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Viscosity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass measured by laser viscometer

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ABSTRACT

The viscosity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass was measured by using a parallel plate rheometry laser viscometer. The isothermal measurements show that the viscosities increase from 10^{12} to 10^{13} Pa s with temperature varying from 668 to 738 K, which can be described by VFT equation with a VFT temperature of 390 K and the fragility parameter D of 28.85. The viscosity from the isothermal measurement is higher than that from the isochronal measurement.

1. Introduction

Bulk metallic glass (BMG) alloys present enormous application potential in the field of advanced materials due to their unique mechanical, physical and chemical properties, and are attracting more and more interests. Viscosity is one of the most important factors governing the glass forming process. Since the discovery of bulk metallic glass, many methods, such as parallel plate rheometry[1,2], three-point beam bending, penetration viscometer[3], have been applied to measure the viscosity in a relatively high temperature. In the glass transition region, the viscosity of metallic glasses decreases markedly, and the temperature dependence is usually described by the Vogel–Fulcher–Tammann (VFT) formula. Since the formation of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG was firstly reported by Inoue and Zhang [4], its viscosity has been measured by many researchers[3,5–8]. The aim of this paper is to introduce a new method to measure the viscosity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG.

2. Experimental

$Zr_{55}Cu_{30}Al_{10}Ni_5$ (nominal atomic percentage) alloy ingot was prepared from a mixture of pure metals with purities above 99.9% by arc melting in a purified argon atmosphere. Bulk glassy alloy rods with a diameter of 5 mm were prepared by copper mould suction casting method. The glassy state of the as cast rods was confirmed by X-ray diffractometry (XRD). The glass transition temperature (T_g) and the onset temperature of crystallization (T_x) were determined to be 683 and 773 K, respectively.

The viscosity measurement was conducted under an Ar atmosphere by the designed high precision parallel plate rheometry laser viscometer. Fig. 1 is a schematic diagram of the viscometer. For viscosity measurement, cylindrical specimens of 6 mm in height were cut from the as cast rods. A constant load of 78 N was applied to the sample through the force applying system. The length change of the sample is measured through a Michelson laser interferometer (SP120D, SIOS Messtechnik) by recording the displacement of the surface of the load. The thermal expansion of the system is measured with the same respective heating rate as the viscosity measurement and deducted from the result. A holding system is used to ensure an effective laser interferometry. Two thermal couples are placed under the sample to measure the temperature.

Doolittle [9] found that the relation among viscosity (η), real stress (σ) and strain rate ($d\varepsilon/dt$) can be described as

$$\eta = \frac{\sigma}{3(d\varepsilon/dt)}, \tag{1}$$

in which $\sigma = FL/A_0L_0$, and $\varepsilon = -\ln(L/L_0)$, where A_0, L_0, F and L are the initial cross-sectional area, initial length, applied constant load, and the instantaneous length, respectively. These experiments were performed under isochronal and isothermal conditions to measure equilibrium viscosity.

3. Results and discussions

Fig. 2 shows the length change of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG sample during an isochronal measurement with a heating rate of 1 K/min. The temperature ranges from 705 to 728 K. The total length change is about 450 μm. The deformation rate increases with the temperature, indicating that the viscosity decreases. The isothermal measurements are carried out at temperatures 668–738 K after sufficient long time pre-heating below T_g. Fig. 3 shows the length change curves with time.

From the length change of the specimen (Figs. 2, 3), the viscosities of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG are plotted in Fig. 4 as a function of the temperature. The viscosity values are between 10^{10} to 10^{13} Pa s within the temperature window 683–738 K. The viscosities of

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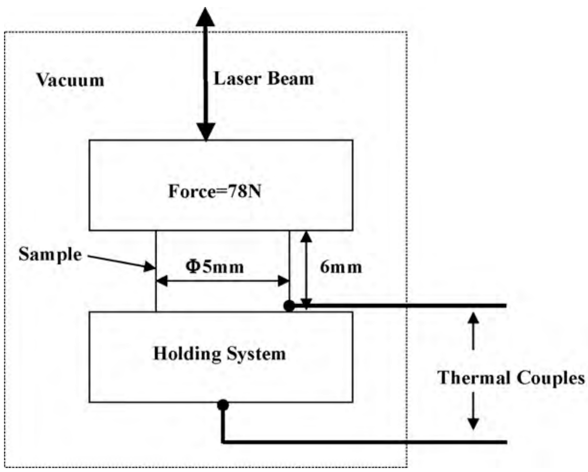

Fig. 1. Schematic diagram of the one-beam laser viscometer.

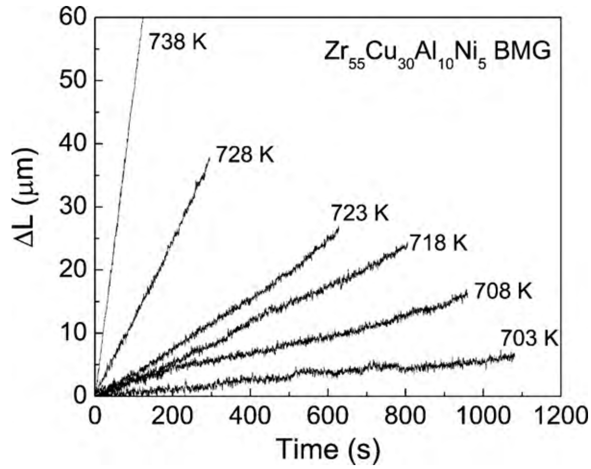

Fig. 3. The length change of $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glass with time at isothermal measurement.

$Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG measured in this work are similar to results of Zhu et al. [7].

The temperature dependence of equilibrium viscosity of glassy alloy above T_g can be described by Vogel–Fulcher–Tammann (VFT) relationship:

$$\ln\,\eta = \ln\eta_0 + \frac{DT_0}{T - T_0}, \qquad (2)$$

where D and T_0 are fragility parameter and VFT temperature, respectively. It can be seen that the temperature dependence of the viscosity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glass (Fig. 4) accords with the VFT relationship at 683–738 K. Fitting the isothermal data points with VFT relationship gives a VFT temperature of 390 K and the fragility parameter D of 28.85, which is similar to the result measured by different method of the same bulk metallic glass [8].

In principle, the fragile parameter D is defined as the slope at T_g for the curve $\log(\eta)$ against T_g/T, which reflects how closely the system obeys the Arrhenius law. Normally the D ranges from 2 to 100 when the liquid changes from fragile liquid to strong liquid. From Fig. 4 the fragile parameter of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass can be derived as about 39, which deviates from the fitting result. The viscosity of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG reaches 10^{12} Pa s at ~700 K (Fig. 4), which implies the supercooled liquid becomes glass through a viscous slow down. This value is a little higher than the calorimetric T_g (683 K) measured from DSC scan at a heating rate of 0.67 K/s in this work.

It can be found that the viscosity data point at 668 K (below T_g) deviates (Fig. 4), which is due to the incompletion of structural relaxation. Fan et al. [10] found that the viscosity of a $Pd_{43}Ni_{10}Cu_{27}P_{20}$ BMG during isothermal annealing increases gradually with annealing time and reaches almost a constant value after long annealing time indicating the relaxation from the amorphous solid state into the equilibrium supercooled liquid state. Zumkley et al. [11] reported that incompletely relaxed BMG exhibits lower diffusivities at temperatures below T_g than that after a long-term annealing. Within the temperature range of $T_g < T < T_x$, the relaxation time for a supercooled liquid is much shorter than the time scale allowed by the experimental conditions. Therefore, equilibrium viscosity can be directly measured by linearly heating the samples, and the isothermal and isochronal measurements should give similar value of viscosities. However, Fig. 4 shows the viscosities of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG measured under isothermal test is higher than those under continuous heating.

The isothermal and isochronal measurements of the viscosities with temperature are almost parallel (Fig. 4), therefore these differences should not result from the structural relaxation. The isothermal measurements took time for temperature stabilization. The BMG specimen might has slightly crystallized which is not able to be confirmed by XRD, and the viscosity become higher than the equilibrium value. On the other hand, during an isochronal test, the average temperature of the specimen might be a little higher than those in the isothermal test due to a heterogeneity of the sample

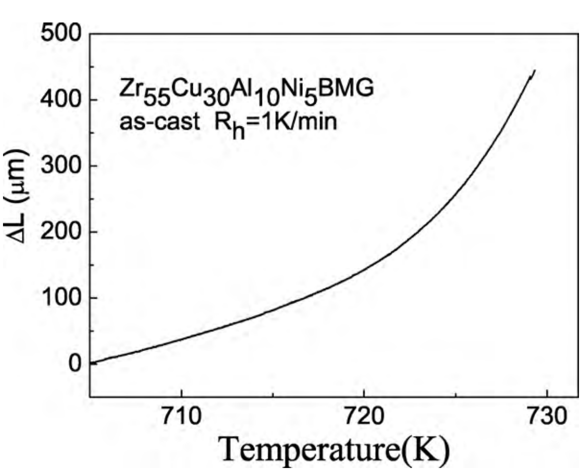

Fig. 2. The length change of $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glass with time under a heating rate of 1 K/min.

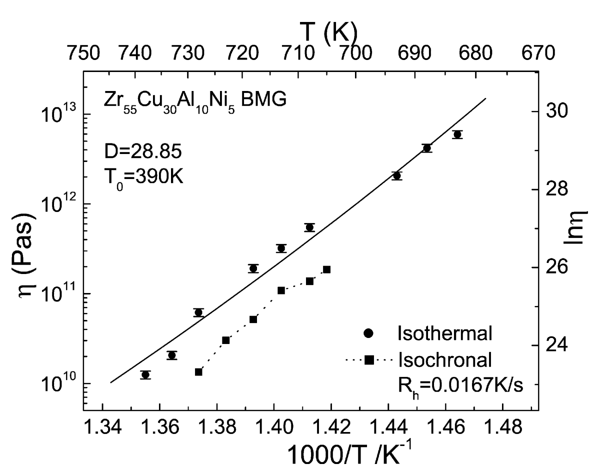

Fig. 4. Viscosities of $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glass measured at isochronal and isothermal annealing. The solid line is a VFT fit to isothermal data points.

temperature. Therefore with increasing the heating rate, the viscosity decreases significantly [3]. The isochronal measurement in this work was done under 1 K/min, so the viscosity values are lower than those from isothermal measurements, but higher than those from the measurement with a heating rate of 100 K/min by Yamasaki et al. [3].

4. Conclusions

(1) Isochronal measurement of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG at the heating rate of 1 K/min shows that large relative displacement about 450 μm was obtained from 705 to 728 K. Isothermal measurement indicates that the length change at each testing temperature kept linear with time.

(2) The viscosity from the isothermal measurement is higher than that from the isochronal measurement. This is attributed to the heterogeneity of the sample temperature during an isochronal annealing.

(3) The viscosity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG can be described by a VFT equation with a VFT temperature of 390 K and a fragility parameter D of 28.85.

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References

[1] S.M. Karim, L. Rosenhead, Rev. Mod. Phys. 24 (1952) 108–116.
[2] G.J. Diennes, H.F. Klemm, J. Appl. Phys. 17 (1946) 458.
[3] T. Yamasaki, S. Maeda, Y. Yokoyama, D. Okai, T. Fukami, H.M. Kimura, A. Inoue, Intermetallics 14 (2006) 1102–1106.
[4] A. Inoue, T. Zhang, Mater. Trans. JIM 37 (1996) 185–187.
[5] H. Kato, A. Inoue, H.S. Chen, Appl. Phys. Lett. 79 (2001) 4515–4518.
[6] Y. Kawamura, T. Shibata, A. Inoue, Appl. Phys. Lett. 69 (1996) 1208–1211.
[7] S.L. Zhu, X.M. Wang, F.X. Qin, A. Inoue, Intermatallics 15 (2007) 885–890.
[8] S. Maeda, T. Yamasaki, Y. Yokoyama, D. Okai, T. Fukami, H.M. Kimura, A. Inoue, Mater. Sci. Eng. A 449–451 (2007) 203–206.
[9] A.K. Doolittle, J. Appl. Phys. 22 (1951) 1472.
[10] G.J. Fan, H.-J. Fecht, E.J. Lavernia, Appl. Phys. Lett. 84 (2004) 487–489.
[11] T. Zumkley, V. Naundorf, M.P. Macht, G. Frohberg, Scr. Mater. 45 (2001) 471–477.