavior at room and high temperature is studied. The evolution of the microstructure during crystallization is characterized in detail. The viscosity as a function of crystalline phase content in the supercooled liquid state is investigated by indentation creep testing. The deformation behavior at room temperature is studied by three-point bending tests.

2. Experimental

A Zr-based commercial BMG (LM-1B) with the composition $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ was studied. The diameter and the length of the cylindrical specimens were 9 and 85 mm, respectively. Isothermal heat treatments were carried out under argon flow in a Setaram calorimeter. The crystalline phases were identified by X-ray diffraction using a Philips Xpert powder diffractometer with $Cu-K\alpha$ radiation. The microstructure of the samples was investigated using a Philips CM-20 transmission electron microscope (TEM) operated at 200 kV. The chemical composition was investigated by energy-filtering TEM (EFTEM). The effect of crystallization on the creep behavior was studied by isothermal indentation tests carried out in a Setaram TMA-92 thermo-mechanical analyzer. The indentation measurements were carried out on specimens of 3 mm height by using a flat end cylindrical punch of 1.2 mm diameter under constant load of 0.5 N which corresponds to 0.4 MPa pressure. The effect of crystallization on the deformation behavior at room temperature was studied by three-point bending tests on 14 mm long samples of 1.6 mm height and 2.3 mm width. The tests were carried out using a computer-controlled hydraulic mechanical testing MTS 810 machine with a spanning distance of 10.4 mm and at a displacement rate of 0.005 mm s^{-1} .

3. Results and discussion

Figure 1 shows a DSC thermogram recorded during isothermal annealing at 682 K. The heat flow versus time curve contains two exothermic peaks. The phase composition was determined by X-ray diffraction at the points marked by dots on the thermogram. Figure 2 shows the X-ray diffractograms corresponding to the as-received state and the last four points in the DSC thermogram in Fig. 1. The X-ray diffraction pattern obtained after annealing for 1300 s contains an amorphous halo and the peaks of a quasicrystalline (QC) phase [7]. The diffractograms corresponding to shorter annealing times (not shown here) have the same peak structure but with weaker reflections 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. The second exothermic peak on the DSC thermogram is related to the crystallization of stable phases, namely Be_2Zr , Zr_2Ni , Zr_2Cu and $NiTi$. At the end of the second crystallization peak (the annealing time is 4900 s) a significant amount of QC phase re-

mained in the microstructure which disappeared completely after prolonged (55 000 s) heat-treatment while the fractions of Zr_2Cu and Be_2Zr increased. This transformation of the remaining QC phase was probably so slow that the heat release was not detected after the second DSC peak. Figure 3 shows a TEM image of the microstructure as well as elemental maps for Cu, Be, and Ti for the sample annealed until the end of the first exothermic peak. Due to an edge overlap, the elemental map of Cu is also influenced by the amount of Ni. The elemental maps reveal that the QC particles are enriched in Ti and depleted of Be and Cu. Similar compositional differences between the amorphous and the QC phases were observed by Wollgarten and coworkers [7] for $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$.

Figure 4 shows a TEM image of the microstructure and elemental maps for Cu, Be, and Ti after the second exothermic peak. In contrast to other elements, Ti retained its distribution of the state after the first crystallization peak when it was in QC grains. The locations of highest Be concentration are between the Ti-rich volumes as Be_2Zr crystallizes from the liquid phase. The Cu and Ni (not shown here) distributions are complementary to Be because Zr_2Ni and

Zr_2Cu also crystallize beside Be_2Zr during the second crystallization peak. High Cu and Ni concentrations are found both in the Ti-rich and Ti-poor regions indicating that Zr_2Ni and Zr_2Cu crystallize both from the liquid phase and QC grains. This suggests that there are deviations from the strong stoichiometry in Zr_2Ni and Zr_2Cu phases and they can be taken rather as $Zr_2Ni(Cu, Ti)$ and $Zr_2Cu(Ni, Ti)$.

The viscosity (η) as a function of crystalline volume fraction was measured by isothermal indentation test. The viscosity was determined as one-third of the ratio of the equivalent stress and strain rate [8]. The equivalent stress

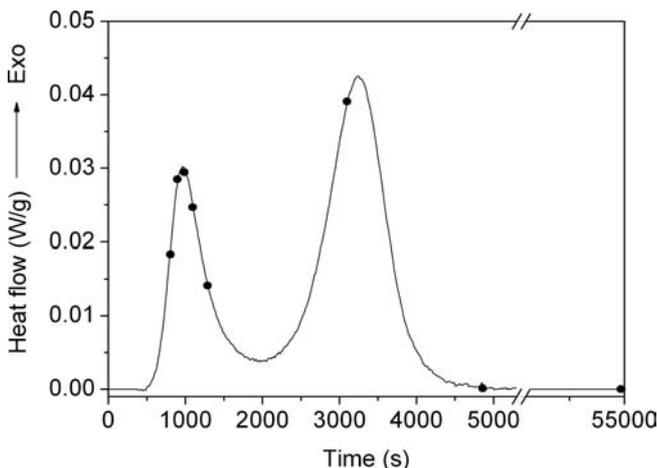


Fig. 1. The heat flow as a function of time during isothermal annealing at 682 K. The dots mark the states where the crystalline phase composition and the bending behavior at room temperature were investigated.

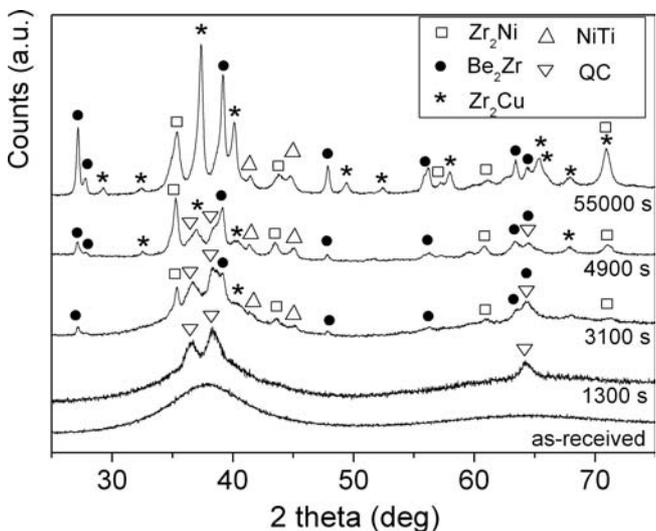


Fig. 2. X-ray diffraction patterns for different times of isothermal annealing at 682 K. QC: quasicrystalline phase.

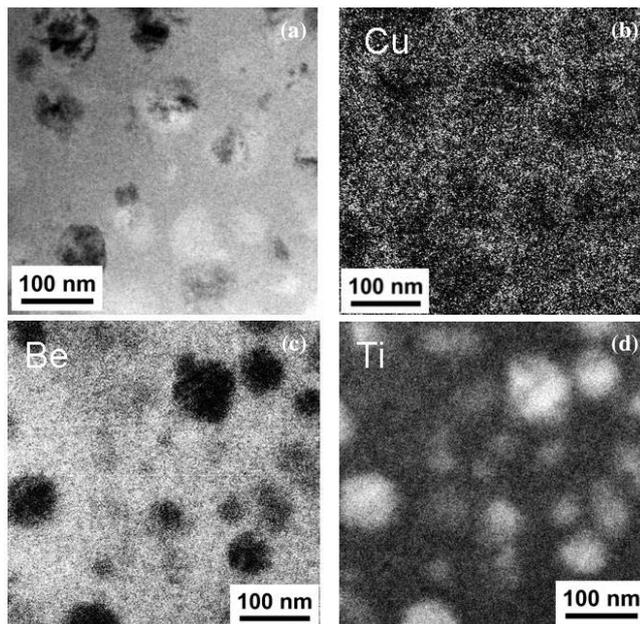


Fig. 3. (a) TEM image and elemental maps obtained by EFTEM for (b) Cu, (c) Be, and (d) Ti of a sample annealed up to the end of the first crystallization peak at 682 K. (The lighter the grey, the higher the concentration of elements.)

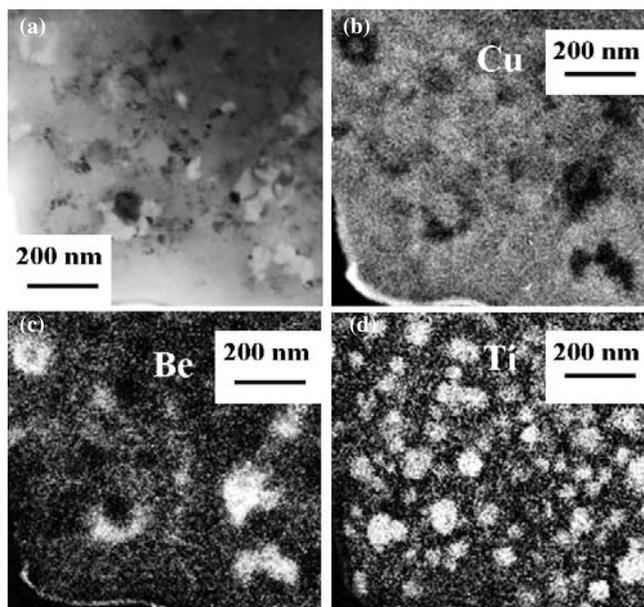


Fig. 4. (a) TEM image and elemental maps obtained by EFTEM for (b) Cu, (c) Be, and (d) Ti of a sample annealed up to the end of the second crystallization peak at 682 K. (The lighter the grey, the higher the concentration of elements.)

and strain rates were obtained as one-third of the applied pressure, and the indentation rate normalized by the diameter of the cylindrical punch, respectively [8]. At any time during isothermal annealing, the volume fraction of crystalline phases was estimated by the relative released heat (H_{rel}) which was determined as the ratio of the heat released till that time and the total heat released during crystallization, i. e. the area under the two DSC peaks. Previous study revealed that H_{rel} and the volume fraction of QC phase agreed within the experimental error at least till the end of the first crystallization peak [9]. Figure 5 shows the reciprocal of the normalized viscosity, η_{L0}/η , where η_{L0} is the viscosity of the liquid phase before the onset of crystallization, as a function of H_{rel} . In this figure the theoretical function describing the reciprocal normalized viscosity of a suspension of monodisperse undeformable particles proposed by Hsueh and Becher (see Eq. (14) in [10]) is also presented by a dashed line. Comparing the experimental and theoretical curves it can be established that the increase in viscosity during crystallization is mainly caused by the increase in the hard crystalline fraction. The higher experimental viscosity compared with the theoretical values during the first

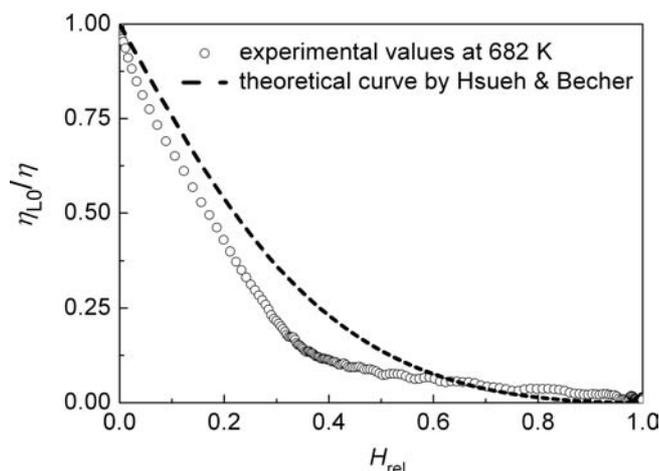


Fig. 5. The reciprocal normalized viscosity as a function of the relative released heat at 682 K. The dashed line represents the theoretical curve proposed by Hsueh and Becher [10].

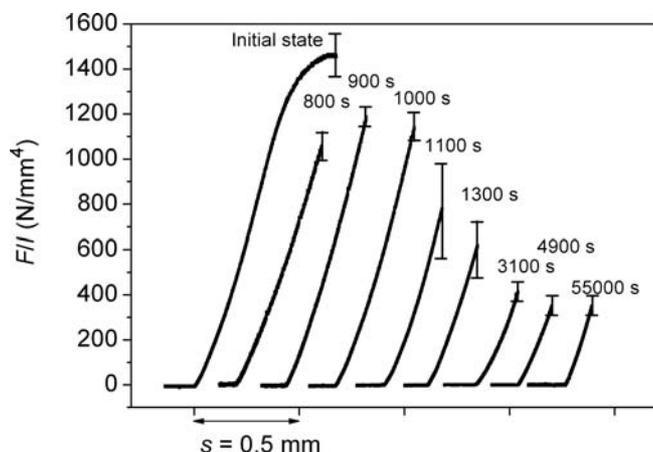


Fig. 6. Results of three-point bending tests for samples annealed for different times at 682 K. F/II is the applied force normalized by the second moment of area and s is the deflection. The error bars indicate the uncertainties of maximum values of F/II .

exothermic peak can be explained by the increase of Be:Ti ratio in the liquid phase which may increase its viscosity [1, 9]. In the second step of crystallization the formation of Be_2Zr reduces the Be:Ti ratio in the liquid phase which may cause a decrease in liquid viscosity. The theoretical curve is not valid for high crystalline fractions (above 0.5–0.6) and when contiguity of the crystalline particles occurs [10].

Figure 6 shows the results of three-point bending tests at room temperature for different annealing times at 682 K. To permit direct comparison of specimens with slightly different cross-sections, the bending force normalized with the second moment of area (F/II) is plotted as a function of deflection. It can be seen that while the initial sample shows plasticity, the crystallized specimens failed in the elastic deformation regime. The large decrease in strength during the first crystallization peak can be explained by a loss of free volume in the beginning of crystallization [11] and an increase in viscosity due to changes of chemical composition in the amorphous phase [4]. This may make stress relaxation by means of viscoplastic flow more difficult (e. g. in a crack tip region). In the second step of crystallization the deviations from the perfect stoichiometry in the crystalline phases may result in internal stresses which may be the reason for the slight additional strength reduction.

4. Conclusions

It was found that $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ BMG annealed at 682 K crystallizes in two steps. In the first step a quasicrystalline phase formed while in the second step stable crystalline phases developed partly from the liquid phase and partly by transformation from the quasicrystals. The viscosity increases during crystallization mainly due to the increase in the volume fraction of hard crystalline grains, although the change of chemical composition in the liquid phase also affects the viscosity. The room temperature bending strength decreases mainly in the first crystallization step which in the initial stage can be attributed mainly to a loss of free volume and an increase in liquid phase viscosity. In the second step the additional strength reduction may be due to formation of weak interphase regions between the contiguous crystalline grains and internal stresses resulting from compositional variations and deviations from stoichiometry in the crystalline phases.

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References

- [1] T.A. Waniuk, R. Busch, A. Masuhr, W.L. Johnson: *Acta Mater.* 46 (1998) 5229.
- [2] A. Inoue: *Mater. Sci. Eng. A* 304 (2001) 1.
- [3] B.C. Wei, G.S. Yu, W. Löser, L. Xia, S. Roth, W.H. Wang, J. Eckert: *Mater. Sci. Eng. A* 375 (2004) 1161.
- [4] C.A. Schuh, T.C. Hufnagel, U. Ramamurty: *Acta Mater.* 55 (2007) 4067.
- [5] L.-Q. Xing, Y. Li, K.T. Ramesh, J. Li, T.C. Hufnagel: *Phys. Rev. B* 64 (2001) 180201(R).
- [6] D. Fátay, J. Gubicza, J. Lendvai: *J. Alloys Comp.* 434–435 (2007) 75.

- [7] M. Wollgarten, S. Mechler, E. Davidov, N. Wanderka, M.-P. Macht: *Intermetallics* 12 (2004) 1251.
- [8] D. Fátay, J. Gubicza, P. Szommer, J. Lendvai, M. Blétry, P. Guyot: *Mater. Sci. Eng. A* 387 (2004) 1001.
- [9] J. Gubicza, J.L. Lábár, E. Agócs, D. Fátay, J. Lendvai: *Scripta Mater.* 58 (2008) 291.
- [10] C.-H. Hsueh, P.F. Becher: *J. Am. Ceram. Soc.* 88 (2005) 1046.
- [11] D. Suh, R.H. Dauskardt: *J. Non-Cryst. Solids* 317 (2003) 181.

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Bibliography

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