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Viscoelasticity of Cu- and La-based bulk metallic glasses: Interpretation based on the quasi-point defects theory

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ABSTRACT

The dynamic mechanical relaxation of metallic glasses is closely associated with the physical and mechanical properties. In the current work, the dynamic mechanical relaxation behaviors of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses are investigated by mechanical spectroscopy. In general, metallic glasses display two relaxation modes: main (α) relaxation and the slow secondary (β) relaxation. The α relaxation is linked to the dynamic glass transition phenomenon and viscous flow while the slow β relaxation is associated with many fundamental issues, such as diffusion and glass transition phenomenon. The experimental study shows $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glass displays a noticeable slow β relaxation. Contrarily, the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass relaxation process takes the form of an "excess wing". In the framework of quasi-point defects (QPD) theory, the dynamic mechanical response of the metallic glasses is discussed.

1. Introduction

Application of constant stress on a glass induces creep through three simultaneous deformation mechanisms: elastic, viscoelastic and viscoplastic. Due to its metastable state, the viscoelastic properties are one of the key concerns in glass-forming liquids. Metallic glasses, also called amorphous alloys, have been attracting tremendous research interest due to their specific combination of structural and functional properties, such as superb strength, high elastic limit, excellent thermoplastic formability, good corrosion resistance, and superior biocompatibility [1–5].

The understanding of the viscoelastic behavior of metallic glasses is very important for both the fundamental research and engineering application. Mechanical spectroscopy or dynamic mechanical analysis (DMA) is a powerful tool to investigate the viscoelastic behavior and dynamic mechanical relaxations of metallic glasses and metallic glass matrix composite [6–10]. Interestingly, metallic glasses show two relaxation kinetics processes, which are called main relaxation (α relaxation) and secondary relaxation (β relaxation) [11,12]. On the one hand, it is widely accepted that α relaxation is connected with the dynamic glass transition and the viscous flow behavior, which corresponds to the cooperative atomic movements. On the other hand, the β relaxation is closely related to local atomic motion, which appears at lower temperature or higher frequency [13–15]. It has been regarded that the β relaxation acts as a precursor of the main α relaxation [7,14,16–19]. Many investigations proved that the β relaxation process is closely linked to internal physical and mechanical properties of metallic glasses [6–8,14,20]. However, the physical mechanism and nature of mechanical relaxation in metallic glasses is still unclear and requires further study.

Here we analyze the dynamic mechanical response of two archetypal metallic glasses. $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses were investigated by mechanical spectroscopy. We found that compared with the $Cu_{46}Zr_{45}Al_7Y_2$ metallic glass, $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ metallic glass displays an evident β relaxation below glass transition temperature T_g. The observed dynamic mechanical relaxation behaviors are analyzed within the framework of the quasi-point defect theory. It is found that the experimental results are in good agreement with the predictions of the quasi-point defect theory.

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2. Experimental procedure

$Cu_{46}Zr_{45}Al_7Y_2$ (at%) and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ (at %) bulk metallic glasses were chosen as model alloys due to their high glass forming ability (GFA) and excellent thermal stability [21,22]. The metallic glasses were prepared by copper mold suction casting technique in a melting equipment under purified argon atmosphere. All the ingots of model alloys were re-melted at least 5 times to keep chemical homogeneity.

The amorphous nature at ambient temperature of the Cu- and La-based bulk metallic glasses was tested by X-ray diffraction (XRD), using Cu Kα radiation produced in a commercial device (XRD, Philips PW3830). The thermal stability of the metallic glasses was examined by differential scanning calorimetry (DSC, Netzsch DSC 200F3) at a constant heating rate of 3 K/min. The thermal parameters, such as glass transition temperature T_g, crystallization onset temperature T_x and super-cooled liquid temperature range (ΔT, $\Delta T = T_x\text{-}T_g$) were obtained based on the experimental results.

Mechanical spectroscopy or dynamic mechanical analysis was used to study the bulk properties (i.e., modulus, compliance, internal friction) of materials. In the current research, dynamic mechanical behavior of the metallic glasses was studied by commercial dynamic mechanical analysis (DMA, TA Q800) and an inverted torsion pendulum for internal friction measurements (homemade apparatus in INSA de Lyon, France). The dynamic mechanical relaxation behavior of the metallic glasses have been described in the previous literature [23]. When the sinusoidal stress $\sigma = \sigma_0 \sin(\omega t)$ (σ_0 is the initial stress, ω is the angular frequency and $\omega = 2\pi f$, where f is the driving frequency) is applied to the sample, the strain in the materials can be measured. The mechanical response of the sample is $E = \sigma/\varepsilon$, which consists in two parts: the storage modulus E' and the loss modulus E''. Similarly it is also define shear storage and loss moduli during the deformation as G' and G''. The phase lag δ between the applied stress and the recorded strain depends on the material, frequency and temperature. While elastic materials show no phase lag ($\delta = 0$), positive phase lags are due to the viscoelastic behavior during the deformation.

According to deformation modes of the instrument, in complex notation, on the one hand, for the DMA Q800 (measured at single cantilever bending model), one can write the complex modulus $E^* = E' + iE''$, where E^* is the complex modulus. On the other hand, for the inverted torsion pendulum apparatus (tested at torsion model), the complex shear modulus $G^* = G' + iG''$, where G^* is the complex shear modulus. As a consequence, the loss factor (also called internal friction) or mechanical damping $\tan\delta = \frac{E''}{E'} = \frac{G''}{G'} = \frac{1}{2\pi}\frac{\Delta W}{W}$ is also determined. It needs to be mentioned that the energy loss (ΔW) induced during one loading cycle, which reveals the atomic or molecular mobility, is then directly connected to the phase lag δ.

The dimension of experimental samples for the DMA TA Q800 and the inverted torsion pendulum testing is around 30 mm (length) × 3 mm (width) × 1 mm (thickness). Experiments were carried out in two modes: (I) Isochronal measurements were performed in DMA TA Q800 at a constant heating rate of 3 K/min with a different driving frequencies (i.e., 1, 2, 4, 8 and 16 Hz). (II) Isothermal tests were carried out at the inverted torsion pendulum under frequency ranges from 10^{-2} to 2 Hz.

3. Experimental results

3.1. XRD analysis and thermal properties of the metallic glasses

Fig. 1 shows XRD patterns of the $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses. The XRD patterns display the typical profile of glassy materials, with no detectable sharp Bragg peaks, which indicates that the whole volume of the metallic glass samples is in amorphous state. The thermal properties of the studied

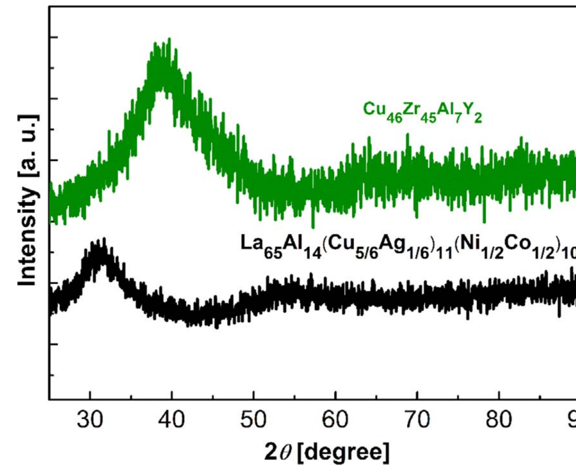

Fig. 1. XRD patterns of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses.

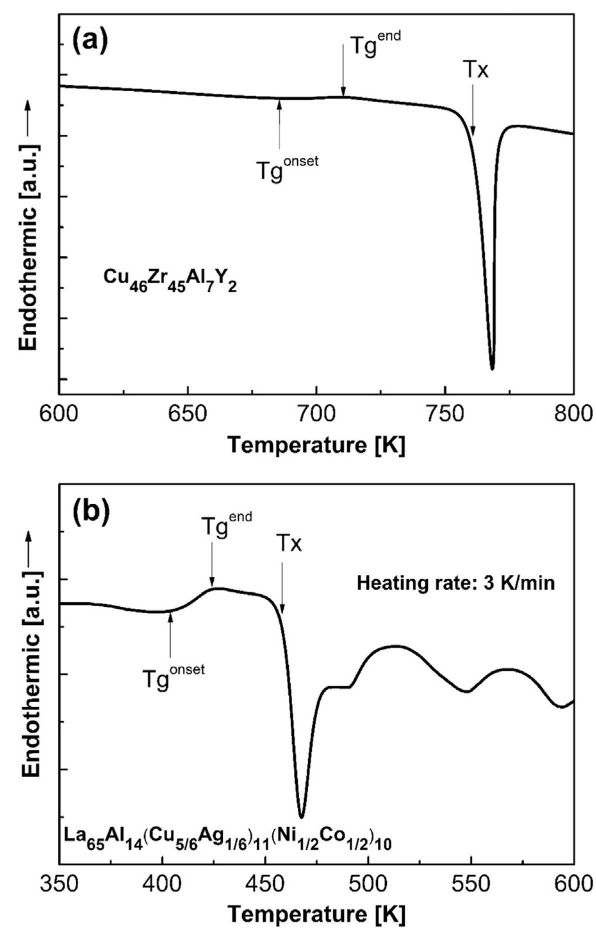

Fig. 2. DSC curves of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses (heating rate is 3 K/min).

bulk metallic glasses were investigated by the DSC technique at a constant heating rate of 3 K/min. The corresponding DSC curves are shown in Fig. 2 and the glass transition temperatures (T_g) and the onset temperature of crystallization (T_x) are defined. The characteristic temperatures T_g and T_x of the two studied alloys are listed in Table 1. The current DSC results are in excellent agreement with previously reports [21,22].