Journal of Non-Crystalline Solids 358 (2012) 150–154

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Investigation of viscosity and crystallization in supercooled-liquid region of Zr-based glassy alloys

Yan Li [a], Ran Li [a], Shujie Pang [a], Bingqing Chen [a], Konstantinos Georgarakis [b], Alain Le Moulec [b], Gavin Vaughan [c], Tao Zhang [a,*], Alain R. Yavari [b]

[a] Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, 100191 Beijing, China
[b] Euronano, SIMaP-CNRS, Institut National Polytechnique de Grenoble, 1130 rue de la Piscine, BP 75, 38402 St-martin-d'Heres Campus, France
[c] European Synchrotron Radiation Facilities (ESRF), 38402 Grenoble, France

ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form 29 August 2011
Available online 28 October 2011

Keywords:
Bulk metallic glass;
Viscosity;
Synchrotron;
Poisson's ratio

ABSTRACT

Using viscosity measurement method and in-situ heating synchrotron radiation, the viscosity of the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ (x = 0, 0.5, 1, 2) bulk metallic glasses (BMGs) in their supercooled liquid regions (SLRs) and the in-situ heating nucleation were investigated, respectively. In the SLR, the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ metallic glass which shows distinct plastic strain in compression exhibits higher viscosity than the other three BMGs, however their Poisson's ratios are almost the same. The synchrotron diffraction results show that crystallization happened in the SLR of the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ glassy alloy, which could be the reason for the higher viscosity and larger plastic strain in compression compared to the other three alloys. The fracture surfaces of the glassy alloys were observed and analyzed.

1. Introduction

Glasses can be roughly classified into two categories according to Angell's theory [1]: strong glass and fragile glass. For many glass formers with good glass-forming ability (GFA), the undercooled liquid is strong and the viscosity doesn't decrease a lot comparing to the fragile liquid [2]. Bulk metallic glasses (BMGs) have been preferred to crystalline alloys for several application areas due to the unique combination of high yield strength, high hardness, large elastic strain limit and high fatigue resistance [3–7]. However, for Fe [8], Co [9], Zr [2,10,11], Mg [12], La [13], Ca [14] and Cu [15] based metallic glasses with good GFA, the deformation was usually localized in shear bands and the catastrophic brittle fracture occur without obvious plastic strain. As the two most important factors of BMGs, GFA and plasticity are expected to show positive dependence on each other for engineering applications.

Investigations have been carried out on the intrinsic ductility of BMGs [16]. A large Poisson's ratio ν or K/G value (G and K are shear and bulk modulus, respectively) has been regarded as the characterization parameter of BMGs with good plasticity [17]. Recently, Poon et al. [18] have proposed using the shear modulus fluctuations (G^*/G) at the shear transformation zone (STZ) scale to represent the plasticity of BMGs. However, the process of shear localized deformation via shear banding of BMGs should also be considered. In the process of shear localization, the bands will experience extreme conditions, such as high strain and heating rate, and the local temperature in the shear bands may increase to the glass transition temperature (T_g) or even the melting temperature (T_m) of the alloy followed by rapid quenching [19–21]. The viscosity variation or nanocrystallization induced by the increased local temperature and large strain in shear bands could promote the generation, propagation and arrestment of them [22], and therefore produce a positive effect on the macroscopic plasticity. In this work, the viscosity and crystallization behavior in the supercooled liquid region (SLR) of the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ (x = 0, 0.5, 1, 2) bulk metallic glasses (BMGs) were investigated. The $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ glassy alloy with high GFA and large plastic strain shows large viscosity in the SLR due to the precipitation of crystals.

2. Experimental

The $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ (x = 0, 0.5, 1, 2) master alloys were produced by arc melting the mixture of the high purity elements under argon atmosphere. Cylindrical glassy samples with 2.5 mm in diameter were prepared by copper mould casting method. The glass transition and crystallization behaviors of the metallic glasses were investigated by differential scanning calorimeter (DSC) at a heating rate of 0.33 K/s protected by argon gas flow. The compression test specimens with a length to diameter ratio of 2:1 were cut from the cylindrical samples. Quasi-static compressive tests were performed on a material test system (MTS) at a strain rate of 4.2×10^{-4} s^{-1} at room temperature. With the same shape and length to diameter ratio, elastic moduli of these BMGs were measured by resonant ultrasound spectroscopy. The fracture

* Corresponding author. Tel.: +86 1082316192; fax: +86 1082339705.
E-mail address: zhangtao@buaa.edu.cn (T. Zhang).

0022-3093/$ – see front matter
doi:10.1016/j.jnoncrysol.2011.08.031

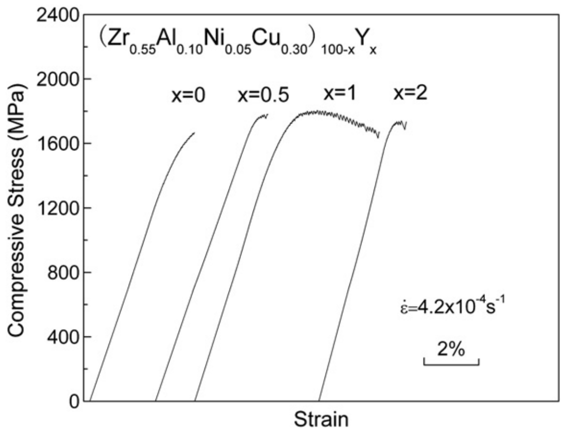

Fig. 1. Compressive stress–strain curves of $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ metallic glassy system. $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ MG shows clear plastic flow and larger plastic strain than others.

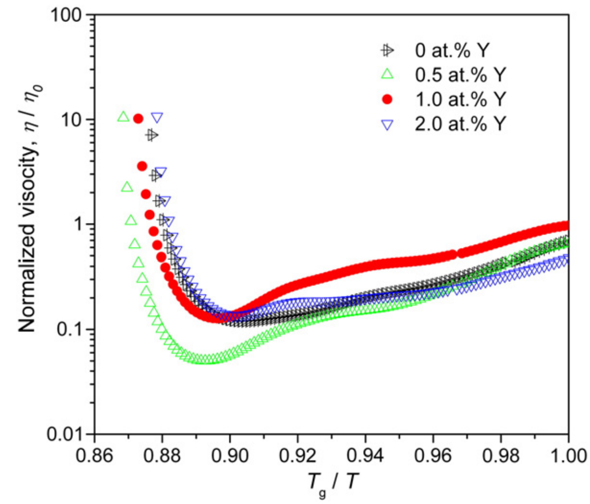

Fig. 2. TMA curves of $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ metallic glassy system in their SLR. $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ MG exhibits higher viscosity η than other alloys, which match the high plasticity in compression.

surfaces after the compression tests were observed by scanning electron microscopy (SEM).

Viscosity in the supercooled liquid region of the BMGs was measured using parallel plate rheometry in a Perkin–Elmer TMA7 analyzer with a quartz penetration probe and a static force of 2.6 N in argon atmosphere. The heating rate was 0.33 K/s. By measuring the penetration of the probe versus temperature for the samples which completely fill the space between quartz probe and lower plate, the viscosity is given by the Stenfan equation [23,24]

$$\eta = \frac{-2Fh^3}{3\pi a^4 (dh/dt)} \quad (1)$$

where η is the viscosity, F the applied load, h the height of the sample, and a is the radius of the plates. The aspect ratio $A = h/a$ is about 0.033.

Structures of the glassy alloys in the supercooled liquids were studied by high energy synchrotron radiation. Rectangular plates with 0.5 mm in width cut from metallic glasses were sealed in quartz capillaries under the protection of argon flow. The capillaries were placed on a computer-controlled Linkam hot stage. The plates were detected by high energy synchrotron radiation on the ID11 beam line of the European Synchrotron Radiation Facilities (ESRF) with in-situ heating and cooling cycles. The beam was monochromatized using a liquid nitrogen-cooled double crystal silicon monochromater. The photon energy was 93.15 keV corresponding to an X-ray wavelength of about 0.01331 nm. The diffraction spectra were acquired in transmission through the quartz capillary in the Linkam hot-stage by a 2D CCD camera. The heating and cooling rate in the Linkam was 0.5 K/s. Acquisition and data processing times were such that a full spectrum was obtained about every 10 s.

3. Results

The $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ (x = 0, 0.5, 1, 2) metallic glasses show good GFA and the critical diameter of fully glassy cylinder is 12 mm when 1 at.% Y is doped [25]. Interestingly, the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ glassy alloy exhibits the highest plasticity in compression in the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ (x = 0, 0.5, 1, 2) system. As shown in Fig. 1, the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ alloy shows compressive plasticity up to 3.5% with distinct serrations in the curve indicating that the stress fluctuation is in the range of 1% of the yield stress [20], while the plastic strains of the other three BMGs are less than 1% before catastrophic fracture. In this system, the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ alloy exhibits the predominance in GFA and plasticity simultaneously.

As mentioned above, Poisson's ratio (ν) and G/K have been used as the parameters for the evaluation of plasticity. In the present work, the critical diameters, thermal and mechanical properties and elastic moduli of the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ (x = 0, 0.5, 1 and 2) metallic glasses are measured and summarized in Table 1. These alloys exhibit higher ν (0.37) than the critical value of 0.32 and the variations of ν and G/K in this system are negligible in the system. Though the Zr-based glassy alloys exhibit similar Poisson's ratio, they show different plastic performances. According to the results shown here, ν can hardly be regarded as a very accurate parameter or sufficient condition for evaluating the plasticity of this glassy alloy system.

The measured viscosity of the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{100-x}Y_x$ metallic glasses was normalized by the value of $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ at its glass transition temperature (η_0). In Fig. 2, the normalized viscosity, η/η_0 is plotted as a function of T/T_g of the four alloys respectively. It is observed that in their own SLR, the normalized viscosity decreases with the increase in temperature and the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ shows the highest value among the alloys. All the alloys present a sharp increase in viscosity at their T_x, which is induced by crystallization.

In order to investigate the cause of its high viscosity, the $(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$ glassy alloy was detected by high energy synchrotron radiation with in-situ heating equipment. Fig. 3(a, b) shows the X-ray diffraction ring-like patterns and spectra of the alloy at different temperatures in the SLR during in-situ heating, respectively. At the temperature of 682 K, no obvious crystallization happened seen the spectra in Fig. 3(b). When the temperature is higher than 694 K, the presence of crystalline phase in the glassy matrix can be noticed judged from the

Table 1
Thermal and mechanical properties and elastic modulus of Zr-based metallic glasses.

Samples (at.%)	T_g (K)	T_x (K)	ΔT_x (K)	Poisson's ratio ν	E (GPa)	G (GPa)	K (GPa)	G/K	σ_f (MPa)	ε (%)
$Zr_{55}Al_{10}Ni_5Cu_{30}$	687	759	72	0.371 ± 0.0004	86	31	111 ± 0.4	0.28	1648 ± 92	0.2 ± 0.08
$(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99.5}Y_{0.5}$	676	754	74	0.371 ± 0.0002	85	31	110 ± 0.5	0.28	1722 ± 76	0.5 ± 0.07
$(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{99}Y_1$	678	750	72	0.371 ± 0.0004	83	30	108	0.28	1697 ± 112	3.5 ± 0.21
$(Zr_{0.55}Al_{0.1}Ni_{0.05}Cu_{0.3})_{98}Y_2$	675	745	70	0.371 ± 0.0004	81	29	104	0.28	1712 ± 109	0.7 ± 0.08