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Modulation of β-relaxation by modifying structural configurations in metallic glasses

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ABSTRACT

β-relaxation and mechanical properties of La-based metallic glasses are investigated by modulation of quenching rate of the MGs. We find that the quenching rate has a remarkable effect on the β-relaxation behaviors and the mechanical properties of the metallic glasses. The β-relaxation shows a strong dependence on the cooling rate of the sample preparation, indicating that there is a correlation between the concentration of the potential flow units and the β-relaxation behaviors. The results imply that the β-relaxation is closely correlated with the inhomogeneous microstructure or the density of the potential flow units in the metallic glasses.

1. Introduction

At sufficiently high temperatures, glass-forming liquids show only one dominant relaxation mode, while in supercooled liquid state, the relaxation splits into α- and β-relaxations [1–5]. The α relaxation is frozen below the glass transition temperature T_g, while the β-relaxation still exists below T_g, which is the source of the dynamics in glassy state and has practical significance to many features and properties of glassy solids [6–10]. The relaxation dynamics of the supercooled liquids and glassy solids are an important issue in condensed matter physics, and the understanding of the structural and physical origins of the β-relaxation is critical for clarifying the glass transition phenomenon, the mechanical properties, the stability and the crystallization of metallic glasses [4–8,11–13].

Intensive work on the β-relaxation has been done in non-metallic glasses such as glassy polymers [14,15]. However, the underlying mechanism leading to the β-relaxation is still in debate due to the complex intramolecular effects in polymer glasses. It is difficult to correlate the static structural features with the relaxation process in these glasses, and the structural origin of the slow β-relaxation is generally explained in terms of intra- and inter-molecular motions that remain active even when the whole system is frozen into the glassy state [16–19]. Metallic glasses (MGs) are regarded as relatively simple glasses because their structures are close to the dense random packing of spheres. Recently, the β-relaxation is found to be the intrinsic and universal feature of the metallic supercooled liquids and metallic glassy solids [4–8, 18–21]. The β-relaxations in different MGs can exhibit as either E'' peaks [22–24] or broad humps [21], or excess wings that almost merge into the α-relaxations. It has been suggested that the relaxation of the MGs depends on fragility, chemical bonding, and atomic size disparity, and constitutes atom diffusivity [18–20], and the MG could be a model system for studying the nature and origin of the β-relaxation [21].

In this paper, by a close scrutiny of the β-relaxation in several prototypical MG systems, we show that the amplitudes of the β-relaxation have a strong dependence on the quenching rate of the sample preparation. The findings suggest the clear connections among the cooling rate, the structural heterogeneity, the concentration of flow units, and the intensity of the β-relaxation in the MGs. The implications of the results for understanding the structural origins and the mechanisms of the β-relaxation in MGs are discussed.

2. Experiments

We selected three MGs of $La_{60}Ni_{15}Al_{25}$, $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$ and $La_{55}Ni_{15}Al_{25}Cu_5$, which have good glass-forming ability, markedly different β-relaxation behaviors and microstructural characteristics. The MG samples were prepared by arc melting in a Ti-gettered argon atmosphere and subsequently sucked into a Cu mold to obtain cylindrical rods with 2–5 mm in diameter, or sheets with 1–2 mm in thickness [21–23]. The corresponding ribbon samples were prepared by melt spinning. The structures of the as-cast alloys were ascertained by X-ray diffraction (XRD) in a MAC M03 XHF diffractometer with Cu Kα radiation. Thermal analysis was carried out using different scanning calorimetry (DSC, PerkinElmer DSC8000) at a heating rate of 0.33 K/s under a constant flow of high purity argon gas. The DSC was calibrated according to the melting points of indium and zinc. The onset temperatures of the glass transition T_g and the crystallization event T_x of $La_{60}Ni_{15}Al_{25}$, $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$ and $La_{55}Ni_{15}Al_{25}Cu_5$ are 460, 418, 465

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and 510, 443, 532 K, respectively. Dynamic mechanical measurements were performed using a TA DMA Q800 by the single-cantilever bending method for rod and sheet samples, and the film tensile method for ribbons in a nitrogen-flushed atmosphere. The storage modulus E' and loss modulus E'' were measured by a temperature ramp mode at a heating rate of 3 K min^{-1}, a strain amplitude about 0.02% and a varied testing frequency f. The Vickers micro-hardness (HV) was determined using an EVERONE MH series unit.

3. Results

Fig. 1(a) shows the master curves of the broadband loss spectra in the frequency domain at five temperatures for $La_{60}Ni_{15}Al_{25}$ bulk MG with a diameter of 2 mm obtained by the time–temperature superposition (TTS) principle [5]. One can see that the α-relaxation exhibits a dominant loss peak which shifts to high frequencies with increasing temperatures and is associated with dynamic glass transition process. Besides the α-peak, a secondary relaxation process with pronounced additional peaks at higher frequencies as indicated in Fig. 1(a) is the so-called β-relaxation. The pronounced β-relaxation peak makes the La-based MGs a model system to investigate the features and origin of the β-relaxation, due to the possibility for modulating the amplitudes and positions of the β-relaxation by annealing and other ways [22,23]. The inset in Fig. 1(a) shows the fitting of Arrhenius equation of $f = f_0\exp(-E_\alpha/RT)$, where f_0 is the pre-factor. The activation energy E_α for the α-relaxation was determined to be about 283 kJ/mol. Fig. 1(b) displays the temperature dependence of the primary α-relaxation and the secondary β-relaxation at the different frequencies. A sharp maximum of E'' appearing at T_α (480 K) is generally referred to α-relaxation. A pronounced additional peak of β-relaxation as indicated in Fig. 1(b) can also be clearly seen. The temperature/frequency dependent E'' increases markedly with increasing testing frequency/temperature during isochronous/isothermal routes, while the peak intensity increases only slightly. The inset in Fig. 1(b) shows the fitting of Arrhenius equation $f = f_0\exp(-E_\beta/RT)$, where the activation energy E_β for the β-relaxation was determined to be about 105 kJ/mol. The value coincides with an empirical law for the activation energy of β-relaxation [$E_\beta \approx (26 \pm 2)RT_g$] [22].

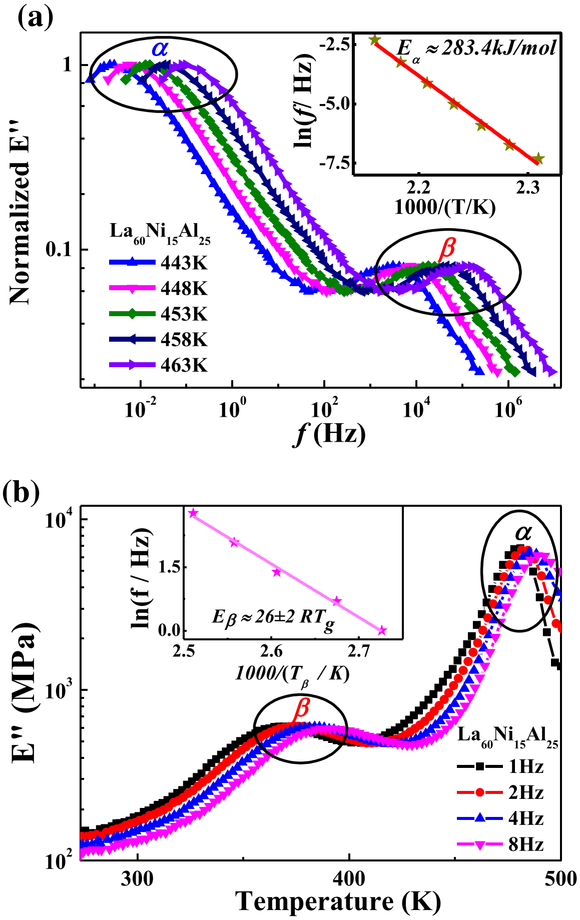

Fig. 1. (a) The frequency dependent loss modulus at different temperatures for $La_{60}Ni_{15}Al_{25}$ MG in extremely broadband measurements by the TTS principle. The inset is the Arrhenius plot of frequency of the α-relaxation peak vs the peak temperature; (b) The temperature dependence of loss modulus measured by DMA for $La_{60}Ni_{15}Al_{25}$ at different frequencies, the inset is the Arrhenius plot of the frequency vs peak temperature of the β-relaxation peak.

It is suggested that the microstructural origin of β-relaxation is related to the inhomogeneous microstructure and can be regarded as the motion of the loose atom groups in the soft regions or potential flow units of MGs [22–27]. Both the β-relaxation and the activation of the flow units relate to the dynamics of the nano-scale structural inhomogeneous or liquid-like sites in MGs where the atomic packing is relatively loose [4,18,25]. To experimentally investigate the relation between the inhomogeneous microstructure and the β-relaxation, we modify the microstructure of the MGs by quenching the La-based MGs with different cooling rates. Thus, we can obtain the MGs with different structural configurations or different fractions of the potential flow units, and then study the change of the β-relaxations and the density variation of the flow units as well. We quenched the MGs with cooling rates of ~10^6 K/s (for the ribbon) and ~10^2 K/s (for the rod). The cooling rate X of the samples was roughly estimated by [28]: $X = dT/dt$ (K/s) $= 10/D^2$, where D (in the unit of cm) is the critical dimension. Fig. 2 presents the typical DSC curves of the $La_{60}Ni_{15}Al_{25}$ MG specimens quenched with different cooling rates. The DSC curves show that there are broad exothermic peaks of the as-cast ribbon and rod glassy samples. However, the ribbon sample with the faster cooling rate has a larger exothermic peak, the rod samples with much lower cooling rate exhibit the much smaller exothermic peaks. The released enthalpy increases with the increase of the cooling rates. These results demonstrate clearly that the different cooling rates make the different microstructures of the MGs. From the free volume model, a proportionality exists between the exothermic enthalpy and the change of free volume or the change of the concentration of defects during the relaxation processes [29], which also suggests that the microstructure change is indeed induced by the cooling rate [3].

Fig. 3 shows the effect of cooling rate on the behaviors of the β-relaxation in $La_{60}Ni_{15}Al_{25}$ MG by dynamic mechanical measurements. The curves also indicate a large difference of the β-relaxation behaviors, although there is a weak cooling rate dependence of the positions of the

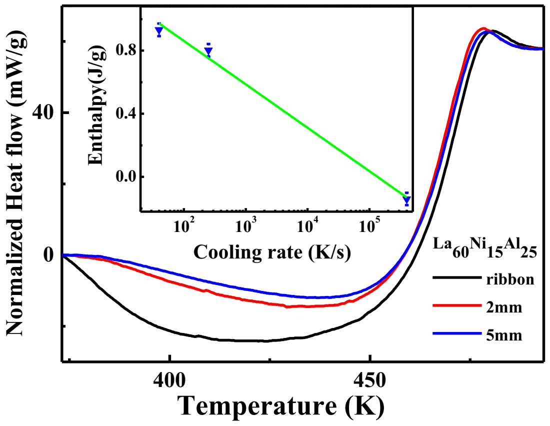

Fig. 2. The normalized heat flow of the $La_{60}Ni_{15}Al_{25}$ MG for the ribbon and rod samples measured by DSC. The inset is the quenching rate dependent enthalpy.

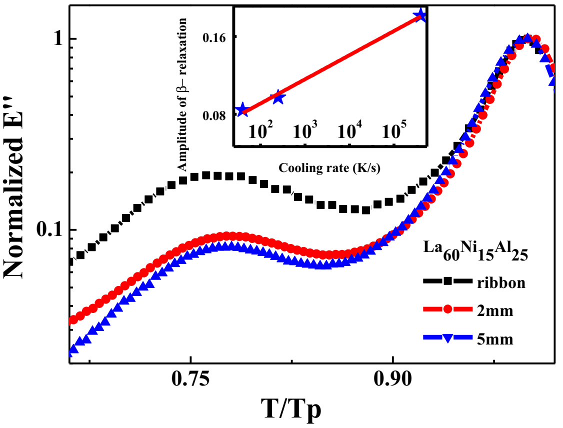

Fig. 3. The normalized E'' of the $La_{60}Ni_{15}Al_{25}$ MG for the ribbon and rod samples measured by DMA. The inset is the quenching rate dependent amplitudes of the β-relaxation.

β-relaxation. Comparing the peaks of the β-relaxations for the ribbon and rod samples, we can see the amplitudes of β-relaxations are strongly dependent on the cooling rates of the samples. The amplitude of the β-relaxation for the ribbon sample is the most pronounced, while for the rod sample with diameter of 5 mm it is much smaller. There is an approximate correlation between the amplitudes of β-relaxation and the cooling rate as shown in the inset of Fig. 3. The different amplitudes of β-relaxations between the samples with the different quenching rates correspond to the different concentrations of the defects frozen in the MGs. Therefore we can infer that the change of the β-relaxation is due to the change of the "defects" or the flow units frozen in the glasses. In other two MGs, $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$ and $La_{55}Ni_{15}Al_{25}Cu_5$, we can see the similar results as presented in Fig. 4. The cooling rate has a significant effect on the behaviors of the β-relaxation in these MGs. The ribbon with a larger exothermic peak has a more pronounced β-relaxation too. The results further confirm that the cooling rate has an effect on β-relaxation and the concentration of flow units which are universal in metallic glasses.

We further investigate the change of the concentration of the flow units with cooling rates, its effect on the β-relaxation and the mechanical properties of the microhardness of MGs. Fig. 5 exhibits the *HV* value change of the La-based MG upon the cooling rate. The values of *HV* monotonically increase with decreasing cooling rate X and it reaches to an equilibrium value when the cooling rate is slow sufficiently. The variation tendency can be described by: $HV(X) = H_0\exp(-bX)$, or $HV(X) = H_0/(1+c)$, where H_0 is the microhardness when the cooling rate approaches zero, c corresponds to the concentration of the flow units, and b is a constant.

4. Discussions

Recently, a relation between the effective concentration of the flow unit c and some properties such as elastic moduli, density, microhardness and plasticity of MGs has been found, and it can be expressed as [30–32]:

$$P(c) = P_0/(1+c), \tag{1}$$

where $P(c)$ represents the properties such as elastic moduli, density, or hardness of MGs; P_0 is a certain property when the effective concentration of the flow units approaches zero. The relationship is helpful for understanding the softening phenomenon, structural heterogeneous, β-relaxation, evolution process of the flow units, and widespread mechanical behavior of MGs. Granato et al. proposed an interstitialcy model to explain the shear modulus G change upon structural relaxation and

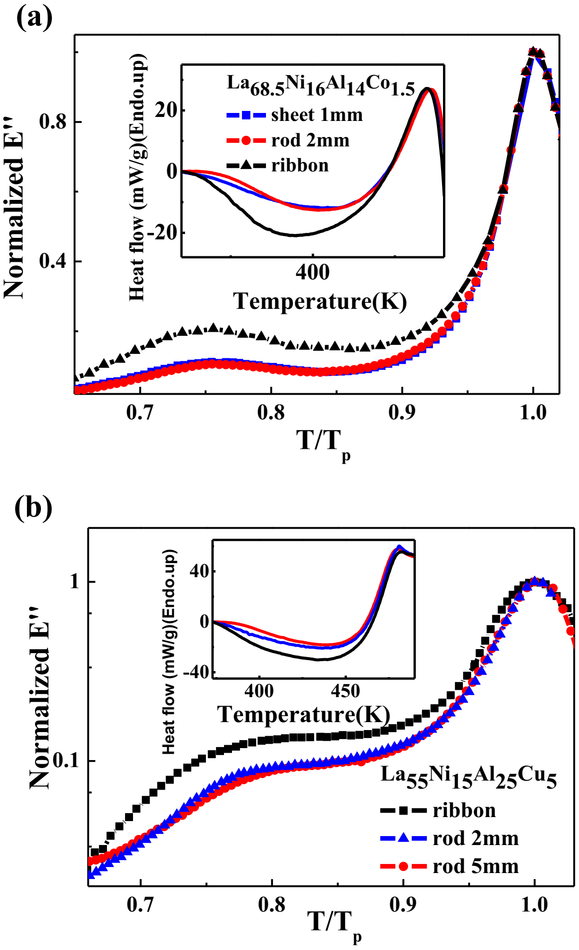

Fig. 4. (a) The normalized E'' of $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$ MG measured by DMA, and the inset is the normalized heat flow of the $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$ MG; (b) The normalized E'' of $La_{55}Ni_{15}Al_{25}Cu_5$ MG measured by DMA, and the inset is the normalized heat flow of the $La_{55}Ni_{15}Al_{25}Cu_5$.

the concentration of defects of MGs and gives an exponential decrease of G in the form of [26]:

$$G = G_0 exp(-\beta' c), \tag{2}$$

where G_0 is the shear modulus of the perfect crystal, β' is a shear softening parameter and c is the total concentration of dumbbell interstitials

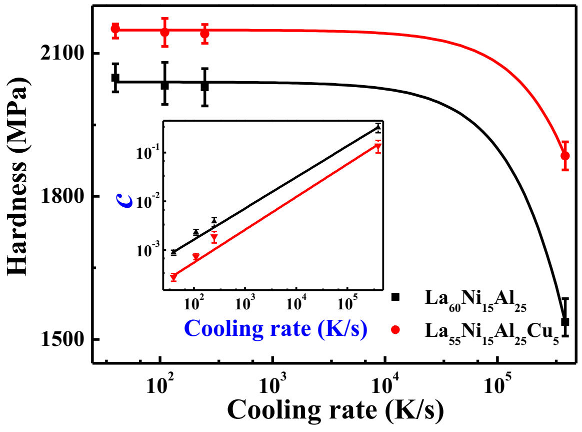

Fig. 5. The quenching rate dependent Vickers micro-hardness of $La_{60}Ni_{15}Al_{25}$ and $La_{55}Ni_{15}Al_{25}Cu_5$ MGs. The inset is the quenching rate dependence of the concentration of the flow units.

defects. The previous studies have shown that for MGs and non-metallic glasses, a rough proportionality between E and G in a relation of $E/G \approx 8/3 \approx 2.67$ [27], and a good correlation between HV and E of $E/HV \approx 20$ exists [27,33,34]. Yamane's and Chen's theoretical analysis also show that Vickers hardness has a linear correlation with the G [35,36]. Based on these correlations, the relationship between c and HV in MGs can be expressed as:

$$HV = H_0 exp(-\beta' c). \tag{3}$$

The free volume model can also describe the effect of cooling rate on the concentration of defects c_f as [37]:

$$c_f = \frac{k}{(T - T_0)^2} \frac{dT}{dt}, \tag{4}$$

where k is a constant, T_0 is the temperature at which the free volume disappears. Comparing Eq. (1) to Eq. (4), we can see that they are similar in essence, and can be used to fit the HV of the MG with different cooling rates. From Eqs. (1)–(4), two interesting extreme cases deserve to be mentioned: When $X = \mathrm{d}T/\mathrm{d}t \to 0, c \to 0, HV(X) \to H_0$, which is a constant corresponding to the hardness of perfect elastic MG without flow units; When $X \to \infty$, $c \to \infty$, $HV(X) \to 0$, in this case the MG approaches more unstable glassy state which is almost full of defects or flow units and in a very high energy valley in energy landscape. For the general case with a finite cooling rate, it can be thereby inferred that the corresponding metallic glassy structure is essentially like a solid-like region and liquid-like flow unit composite that attributes to its mixed mechanical responses. With the increase of cooling rate, the concentration of flow units increases, and the HV decreases and the β-relaxation becomes more pronounced.

As illustrated in this study, the β-relaxation mainly originates from the local flow units in MGs, and the MG with the high concentration of flow units has more pronounced β-relaxation, which confirms that the concentration of flow units is a key parameter for description the β-relaxation and mechanical properties of MGs. This accords with the recent report that the β-relaxation is associated to the shear transformation zones (STZs) [38] of the basic flow units and is related to the self-diffusion of the smallest constituting atoms only in the loosely packed regions (or weak bonded regions),which is in agreement with observations that MGs with pronounced β-relaxations often have high nano-scale density fluctuations corresponding to high density of flow units [39–42].

5. Conclusions

In summary, we find that the amplitudes of the β-relaxations measured by DMA in our frequency/temperature range, the mechanical properties and the concentration of flow units show strong dependence on the cooling rate of the La-based MGs. With the increase of cooling rate, the amplitudes of β-relaxations of the La-based MGs become more pronounced and the hardness decreases due to the increase of the concentration of flow units. The general relationship between the amplitudes of β-relaxations, mechanical properties, the concentration of flow units of the La-based MGs and the cooling rate further validates that the structural inhomogeneity or the density of the flow units is the origin of the β-relaxation in metallic glasses.

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