Materials Science & Engineering A 620 (2015) 352–358

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Homogeneous viscous flow behavior of a Cu–Zr based bulk metallic glass composites

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ARTICLE INFO

Article history:
Received 8 July 2014
Accepted 20 September 2014
Available online 30 September 2014

Keywords:
Bulk amorphous alloys
Composites
Mechanical characterization
High temperature deformation

ABSTRACT

In this paper, $Cu_{40}Zr_{44}Ag_8Al_8$ bulk metallic glass composites (BMGCs) consisting of various volume fraction of nanocrystals embedded in the amorphous matrix was synthesized by controlled annealing treatment of an as-cast BMGCs. The high temperature compression behaviors of the BMGCs were characterized in the supercooled liquid region. Results show that the flow stresses keep increasing after an initial decrease with extension of the annealing time. With annealing the values of activation volume V_{act} is determined to be increasing from 283.6216 Å^3 to 305.553 Å^3, suggesting that the jump of atoms is a cooperative process during the high-temperature deformation. Flow behavior of the BMGCs annealed for less than 8 min transform from Newtonian to non-Newtonian dependant on the stain rate and can be successively fitted by the visco-plasticity model. Fitting results indicate that deformation behaviors of these samples are governed by homogeneous flow of the amorphous matrix and indeed determined by the viscosities in the Newtonian flow stage. However, the BMGCs annealed for 8 min exhibit a non-Newtonian flow over the entire compression process and fail to be fitted by the visco-plasticity model. Micrographs of the sample reflect an impinged structure, indicating that high temperature deformation behavior of the BMGCs with high volume fractions of particles is indeed controlled by that of a backbone of particles.

1. Introduction

Compared with the traditional alloys, bulk metallic glasses (BMGs) have been paid worldwide attentions due to their prominent mechanical properties, including high compressive fracture strength (~2 GPa), large elastic strain (~2%), high tensile strength (~6 GPa), excellent corrosion resistance and good soft magnetic property [1–3]. Furthermore, the presence of a large supercooled liquid region (SLR) and a high thermal stability provides new opportunities for high temperature forming. Previous studies have shown that BMGs exhibit superplastic behavior in the SLR. The homogeneous flow behavior of BMGs at high temperature transit from Newtonian to non-Newtonian, depending on testing stain rate and temperature. Moreover, it is shown that the homogeneous flow behavior of BMGs can be quantitatively described by the transition state theory [4,5].

However, seldom experimental results about the homogeneous flow behavior of BMGCs have been presented up to now, keeping in mind that it is the BMGCs consisting of secondary particles in the amorphous matrix always exhibit improved properties at room temperature [6,7]. In the previous investigations, Fu et al. [8] found that rheological behavior of the Zr–Cu–Al BMGCs with various crystal volume fractions ($\nu_f = 0$–20%) can be explained in terms of the transition state theory, in which Newtonian behavior followed by a transition to non-Newtonian behavior. However, in the experiments of Wang et al. [9], the partially crystallized BMGCs Vit 1 just only reveals non-Newtonian flow and the stress–strain rate relation obeys the sin *h* law, even though the crystal volume fractions is only 10%. The exact deformation mechanism of BMGCs is still unclear.

In the present study, compression tests will be carried out to present the high temperature deformation behavior of partially crystallized $Cu_{40}Zr_{44}Ag_8Al_8$ BMGCs and more precisely to discuss the influence of the crystals on high temperature flow behavior of the BMGCs. Deformation behavior of four different volume fractions of in situ particles are compared and a visco-plasticity model based on free volume theory was applied to explain the cause of the influence.

2. Experimental

Master ingots with a nominal composition of $Cu_{40}Zr_{44}Ag_8Al_8$ (in atomic percentage) were prepared by arc melting of pure

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http://dx.doi.org/10.1016/j.msea.2014.09.080
0921-5093/© 2014 Published by Elsevier B.V.

metals (99.999% purity) for 3 times in a high purity argon atmosphere, followed by suction casting into a water-cooled Cu mold to get rods with a diameter of 6 mm and length of 30 mm under 7 kW of power and negative pressure of 0.02 MPa by the electro magnetic levitation suction casting equipment. The investigated BMGCs with various volume fractions of nanocrystals dispersed in the amorphous matrix were synthesized by isothermally annealing the as-cast samples at the temperature of 738 K in the supercooled liquid region for different times (0, 3, 5, 8 min).

The thermal characteristic parameters of the BMGCs were determined by differential scanning calorimeter (DSC, NETZSCH STA 449C Instruments) at the heating rate of 20 K min^{-1}. T_g was determined to be 706 K for the sample, whereas T_x was 784 K. The thermal parameters are comparable to those studied by Liu et al. Hence the sample exhibits a large SCL region up to 78 K. The microstructure of the BMGCs were investigated by X-ray diffractometer (XRD, Japan Nikkaku D/max-2400, Cu K_α) and scanning electron microscopy (SEM, JSM-6700F). The etched solutions were 1% hydrofluoric acid aqueous solution for SEM observation.

To minimize the experimental errors for various strain rates between different experimental conditions and samples, strain rate jump compression tests were carried out. For compression tests, cylindrical samples with an aspect ratio of 1:2 were cut from the rods by a diamond slicing machine and both compressive sides were polished in order to be parallel. High temperature compression tests were conducted using a Gleeble 3500 machine at T_a=721 K in the SCL region. Thermocouples were welded in the middle of the samples to detect in situ the test temperature. To minimize or avoid crystallization during the heating stage, the tests should be conducted as soon as possible. First heat the samples quickly to T_a −40 K at the rate of 10 K s^{-1}. Then heat them to T_a at the same rate of 20 K min^{-1} as used in DSC measurements, considering the fact that T_g is not a unique physical property of the glass but rather a rate dependent kinetic quantity. Compression testing started only after the samples were maintained at T_a for 30 s to homogenize temperature. The investigated true strain rate interval was from 2.5×10^{-4} to $1\times10^{-2}\ \text{s}^{-1}$.

3. Results and discussion

3.1. Materials characterization

Fig. 1 shows XRD pattern of the as-cast $Cu_{40}Zr_{44}Ag_8Al_8$ sample. The XRD pattern showed a broad halo peak, characteristic of the amorphous phase. Fig. 2 shows SEM observation of the BMGCs isothermally annealed at 738 K for 0, 3, 5, 8 min. SEM image of the as-cast sample reveals a few nano-sized precipitates in the range of 20–50 nm embedded in the amorphous matrix, as shown in Fig. 2(a). In contrast, SEM images of the other three annealed samples show that particles with a spherical size about 500 nm have precipitated from the amorphous matrix, as shown in Fig. 2(b)–(d). Especially for the sample annealed for 8 min, particles precipitate from the amorphous matrix in a large number and start to impinge to each other.

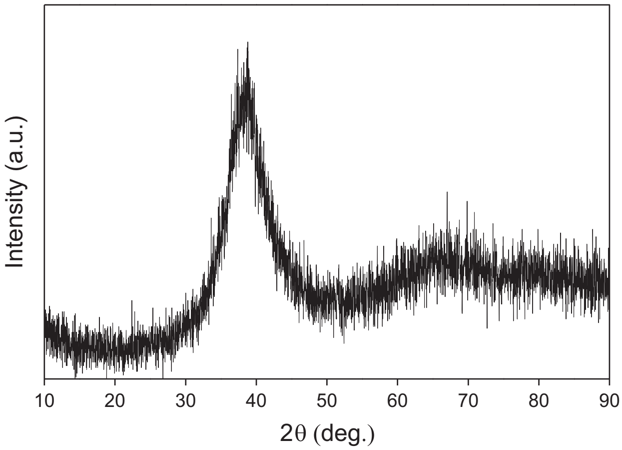

Fig. 1. XRD pattern of the as-cast $Cu_{40}Zr_{44}Ag_8Al_8$ sample.

3.2. Deformation behavior of the as-cast samples

In order to determine the rheology information of the BMGCs, strain rate jump tests were carried out at the temperature of 721 K and the Backofen function is introduced [10].

$$\sigma_{\text{flow}} = K\dot{\varepsilon}^m \tag{1}$$

where σ_{flow} is the flow stress, K is a constant, $\dot{\varepsilon}$is the strain rate and m is the strain rate sensitivity exponent.

Taking the logarithm leads to the relationship

$$\lg\sigma = m\lg\dot{\varepsilon} + \lg K \tag{2}$$

a straight line, whose slope yields the value m.

According to Refs. [10,11], the flow stress is defined as the peak-yield stress in order to minimize the elastic contribution (the elastic strain rate $\dot{\sigma}/E=0$ at the peak stress). Thus to ensure that the stresses can reach to the peak-yield points and the measurements are performed within the shortest time in order to avoid structural modification taken place in the amorphous matrix, a strain interval of 0.04 is chosen for each strain rate. In the compressive process, drum shape is formed on the side surface of the cylindrical billet, which is similar to the upsetting process of the alloy [12]. The photograph of the deformed sample is shown in the inset of Fig. 3. The sample keeps a smooth surface without any cracks until the tested strain reached ε=36%, indicating the BMGCs process a homogenous flow behavior during high temperature deformation.

Fig. 3 shows true stress versus true strain curve of the as-cast samples obtained by strain rate jump compression test performed at 721 K. It is noted that even at the highest strain rates the material still exhibits fully homogenous deformation behavior, which indicates a good compressibility of the BMGCs. The steady state plastic flow was observed at low strain rate. However, when the testing strain rate is increased (e.g. $\dot{\varepsilon}=2.5\times10^{-4}\ \text{s}^{-1}$), stress overshoots are observed whose amplitude is obviously increasing with the strain-rate, as had been extensively studied [13,14].

3.3. Viscosity flow behavior of all the BMGCs

Fig. 4 shows stress–strain curves of all the BMGCs. Deformation curves of the annealed samples are quite similar to that of the as-cast sample, which is seriously dependent on the testing strain rate. As the strain rate increasing, steady state plastic flow changes to obvious stress overshoots. Furthermore, it is remarkable to note that the flow stresses keep increasing after an initial decrease with extension of the annealing time.

According to Kim [15], due to the differences in the thermal and elastic properties between particles and amorphous matrix, residual stress can arise during the sample preparation. He demonstrated the higher compressive strength in W-rich particle-reinforced Ti-based BMGCs as being the result of the generation of tensile residual stress in the amorphous matrix upon cooling during sample preparation. In the case of ceramic particle-reinforced alloy composites [16], it has been explained that it is also the tensile residual stress that contribute to the high compressive strength. A similar effect is expected to work in the as-cast $Cu_{40}Zr_{44}Ag_8Al_8$ BMGCs. Residual stress would normally be left