Effects of ultrasonic vibration on thermal stability, dynamic mechanical behaviors and nanomechanical behaviors of a La-based bulk metallic glass

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***Abstract*—The effects of room-temperature ultrasonic vibration on thermal stability, dynamic mechanical behaviors and nanomechanical properties of $La_{65}Al_{14}Ni_5Co_5Cu_{9.2}Ag_{1.8}$ bulk metallic glass (BMG) have been investigated by nanoindentation, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The thermal stability of La-based BMG has not obviously change after ultrasonic vibration, while the annealing results in the decrease of free volume and the increase of glass transition temperature T_g. It is found that a slight increase in storage modulus *E'* below T_g for the annealed sample for 20 h is attributed to the formation of ordered clusters in glassy matrix, but the values of *E'* and loss modulus *E''* of the sample subjected to ultrasonic vibration are lower than the as-cast sample. Ultrasonic vibration leads to the softening of La-based BMG, but does not improve the plasticity.**

Keywords—La-based bulk metallic glass; ultrasonic vibration; structural relaxation; dynamic mechanical behavior; nanoindentation

I. INTRODUCTION

Bulk metallic glass (BMG) is a kind of metastable metallic material which is obtained by rapid cooling of the glass-forming liquid, so it tends to transform into the more stable or equilibrium state by relaxation or aging. This non-equilibrium state of BMG is closely linked with the structural and dynamic heterogeneity [1-5]. It has been revealed by simulations and experiments that nanoscale liquid-like regions acted as flow units exist in elastic matrix regarded as solid-like regions in metallic glasses [6, 7]. The unstable and high mobility of liquid-like region makes it be easily activated by external fields, including applied stress, elevated temperature, ion-irradiation and high pressure [8-13]. The evolution of liquid-like region plays a key role on structural relaxation and properties of metallic glasses.

Recently, ultrasonic vibration is used to process various BMGs [14]. As a typical mode of external force, ultrasonic wave can modify the microstructures and properties of BMGs by introducing the heterogeneity in atomic rearrangement and crystallites. For example, T. Ichitsubo et al. have proved that ultrasonic vibration accelerates the crystallization in Pd-based BMGs even at low temperature below glass transition temperature (Tg) but does not induce the anomalous phases [15]. It has been reported that the hardness and elastic modulus of Zr-based BMG are enhanced by ultrasonic treatment at room temperature [16].

In this work, the effects of room-temperature ultrasonic vibration on thermal stability, viscoelasticity and mechanical behaviors of a La-based BMG with a low glass transition temperature have been investigated.

II. EXPERIMENTAL

Alloy ingots with a nominal composition of $La_{65}Al_{14}Ni_5Co_5Cu_{9.2}Ag_{1.8}$ (at.%) were prepared by arc-melting a mixture of pure elements (the purity above 99.9 wt.%) under high-purity nitrogen atmosphere. Cylindrical rods with a diameter of 5 mm and a length of 60 mm were obtained by copper-mold casting under argon atmosphere. The ultrasonic vibration treatment was carried out by putting the as-cast samples in ultrasonic cleaning machine for 20 h under 40 KHz± 10% working frequency at room temperature. For comparison, the annealed samples were obtained by heating the as-cast one at 343K in a water bath for 20h. The microstructure was confirmed by a Dmax-2500VBX X-Ray diffractometer (XRD) equipped with Cu-Kα radiation. Thermal stability was investigated by a Perkin Elmer-8000 differential scanning calorimetry (DSC) at a heating rate of 20K/min under nitrogen atmosphere. Dynamic mechanical analysis (DMA) were performed using a TA DMA-Q800 by the single-cantilever bending at a frequency of 1Hz with temperature increasing from 223K to 573K at a heating rate of 3K/s. The rectangular samples with sizes of 18 mm × 2 mm × 2 mm were used for DMA measurement. Nanoindentation experiments were carried out in a load control mode using an Ultra nanoindentation tester with a Berkovich diamond tip at room temperature. The maximum load was 30 mN and the loading rate was 6mN/min. At least 6 indents for each sample were performed to ensure the credibility of the data.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns and DSC curves of the as-cast, annealed and ultrasonic vibrated $La_{65}Al_{14}Ni_5Co_5Cu_{9.2}Ag_{1.8}$ BMGs. The XRD patterns in the inset shows a broad diffraction hump without any sharp crystallization peak for all the samples, suggesting that the amorphous structure is obtained for La-based BMGs with various states. It is seen from the DSC curves that, for all the samples, a clear endothermic event corresponding to glass transition is followed by three sharp exothermic peaks resulting from crystallization. The thermodynamic parameters of La-based BMGs with various states are summarized in Table 1. As shown in Fig. 1 and Table 1, the ultrasonic vibration has little effect on the thermal stability of the as-cast La-based BMG. The annealing treatment leads to the enthalpy recovery existing in the DSC curve and the T_g of the annealed sample is relatively lower than that of the as-cast one.

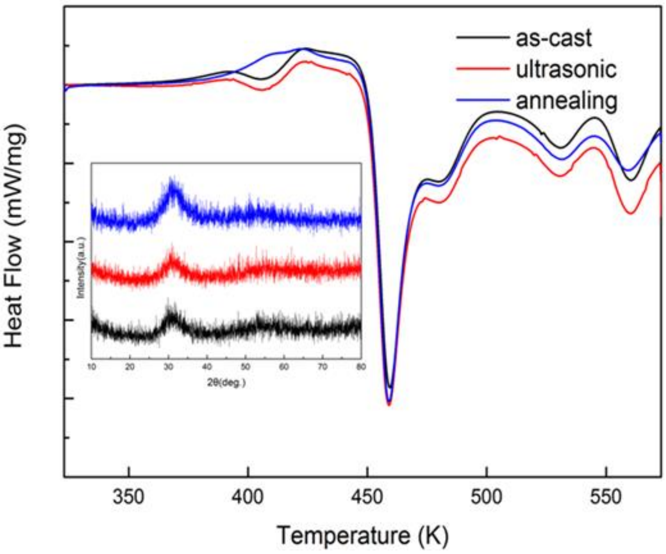

Figure 1 XRD patterns and DSC curves of the as-cast, annealed and ultrasonic vibrated La-based BMGs

Table 1 Thermodynamic parameters of La-based BMGs with various states

State	T_g (K)	T_x (K)	Δ Hg(J/g)	T_p (K)
As-cast	419	451	-1.073	459
Annealed	410	451	0.275	459
ultrasonic	418	452	-1.119	459

DMA is a powerful method to investigate the dynamic mechanical relaxation process of amorphous materials [17]. Figure 2 shows the dependence of the normalized storage modulus E'/E'_a and loss modulus E''/E''_a of the as-cast, annealed and ultrasonic-vibrated $La_{65}Al_{14}Ni_5Co_5Cu_{9.2}Ag_{1.8}$ BMGs on temperature. E''_a and E''_a are the maximum values of the storage and loss modulus of the as-cast sample, respectively. In the temperature range from 200 K to 325 K, all the samples remain in the glassy state as shown by the high value of E'/E'_a and negligible E''/E''_a. when the temperature is further elevated, E'/E'_a decreases obviously while E''/E''_a increases simultaneously. Dynamic glass transition exists in this temperature range. It is obvious that the peak value of E'/E'_a and E''/E''_a of the ultrasonic vibrated sample are lower than those of the as-cast and annealed ones. It is clear that the ultrasonic vibration has different effect on dynamic mechanical behaviors of La-based BMG compared with the annealing.

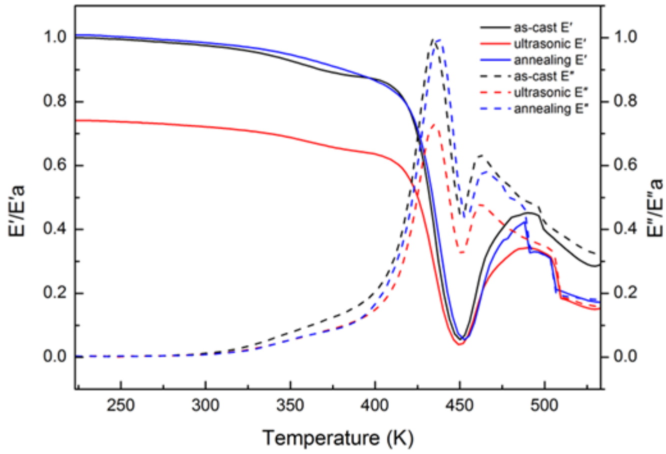

Figure 2 Dependence of the normalized storage modulus E'/E'_a and loss modulus E''/E''_a of the as-cast, annealed and ultrasonic-vibrated La-based BMGs on temperature.

Figure 3 presents the E″ normalized by the peak value varying with temperature scaled by the onset temperature of α relaxation (Tα). The intersection angle θ of two lines before and after β relaxation hump was adopted to characterize the intensity of β relaxation [18]. The θ value is larger, the more pronounced is β relaxation. The θ value of the as-cast sample is about 10°, which is larger than that of ultrasonic vibrated one (about 6°). However, the θ value of the annealed one is negligible due to its low value. The annealing can inhibit the appearance of β relaxation of La-based BMG.

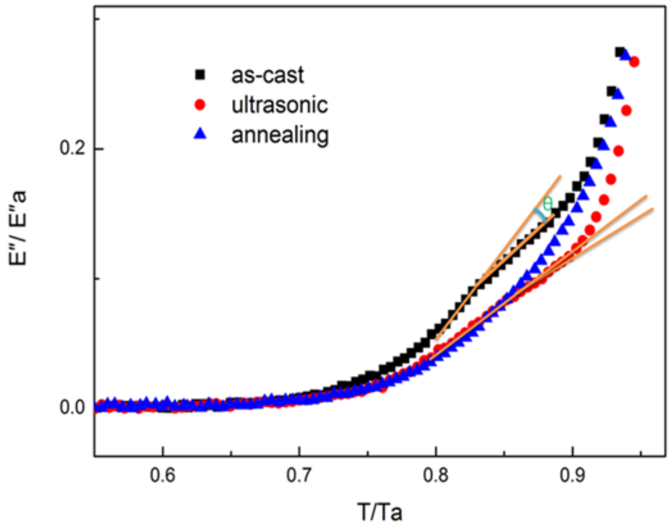

Figure 3 presents the E″ normalized by the peak value varying with temperature scaled by the onset temperature of α relaxation (Tα). The θ is used to characterize the obviousness of β relaxation.

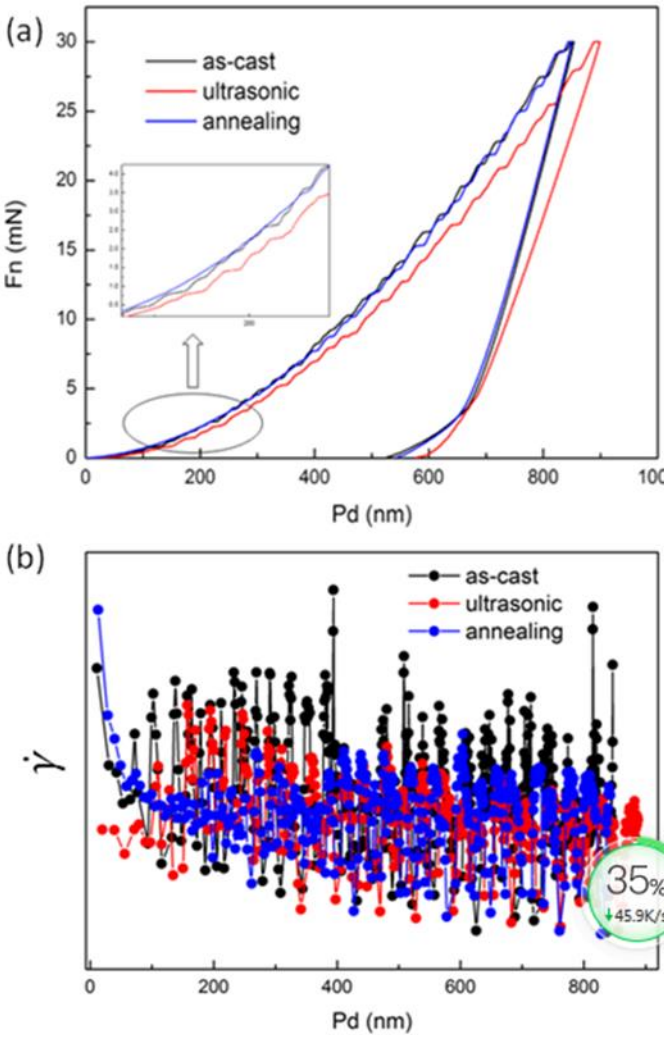

Figure 4(a) Typical load-depth (*P-h*) curves of the as-cast, annealed and ultrasonic vibrated La-based BMGs; (b) Indentation strain rate plotted as a function of indentation depth for La-based BMGs with various states.

The typical load-depth (*P-h*) curves of the as-cast, annealed and ultrasonic vibrated La-based BMGs are shown in Fig. 4(a). The depth of indentation of the ultrasonic vibrated sample is larger than that of the as-cast and annealed ones, indicating the ultrasonic vibration leads to the soften of La-based BMG. The serrated flow or pop-in, which is associated with the activation and propagation of single or multiple shear bands during plastic deformation, is obvious for all the samples. As shown in the inset in Fig. 4(a), the pop-in events are more pronounced in the ultrasonic vibrated and as-cast samples than the annealed one at the early stage of loading. Fig.4 (b) shows the indentation strain rate plotted as a function of indentation depth for the samples with various states. The indentation strain rate is usually defined as follows [19]:

$$\dot{\gamma} = \frac{1}{h}\frac{dh}{dt} \quad (1)$$

where *h* is the depth and *t* is time. Lots of short peaks are found for all the samples in Fig. 4(b), which can be exactly correlated to the serrations or pop-in events in the *P-h* curves shown in Fig. 4(a). These serrations or 'pop-in' events correspond to the nucleation and propagation of single or more shear bands. The elastic to plastic transition during nanoindentation causes short peaks. The annihilation of free volume in the annealed sample can enhance short range ordering and increase the resistance to the movement of shear bands. Therefore, the serration is not obvious in the annealed sample compared with the as-cast one. The ultrasonic vibration induces the rearrangement of atoms in some areas at nanoscale which improves structural inhomogeneity of La-based BMG, so the shock range of the as-cast sample is larger than that of the ultrasonic vibrated one.

IV. Conclusions

In summary, the effects of room-temperature ultrasonic vibration on thermal stability, dynamic mechanical behaviors and micromechanical properties of $La_{65}Al_{14}Ni_5Co_5Cu_{9.2}Ag_{1.8}$ BMG have been investigated. Ultrasonic vibration has little effect on thermal stability of La-based BMG, but the annealing leads to structural relaxation and enthalpy release. The values of storage modulus E' and loss modulus E'' of the ultrasonic vibrated BMG are lower than those of the as-cast and annealed ones. In the glassy state, the E' value of the annealed BMG for 20 h is slightly higher than that of the as-cast one, which is ascribed to the formation of ordered clusters in the amorphous matrix. The ultrasonic vibration leads to the softening of La-based BMG, but does not improve the plasticity.

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