Journal of Non-Crystalline Solids 443 (2016) 103–107

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Thermo-mechanical study of bulk glass forming Zr-Cu-Ni-Al alloys

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ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 25 March 2016
Accepted 2 April 2016
Available online 22 April 2016

Keywords:
Zr-based
Bulk glasses
Viscosity
Glass transition temperature
Quasicrystals

ABSTRACT

The thermal stability and viscous flow behavior of bulk glass forming $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ and $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ alloys are studied. The viscosity experimental results are interpreted based on the free volume model (FVM). The values of the obtained model parameters are used to estimate the glass forming ability (GFA) in terms of Angell parameter, and the fracture strength of the alloys based on its correlation with the glass transition temperature (T_g). The viscosity data are compared with DSC measurements. The two glasses, having similar composition, revealed comparable T_g, but one of them ($Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$) showed substantially lower crystallization temperature due to quasicrystals formation. Higher GFA was obtained for $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ alloy.

1. Introduction

Bulk metallic glasses (BMGs) attracted much attention because of their unique properties and potential engineering applications in electrode materials, die materials, sporting equipment, mobile devices, surgical tools, military industry, etc. [1–4].

Multicomponent Zr-based metallic glasses are well known for their outstanding mechanical properties (high strength, high hardness and exceptional impact resistance) and high glass forming ability (GFA), which allows them to be produced in the form of large dimension BMG relatively easily [5–8]. These bulk metallic glasses are promising materials for biomedical applications such as bone fracture fixation components and artificial joints, where mechanical properties are important in order to avoid stress shielding, but still endure the forces in human body [9,10], and were used to create a pressure sensor with higher sensitivity than the conventional one [11].

Among the number of Zr-based BMGs the Zr-Cu-Ni-Al system is suitable for application, because of the high GFA, low cost, and nontoxicity. The Zr content in the best Zr-Cu-Ni-Al glass formers is found to be around 50–60 at.% [12,13]. It was shown to be a promising material for preparing amorphous micro-components for micro-electro-mechanical systems (MEMS) by hot embossing technology [14]. This and other similar alloys are used in the golf industry with significantly better performance than regular steel or titanium alloys [15].

During heating of BMG its viscosity drastically decreases at the glass transition temperature T_g and further decreases until the crystallization temperature T_x is reached. Many methods were applied to measure viscosity from the equilibrium melt down to undercooled liquid near T_g, such as parallel-plate rheometry, beam bending and capillary flow method [16–20], since the viscosity has a significant influence on the GFA of BMGs. The temperature dependence of the viscosity for various Zr based glasses as well as their thermal behavior by DSC are also studied thoroughly with the aim to predict the compositions with high GFA [21].

In this work we investigate the thermal stability and viscosity (non-equilibrium and quasi-equilibrium viscosity around T_g) of bulk glass forming $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ and $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ alloys using tensile tests equipment. The viscosity is determined at constant hearting rate and compared with DSC results.

2. Materials and methods

2.1. Alloys preparation and characterization

The quaternary Zr-Cu-Ni-Al master alloys were prepared by arc melting the mixture of the pure metals (Zr 99.8, Cu 99.95, Ni 99.95, Al 99.95) under argon atmosphere. Amorphous ribbons were produced by melt-spinning under helium atmosphere of 300 mbar, using quartz crucible and copper quenching wheel with a diameter of 250 mm and surface velocity of 35 m.s^{-1}.

The microstructure of the as-cast and annealed alloys was characterized by X-ray diffraction (XRD) with CuKα radiation. The glass transition

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.04.006
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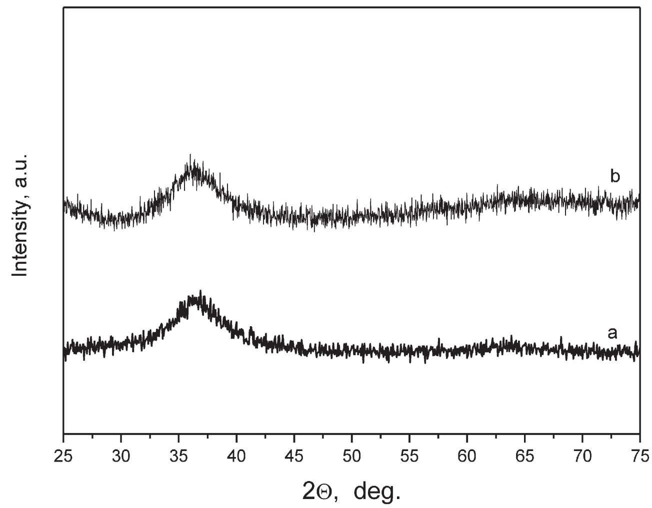

Fig. 1. X-ray diffraction patterns of as-cast $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ a) and $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ b) alloys.

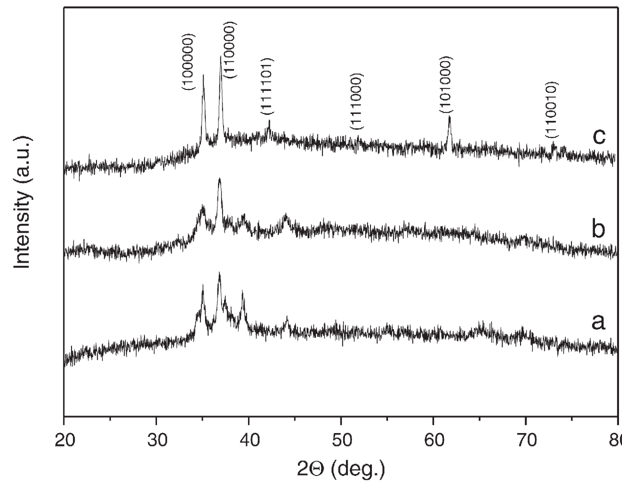

Fig. 3. X-ray diffraction of the alloys after annealing in DSC: a) $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ – 773 K, b) $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ – 773 K, c) $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ – 713 K.

temperature T_g and crystallization temperature T_x and enthalpy were measured by Perkin Elmer DSC 7 at a constant heating rate of 20 K/min.

The viscous flow behavior of the amorphous $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ and $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ alloys was studied by tensile tests homemade equipment using Perkin Elmer thermo-mechanical devise TMS-2 [22]. A silica glass assembly designed for high temperature creep measurement was applied. The measurements were carried out under loads ranging between 50 and 130 g. The length of the samples was kept at 4 mm. The temperature accuracy (± 1 K) of the TMS-2 was calibrated by using strips of pure Sn, Pb, Zn and Al of known melting points.

2.2. Theoretical background of the viscosity measurements and their interpretation

The basic assumption of the free volume model (FVM) used for interpretation of the viscosity experimental data is that viscous flow takes place through thermally activated events at specific sites in the structure, called flow defects. Duine et al. [23] have shown that the most generalized temperature dependence of the viscosity η of an amorphous alloy can be represented as:

$$\eta = \eta_0 T \exp\left(\frac{Q_\eta}{RT}\right)\left(\frac{1}{c_f}\right). \tag{1}$$

Here Q_η is the activation energy for the viscous flow, η_0 is a pre-exponential factor and c_f is the concentration of the flow defects. The equilibrium concentration of flow defects $c_{f,eq}(T)$ is given by.

$$c_{f,eq}(T) = \exp\left(-\frac{B}{T-T_0}\right), \tag{2}$$

where B and T_0 are two model parameters which can be related to the empirical constants B_{VFT} and $T_{0,VFT}$ in the classical empirical Vogel-Fulcher-Tammann equation. Combining Eqs. (1) and (2), the so-called 'hybrid' temperature dependence of quasi-equilibrium viscosity η_{eq} is obtained:

$$\eta_{eq}(T) = \eta_0 T \exp\left(\frac{Q_\eta}{RT}\right)\exp\left(\frac{B}{T-T_0}\right). \tag{3}$$

Eq.(3)describes the change of viscosity of glass forming undercooled (metallic) melts in the structural state, where the flow defect concentration follows immediately the changes of temperature. Russew et al. proposed an equation of Bernoulli of 2nd order [22] describing the change of c_f in the glassy alloy with temperature under non-isothermal conditions and at a constant heating rate q in the temperature range around the glass transition temperature T_g is:

$$c_{f,high}^{-1}(T,q) = \left[c_{f,0}^{-1} - \int_{T_0}^{T} Q(T')\exp\left(-\int_{T_0}^{T'} P\left(T''\right)dT''\right)dT'\right]\exp\left(\int_{T_0}^{T} P(T')dT'\right) \tag{4}$$

where $P(T) = -\frac{\nu_r}{q}\exp(-\frac{Q_r}{RT} - \frac{B}{T-T_0})$, and $Q(T) = -\frac{\nu_r}{q}\exp(-\frac{Q_r}{RT})$; ν_r is the attempt frequency, Q_r is activation energy of relaxation, $c_{f,0}$ is the initial defect concentration and R is the universal gas constant. Combining Eq. (1) with Eq. (4), one obtains the temperature dependence of viscosity η in the high temperature range near T_g. The Free Volume Model interpretation of the viscosity experimental data allows specifying the model parameters in Eq. (1) and Eq. (4) by using multi-parameter regression analysis.

One of the basic parameters of the vitreous state is the glass transition temperature T_g, which is usually defined rather arbitrarily as the

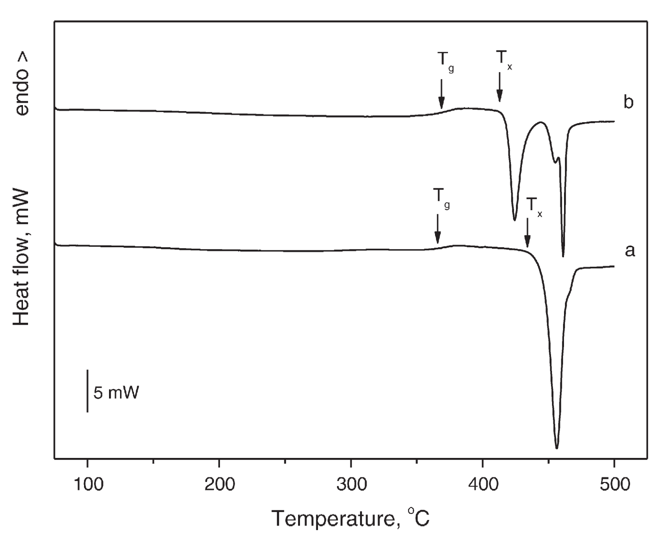

Fig. 2. DSC plots of $Zr_{69}Cu_{12.5}Ni_{11}Al_{7.5}$ a) and $Zr_{68}Cu_{13}Ni_{11.5}Al_{7.5}$ b) melt-spun alloys.