Journal of Alloys and Compounds 549 (2013) 370–374

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Analysis of atomic mobility in a $Cu_{38}Zr_{46}Ag_8Al_8$ bulk metallic glass

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ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 18 October 2012
Accepted 22 October 2012
Available online 1 November 2012

Keywords:
Bulk metallic glass
Dynamic mechanical analysis
Internal friction
Relaxation
Defects

ABSTRACT

Atomic mobility in as-cast and annealed $Cu_{38}Zr_{46}Ag_8Al_8$ bulk metallic glass samples is analyzed by performing dynamic mechanical analysis. The loss factor is directly connected to the energy lost during application of the stress. Structural relaxation process and crystallization lead to a decrease of the atomic mobility in the bulk metallic glass. A physical model, based on the concept of quasi point defects is introduced, to describe the atomic mobility. Movements in amorphous materials are correlated. The correlation factor χ reflects the atomic mobility in bulk metallic glasses: structural relaxation and crystallization lead to a decrease of χ, implying the reduction of atomic mobility. The evolution of elastic, visco-elastic and viscoplastic components after structural relaxation and partial crystallization state during the mechanical response has been obtained. Compared with as-cast state, structural relaxation induced an increase of elastic component and a decrease of visco-elastic component in the metallic glass.

1. Introduction

Mechanical and physical properties of materials are related to the atomic or molecular mobility. This mobility is sensitive to local atomic arrangements, i.e. to the order degree [1–3]. Amorphous materials, e.g. bulk metallic glasses, are in out of equilibrium state characterized by a lack of long-range topological order. However, existence of structural heterogeneity in metallic glasses has been confirmed in recent investigations, namely, short-range order and medium-range order in metallic glasses was observed [4–6]. It should be emphasized that the features of the heterogeneity in metallic glasses depend on thermal treatment. These treatments can induce a progressive elimination of these heterogeneities and thus enhance the order degree. Starting from as-cast samples, annealing induces an evolution towards either structural relaxation (when annealing temperature is below the glass transition temperature T_g) or crystallization (when annealing temperature is above the T_g). In such a scenario, heat treatment leads to atomic movement in metallic glasses and so to modifications of enthalpy and entropy [7–9].

Many theoretical and experimental methods have been introduced to elucidate the mechanisms of atomic mobility in metallic glasses, suggesting that atomic mobility depend on structural heterogeneity of bulk metallic glasses [10–14]. Dynamic mechanical analysis (DMA) is a useful tool to investigate atomic mobility in amorphous materials [7,15]. A periodic stress $\sigma = \sigma_0\cos(\omega t)$ is applied (ω is the angular frequency, and $\omega = 2\pi f$, where f is the frequency). In amorphous materials, the induced deformation is usually not perfectly elastic and includes a visco-elastic component. The resulting deformation writes: $\varepsilon = \varepsilon_0\cos(\omega t + \delta)$, where δ is the phase lag. The visco-elastic phenomenon induces an energy loss ΔW during a cycle, which is directly connected to δ by the simple relation: $\Delta W/W = 2\pi \cdot \tan(\delta)$. From the knowledge of σ, ε and δ, the two components of the shear modulus may be deduced: G′ (storage modulus) and G″ (loss modulus). So the atomic mobility may be approached by DMA. Physical modeling and quantitative description of this mobility have been proposed in the literature. This point will be discussed.

Compared with as-cast state, effect of structural relaxation and partial or total crystallization on the atomic mobility is examined in the present paper. This strategy can help us to answer how to determine and unveil the nature of atomic mobility in metallic glasses.

2. Experimental procedure

$Cu_{38}Zr_{46}Ag_8Al_8$ bulk metallic glass samples were fabricated by suction casting technique with a thickness of 2 mm. All the samples were re-melted several times to promote the homogeneity. This model alloy presents excellent glass forming ability, wide super-cooled liquid region and high mechanical properties. X-ray diffraction (XRD) experiments were conducted at room temperature to examine their amorphous feature by Cu Kα radiation produced by a commercial device (D8, Bruker AXS Gmbh, Germany). Dynamic mechanical measurements were carried out in an inverted torsion mode using a mechanical spectrometer described by Etienne et al. [16] Experiments were performed using a sinusoidal stress, either at a fixed frequency (ranging from 10^{-4} to 1 Hz) during continuous heating with a constant heating rate or at a given temperature with different frequencies. Experimental samples with the dimension of 30 mm (length) × 2 mm (width) × 1 mm (thickness) were prepared using electric discharge machining. All the experiments were performed in a high vacuum atmosphere and strain amplitude was lower than 10^{-4}. The fluctuation of the temperature during the experiments was ±0.1 K.

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http://dx.doi.org/10.1016/j.jallcom.2012.10.113

3. Experimental results and discussion

Fig. 1 displays the evolution of the loss factor during a continuous heating (heating rate: 3 K/min) with a constant frequency (0.3 Hz). Let us first consider the as-cast state. At low temperature, the loss factor is very low, i.e. the atomic mobility is very limited. A maximum is observed at about 730 K, corresponding to the main relaxation observed in all the amorphous materials and related to the dynamic glass transition. Then, in the supercooled liquid region, the loss factor is lower. The second maximum corresponds to the onset of the crystallization. Similar experimental data have been depicted in other based metallic glasses [7,17–20]. From these results we can define adequate annealing conditions inducing various microstructural states: annealing at 660 K (16 h) will induce a structural relaxation, heating to 800 K leads to a partial crystallization, heating to 973 K gives a fully crystalline state.

The main results displayed in Fig. 1 are as follows:

- States 1 and 2 correspond to amorphous states. The loss factor is high and the main relaxation is clearly observed. Structural relaxation reduces the loss factor, i.e. reduces the atomic mobility.
- States 3 and 4: the existence of crystalline particles induces a decrease in the loss factor and the main relaxation is no longer observed. So, microscopically, the formation of non-amorphous particles during heating at high temperature induces a molecular mobility decrease in bulk metallic glasses.
- No pronounced β relaxation peak is detected whatever the state. However, on the low temperature side of the maximum a shoulder is observed, mainly in the as cast-state. Previous experiments called this shoulder "excess wing" and suggested that this excess wing is the high frequency flank of β relaxation loss peak submerged under α relaxation loss peak, indicating that the mechanism of excess wing is the same with β relaxation in glassy materials [21–23].

To further assess the effect of atomic arrangement on the atomic mobility in $Cu_{38}Zr_{46}Ag_8Al_8$ bulk metallic glass, isothermal experiments in $Cu_{38}Zr_{46}Ag_8Al_8$ bulk metallic glass were carried out in the range from 655 to 720 K at various frequencies. Master curves of the loss factor *vs* frequency were obtained with help of the time-temperature superposition principle (Fig. 2) (Reference temperature is 690 K). In order to well describe the experimental phenomena, the as-cast state was regarded as reference state: annealing below T_g induces a limited loss factor decrease, while partial crystallization and total crystallization lead to a more pronounced loss factor decrease. When the specimen is fully crystalline, the loss factor becomes independent on frequency, so the behavior is elastic, the viscoelastic and viscoplastic components are being negligible.

Many models or theories have been proposed to describe the molecular or atomic mobility in amorphous materials, e.g. free volume theory [10,11], Adam–Gibbs theory [24], potential energy landscape (PEL) theory [25] and Argon's theory [26]. Perez introduced a very similar concept of "micro shear domains (MSD)" occurring in weak zones, called quasi point defects [27]. Based on the major assumption that density fluctuations in amorphous materials (polymer, bulk metallic glasses and other non-crystalline solids) could be considered as quasi-point defects, Perez has proposed a theory to describe the physical and mechanical properties in amorphous materials. The defect concentration C_d strongly depends on temperature and could be derived from by Boltzmann statistics. Structural relaxation and atomic mobility could be described according to diffusion-aided annihilation of the defects until new thermodynamic equilibrium is formed when annealing temperature is lower than T_g [27,28]. Movements of atoms (or molecules) are assisted by quasi-point defects and a hierarchical correlation exists, as proposed initially by Palmer et al. [29].

In the framework of this quasi-point defects model, the dynamic modulus as a function of frequency is given by the following equation [30]:

$$G^*(i\omega) = \frac{G_u}{1 + \lambda(i\omega\tau_{mol})^{-\chi} + (i\omega\tau_{mol})^{-1}} \quad (1)$$

where ω is the angular frequency. λ is a numerical factor near unity. τ_{mol} corresponds to the mean duration of the movement of a structural unit over a distance equal to its dimension. χ is a correlation factor, which is associated with the quasi-point defects concentration, ranging from 0 (full order) to 1 (full disorder). $\chi = 0$: maximum order, corresponds to a perfect crystal, any movement of a structural unit requires the motion of all other units. $\chi = 1$: maximum disorder, corresponds to a perfect gas, all the movements are independent on each other.

The loss factor can be expressed as [30]:

$$\ln(\tan\delta) = \frac{U_\beta}{kT} - \chi\ln\omega - \chi\ln\tau^* + \ln\lambda \quad (2)$$

where U_β is the apparent activation energy for the structural unit movement. k is the Boltzmann constant and T is temperature.

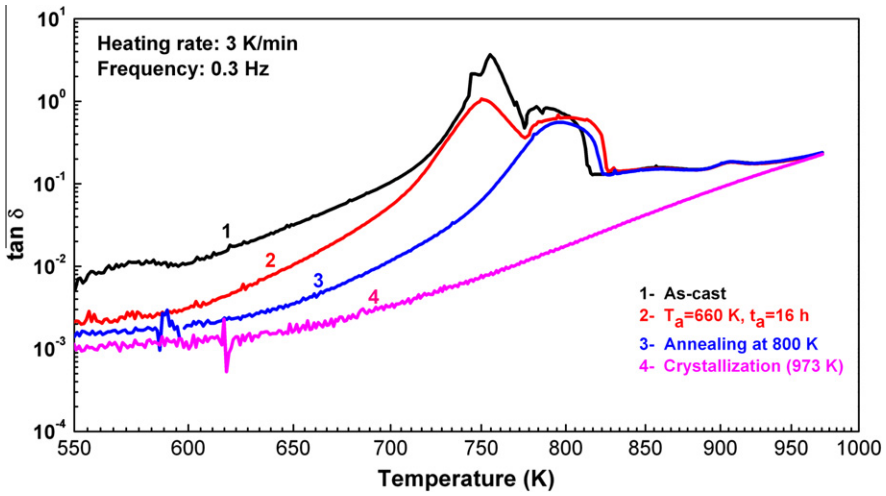

Fig. 1. Temperature dependence of the loss factor tanδ for $Cu_{38}Zr_{46}Ag_8Al_8$ bulk metallic glass in different states: as-cast, structurally relaxed (annealed at 660 K for 16 h), partially crystallized (heating to 800 K) and crystalline (heating to 973 K), respectively. (Frequency is 0.3 Hz and heating rate is 3 K/min.)