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Size effect on beta relaxation in a La-based bulk metallic glass

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A R T I C L E I N F O

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A B S T R A C T

This work studied the effect of the size of specimens on the β relaxation. Taking $La_{70}Ni_{15}Al_{15}$ bulk metallic glass as a model material, via dynamic mechanical analysis, we found that the thickness of specimens can affect the intensity of β relaxation. Specifically, increasing the thickness of specimens can enhance intensity of β relaxation. For this enhancement, we proposed that the involvedly total free volume facilitates the β relaxed process. This finding gives a new insight on the structural relaxation of bulk metallic glasses, especially for understanding of origin of β relaxation.

1. Introduction

Structural relaxation is a ubiquitous phenomenon in glassy materials, such as polymer and recent bulk metallic glasses (BMGs). Below a critical temperature, referring to the onset temperature of crystallization of BMGs (T_x), this relaxation splits into a primary relaxation (α relaxation) and a secondary relaxation (β relaxation) [1–3]. The later has attracted much interest in recent years and many important investigations have correlated it many features and properties of BMGs, such as aging, diffusion and plastic deformation [3,4].

Very recently, there are a great number of researches performing on effect to the β relaxation [5–14]. Yu et al. [6,12] proposed that the enthalpy of mixing can derive β relaxation to display in peak, shoulder and excess wing styles, and come up with a general rule about the behavior of β relaxation in a majority of BMGs. Specially, BMGs where all the atomic pairs have largely similar negative values of enthalpy of mixing have pronounced β relaxation, while positive values, or large fluctuation in the values of enthalpy of mixing suppress β relaxation [6]. On the other hand, physical treatments such as aging and fabrication conditions including thermal history during solidification, also strongly affect β relaxation. Qiao et al. [7,13] experimentally observed that aging and annealing can decrease the intensity of β relaxation in BMGs. Some investigations also found that the length scale associated with β relaxation has been suggested to range from very local (the first atomic shell) to quite extended (several tens of nanometers) [8,9]. Harmon et al. [15] firstly suggested that the isolated shear transformation zone (STZ) events within the elastic matrix closely correlates to β relaxation. Yu et al. [10,11] proposed that the activation energy of STZs and the β relaxation are almost equal, suggesting that the correlation between β relaxation and plastic deformation of BMGs. Zhao et al. [2] suggested that, increasing the cooling rate, the amplitude of β relaxation becomes more pronounced in La-based BMGs.

Aforementioned above showed that the atomic scale structures and the relevant fabrication conditions, *e.g.* mixing enthalpy [16,17] and cooling rate [18–20], can affect β relaxation. In view of these factors regarding to the internal microstructures of BMGs, one can consider these as internal factors. Nevertheless, the external factor, mainly referring to the shape and the scale of the measured BMGs, was reported very little. Interestingly, a number of investigations have disclosed that the sample size effects (aspect ratio) on the deformation behaviors, mostly in plastic deformation of metallic glasses [21–25]. Greer et al. [26,27] explored that the compressive plasticity increases as sample size decreases. Conner et al. [28,29] performed bending experiments through different thicknesses of the BMG samples, and discovered that the shear band spacing on the tensile side increased with the thickness of the plate at a ratio of 0.1. On the other hand, they also suggest that small sample size can induce bending plasticity. In a general viewpoint, under a compressive loading, BMGs with aspect ratios of $< 1.5:1$ deform in an elastic-perfectly plastic manner, while it can become into weak plastic manner when those aspect ratios excess 1.5:1. On the other hand, it has been validated that the plasticity of BMGs strongly correlates with their β relaxation behaviors. In this score, the size effect on the β relaxation may also promote the understanding of their origin and relevant plastic deformation.

In this paper, we investigated the effect of sample size on the β relaxation of La-based BMGs through changing the size of specimens. We revealed that the amplitudes of the β relaxation have a strong

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dependence on the size. The finding suggests a clear connection between the external factor and β relaxation in the BMGs.

2. Experiments

2.1. Materials and methods

The BMGs of $La_{70}Ni_{15}Al_{15}$ was selected for this work because of its good glass-forming ability and pronounced β relaxation behaviors [10]. The master ingot was prepared by arc melting pure elemental of La, Ni and Al (purity: > 99.9 wt%) in a Ti-gettered argon atmosphere and was remelted at least 4 times to ensure compositional homogeneity and subsequently suction-cast into a water-cooled copper mold to produce rectangular plate glassy samples with the dimension of 80 mm×10 mm ×1.25 mm. Then the as-cast plate was sliced into 2 mm wide BMG sheets using the diamond saw, and each face of the sheet was separately ground and polished into 1.0 mm, 1.1 mm and 1.2 mm in thickness for DMA testing by abrasive paper. All specimens for DMA testing were cut from a same BMG plate.

2.2. Characterizations

The amorphous nature of the as-cast alloy was ascertained by X-ray diffraction (XRD) via an X′Pert PRO MPD diffractometer equipped with Cu Kα as radiation. Thermal analysis was performed on the different scanning calorimetry (DSC, PerkinElmer DSC8000) with the heating rate of 40 K min^{-1} under high purity nitrogen flow. DMA measurements were performed using a TA DMA Q800 by the single-cantilever bending method in a nitrogen atmosphere. The storage modulus (E′) and loss modulus (E″) were measured by a temperature ramp mode with a heating rate of 3 K min^{-1}, a strain amplitude about 0.01% and frequency range from 1 Hz to 16 Hz.

3. Results

Fig. 1a shows the XRD pattern of as-cast $La_{70}Ni_{15}Al_{15}$ BMG. The apparently broad diffraction hump without any sharp crystalline peak in the XRD pattern indicates the amorphous nature of the alloy. The DSC curve of as-cast $La_{70}Ni_{15}Al_{15}$ BMG focusing on the glass transition and crystallization behavior is shown in Fig. 1b. It clearly shows that a distinct glass transition followed with crystallization exothermic peaks. The T_g and T_x of as-cast BMG are about 420 K and 443 K, respectively.

Fig. 2a presents the temperature dependence of E′ and E" of $La_{70}Ni_{15}Al_{15}$ BMG at 1 Hz. Remarkably, the E" curve shows two peaks: an α relaxation peak of E" at 430 K and an β relaxation peak at 325 K. It was easily found that both α relaxation and β relaxation peaks have a corresponding decline in the E′ curve. On the other hand, Fig. 2b displays the temperature dependence of α relaxation and β relaxation for $La_{70}Ni_{15}Al_{15}$ with a thickness of 1.0 mm at the different frequencies. The β relaxation peaks remarkably shift to high temperature with the increasing testing frequency and their intensity are approximately equal. However, for α relaxation peak, the peak temperature trend is little variation with the increasing testing frequency, but the intensity rapidly drop with increasing testing frequency.

Fig. 3 indicates the effect of sample size on the behaviors of the β relaxation on the $La_{70}Ni_{15}Al_{15}$ BMG. It clearly illustrates that the amplitudes of β relaxation are strongly dependent on the thickness of specimens. Specifically, accompanying with the increase of thickness, the intensity shifts towards high value.

We obtain the effective activation energy from the Arrhenius equation [3,30].

$$f=f_0\ \exp\left(-\frac{E_\beta}{RT_p}\right) \tag{1}$$

where f_O is the pre-factor, R gas constant, T_P the peak temperature of β relaxation in the E" curve. Taking logarithm, Eq. (1) can derive into

$$\ln f=\ln f_0-\frac{E_\beta}{RT_p} \tag{2}$$

From Eq. (2), activation energy of β relaxation (E_β) can be determined from the slope of ln$f$ *vs.* 1000/T_P.

Fig. 4a shows the activation energy of β relaxation E_β for different thick $La_{70}Ni_{15}Al_{15}$ BMG. The value of E_β for three La-based BMGs with thickness of 1.0 mm,1.1 mm 1.2 mm are 68.12, 69.93, 71.4 kJ/mol, respectively. Alternatively, one can find that E_β increases slightly with increasing thickness (Fig. 4b). There is an approximate correlation between the E_β and the thickness of sample, as shown in Fig. 4b, referring to a good linear relationship.

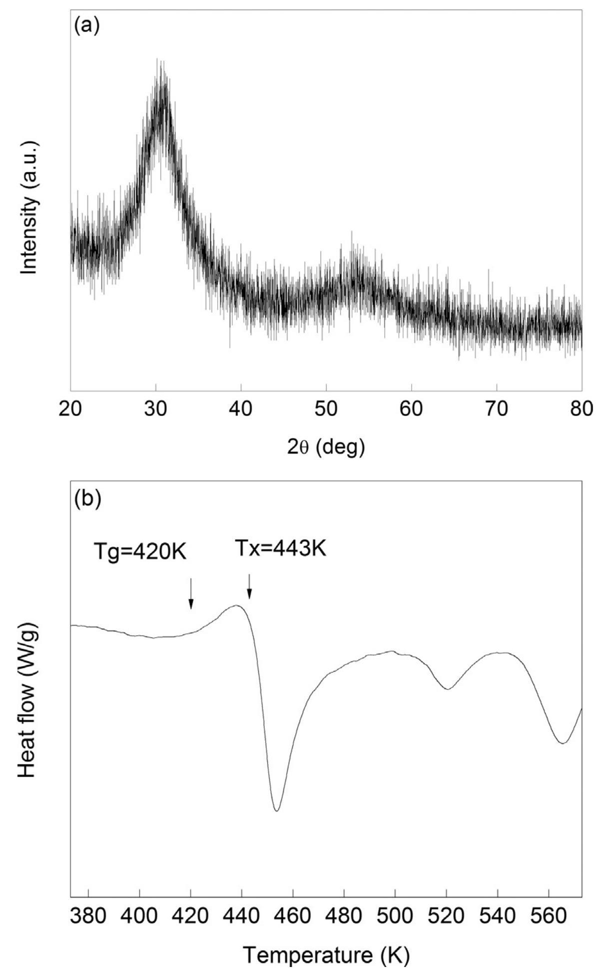

Fig. 1. (a) The XRD pattern and (b) the DSC curve of $La_{70}Ni_{15}Al_{15}$ alloys.

4. Discussion

The different intensity of β relaxation between the samples with the different thickness corresponds to the different concentrations of free volume in the BMGs. β relaxation is a rearrangement process of atoms in a small region, and this is a reversible process. Generally, the atomic rearrangement process become easier and faster with increasing the concentration of free volume [31–33]. As a consequence, β relaxation becomes more pronounced. In the current work, we revealed that the intensity of β relaxation increases with increasing the thickness of specimens. It is worth emphasizing that the concentration of free volume in a given volume is identical because the specimens are from the same as-cast plate. On this basis, one can argue that the involved total free volume may play an important role in the response of β relaxation. Specifically to this work, the involved free volume increases