Characteristics of stress relaxation kinetics of $La_{60}Ni_{15}Al_{25}$ bulk metallic glass

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A B S T R A C T

The β relaxation typically plays an important role in the plastic deformation of glassy materials. Compared with amorphous polymers, most of the metallic glasses do not show evident β relaxation based on mechanical spectroscopy. However, $La_{60}Ni_{15}Al_{25}$ bulk metallic glass (BMG) exhibits a prominent β relaxation process, which could be an ideal model alloy to investigate the correlation between the β relaxation and mechanical behavior of metallic glasses. In this work, compressive properties and stress relaxation at high temperature (below glass transition temperature T_g) were studied. Stress relaxation of $La_{60}Ni_{15}Al_{25}$ BMG was measured by uniaxial compressive tests and mechanical spectroscopy around both α and β relaxation temperature domain. At higher temperatures and sufficiently low strain rate, the flow behavior of the $La_{60}Ni_{15}Al_{25}$ BMG could be simulated by a master curve, showing that the behavior is independent of temperature, especially on the proximity of the β relaxation process. Because the existence of the β relaxation, a high value of the activation volume for the plastic deformation could be ascribed to the existence of a specific atomic arrangement in the $La_{60}Ni_{15}Al_{25}$ BMG. It is found that compressive stress relaxation kinetics parameter remains temperature independent below T_g.

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1. Introduction

Metallic glasses present unique physical, chemical and mechanical properties compared with the conventional crystalline alloys. Profiting from the amorphous structure (i.e. specific random disordered structure of atoms), metallic glasses exhibit relatively high mechanical strength and hardness, good wear resistance, high fracture toughness, low elastic modulus, a high fatigue resistance, as well as a large elastic limit at ambient temperature [1–5]. In addition, metallic glasses show excellent corrosion resistance compared with their crystalline counterparts [6]. From a practical and mechanical viewpoint, metallic glasses are important candidates to be applied as functional and structural materials [7–10]. However, the majority of the monolithic metallic glasses display a catastrophic brittle deformation with limited plastic strain (less than 2%) based on uniaxial compressive tests [1,2,11,12]. To a great extent, the poor plasticity restricts the applications of the metallic glasses as an engineering material.

One fundamental yet longstanding issue in metallic glasses is how to establish the structure–property relationship. Some previous investigations have suggested that the deformation behavior of metallic glasses is linked to the internal structural heterogeneity [13,14]. In general, the mechanical response of materials consists of three different contributions: elastic, visco-elastic and viscoplastic. These contributions depend on temperature and strain rate during the deformation. At a given strain rate, the temperature dependence is as follows:

- At low temperature: the amorphous alloys present an elastic behavior.
- At temperatures close to T_g, the elastic component decreases dramatically, the visco-elastic component reaches a maximum value, which corresponds to the main relaxation observed by dynamic mechanical analysis (DMA), and the viscoplastic component increases.

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- When the temperature is above T_g, the viscoplastic component is the major contribution to the deformation process, when no parasite crystallization phenomenon occurs.

As a potential engineering material, there are many investigations focused on the mechanical properties of the metallic glasses, i.e. compression, tension, bending and fatigue [1–3,9]. The stress relaxation is another important issue to help understand the mechanical properties of metallic glasses. Due to the absence of the crystal lattice and dislocations, it is essential to understand the kinetics of stress relaxation. Recently, some investigations on stress relaxation in metallic glasses have been performed. It is found that the tensile relaxation behavior is independent of the sample thickness for Zr-based metallic glass [15]. Lu et al. proposed a parameter n to describe the structural heterogeneity of metallic glasses based on the stress relaxation [16], which provides a new perspective to understand the relation between the intrinsic structure and dynamic heterogeneity of the metallic glasses. From the linear heating and isothermal tensile stress relaxation experiments of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic glass, Bobrov et al. suggested that stress relaxation is caused by irreversible structural relaxation orientation induced by the external stress [17]. On the other hand, stress relaxation behavior of metallic glasses has been observed at the room temperature. Zhang et al. reported stress relaxation of the $La_{62}Al_{14}Cu_{11.7}Ag_{2.3}Ni_5Co_5$ BMG at ambient temperature, which supports that stress relaxation behavior depends on the physical aging below T_g [18]. Furthermore, negative stress relaxation in Fe-based metallic glass at room temperature is attributed to the "mechanically induced" annealing [19]. However, a comprehensive understanding to the stress relaxation kinetics in metallic glasses at higher temperature (i.e. below T_g) is still ambiguous and lacking.

There is some debate relative to the interpretation of the microscopic deformation mechanisms in glassy materials. These mechanisms exhibit sensitivity to the nature of the material. For example, polymers consist of a chain with side groups or phenol nuclei in the chain; a local deformation can occur through movements of such entities. This kind of local mobility is usually considered as the origin of the β relaxation that can be observed in some polymers. On the other hand, metallic glasses are composed of atoms linked by metallic bonds. Therefore, local movements appear to be more difficult. However, structural heterogeneity in metallic glasses has been observed in recent experiments and numerical simulations, and this heterogeneity can enhance the local movements and mechanical relaxations [13,14,20,21]. It is well accepted that the deformation of metallic glasses is ascribed to dilatation or the free volume [22,23]. It should be noted that the deformation accommodated by plastic rearrangements of atomic regions involving tens or hundreds of atoms, which is termed shear transformation zones (STZs) and have been adopted to interpret the plastic deformation of the metallic glasses [24,25]. Johnson and Samwer proposed a cooperative shear model (CSM) to study the deformation mechanisms. The number of atoms in an STZ of the typical metallic glass was estimated to be around 100–300 based on the theoretical analysis of CSM [26].

Up till now, some questions still remain unclear: (i) It has been observed that many polymers present local relaxation phenomenon (β relaxations in the framework of DMA curve), which can favor deformation below T_g. For instance, polycarbonate displays a large deformation between the peak of β relaxation T_β and T_g (T_β = 250 K and T_g = 430 K), e.g. at room temperature [27]. In contrast, most metallic glasses do not exhibit a pronounced β relaxation peak. Interestingly, the $La_{60}Ni_{15}Al_{25}$ metallic glass investigated in current work is a type of exception, which presents a pronounced β relaxation. Is there any influence of this β relaxation on the compressive behavior, in particular, the stress relaxation?

(ii) During tension or compression tests, stress relaxation experiments can be performed. How does stress relaxation occur in metallic glasses? (iii) Is it possible to use a physical model to describe the stress relaxation of bulk metallic glasses? In particular, direct evidence of stress relaxation in the metallic glasses with a pronounced β relaxation is still missing. In current work, these questions are addressed in the $La_{60}Ni_{15}Al_{25}$ BMG. The stress relaxations in the La-based metallic glass were investigated experimentally.

2. Experimental methods

2.1. Sample fabrication

$La_{60}Ni_{15}Al_{25}$ bulk metallic glass was selected as the model alloy because it shows excellent glass forming ability, high thermal stability and evident β relaxation [28]. Master alloys with a nominal composition of $La_{60}Ni_{15}Al_{25}$ have were prepared by the arc-melting method in a pure argon atmosphere [28]. All master alloys were re-melted several times to ensure chemical homogeneity. Alloy ingots of $La_{60}Ni_{15}Al_{25}$ were used to prepare the BMGs by a copper mold suction casting technique.

2.2. Thermal properties and materials characterization

The thermal properties and relaxation behavior of the as-cast and annealed $La_{60}Ni_{15}Al_{25}$ metallic glasses were studied by differential scanning calorimetry (DSC) (Perkin Elmer, DSC-7) with a heating rate of 20 K/min. Aluminum pans were used as sample holders. For the annealed sample, the metallic glass was heated to 448 K with a heating rate of 20 K/min, then held on this temperature for 16 h, subsequently cooling down to room temperature with the same cooling rate.

X-ray diffraction (XRD) experiments at ambient temperature were performed to characterize the glassy nature by Cu Kα radiation produced by a commercial device (D8, Bruker AXS Gmbh, Germany). The working conditions of XRD experiments are 40 kV and 40 mA for the X-ray tube with a scanning rate of 0.025° per step.

2.3. Dynamic mechanical analysis experiments

DMA is an effective technique to study the mechanical properties of the materials as a function of temperature, frequency and time. In the current research, a dynamic mechanical measurement was performed in an inverted torsion mode by a mechanical spectrometer in a high vacuum atmosphere, as described by Etienne et al. [29]. Experiments were conducted by applying a sinusoidal stress with a constant driving frequency (i.e. 0.3 Hz) and a fixed heating rate (i.e. 3 K/min). Experimental specimens with dimensions of around 30 mm (length) × 2 mm (width) × 1 mm (thickness) were cut by automatic wire cutting machines. In the DMA test, a periodic shear stress was applied and the corresponding strain was measured. The complex modulus ($G = G' + iG''$) was recorded, the storage (G') and loss (G'') shear modulus were determined. The loss factor (also named internal friction) $\tan\delta = G''/G'$. During the DMA experiments, the strain amplitude was lower than 10^{-4}. For the stress relaxation by DMA experiments, the $La_{60}Ni_{15}Al_{25}$ BMG was heated to the temperature T_a = 433 K (the temperature is below T_g) with a heating rate of 3 K/min; then the metallic glass was kept at 433 K for 16 h.

2.4. Compressive tests and stress relaxation at higher temperature

The compression samples with a dimension of φ3 mm (diameter) × 5 mm (height) were mechanically cut from the as-cast rods. Strain rate jump tests in the compressive mode were performed by the MTS 4M testing machine equipped with a high temperature heating furnace [28]. The samples were heated to 20 K below the tested temperature at a heating rate of 20 K/min, followed by heating up to the tested temperature at a heating rate of 10 K/min. The compressive temperature was held for 5 min to ensure thermal equilibration prior to the compressive tests [30]. Compressive stress relaxation behavior of the $La_{60}Ni_{15}Al_{25}$ metallic glass was investigated around T_g at different temperatures.

3. Results and discussion

3.1. Thermal analysis for the La-based metallic glass

In the scenario of the DMA test, the representative loss modulus G'' of $La_{60}Ni_{15}Al_{25}$ as a function of temperature is shown in Fig. 1; a pronounced β relaxation process was observed at lower temperature (~360 K). In addition, the α relaxation was detected at a higher temperature (~500 K). In the framework of the potential energy landscape [31,32], there are two different relaxation processes for glassy materials [7,33–35]: (i) the primary (α) relaxation, observed at the higher temperature domain, which is common nature for the glassy materials and is connected to the dynamic glass transition behavior. (ii)The β relaxation, also called as Johari–Goldstein (JG) relaxation, is observed at a lower temperature region or higher frequency domain in glassy materials. Importantly, there are some interesting physical and mechanical properties linked to the β relaxation in metallic glasses. It should be noted that the nature of the β relaxation is essential to understanding the diffusion, plastic deformation, and glass transition of amorphous materials [36]. Previous investigations demonstrated that the β relaxation is associated with the plastic deformation in La-based metallic glass [13]. In addition, a correlation between the activation energy $U_β$ of the β relaxation in typical metallic glasses and the potential energy barriers of STZs W_{STZ} has been established: $U_β ≈ 26(±2)RT_g ≈ W_{STZ}$ [37]. It is suggested that flow resistance of the β relaxation and STZs in metallic glasses are of the same origin in the microstructure scale. This phenomenon is useful to understand the deformation mechanism and β relation in metallic glasses. Yu et al. proposed that the β relaxation in metallic glasses is connected to the diffusion of the smallest constituent atom [38].
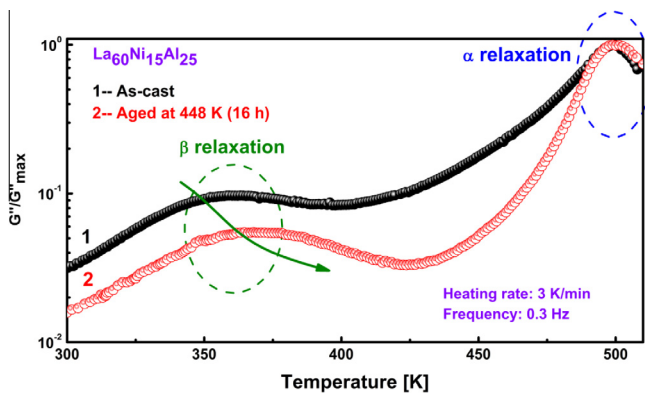
From the perspective of thermodynamics, the energy of the glassy materials will relax to a more stable state when the physical aging is below T_g. Fig. 1 shows the effect of physical aging on the β relaxation and α relaxation in $La_{60}Ni_{15}Al_{25}$ BMG (the annealing temperature is 448 K and annealing time is 16 h), which clearly demonstrates that the intensity of the β relaxation was reduced and induced by physical aging below T_g. In parallel, we observed that the peak of the β relaxation of the La-based metallic glass shifts to higher temperature compared with the as-cast one. On the other hand, the peak position of the α relaxation is independent of the physical aging when annealing is below T_g. The experimental phenomenon is consistent with the previous results [39,40]. As proposed in the previous investigations, the β relaxation of the metallic glasses is ascribed to the structural heterogeneity or local motion of the "defects" [41]. These "defects" are usually termed as flow units [42,43], quasi-point defects [44,45] and liquid-like sites [46,47]. A new energy configuration could be achieved via annihilation and creation of these "defects" for the metallic glasses. It is worth noting that, physical aging below T_g leads to a decrease of the concentration of these "defects". This fact results from the physical aging below the T_g induced decrease of the β relaxation amplitude.

Fig. 2 shows the DSC curves of the $La_{60}Ni_{15}Al_{25}$ BMG at different states (as-cast state and relaxed). The glass transition temperature is 461 K determined by DSC at a heating rate of 20 K/min for the metallic glass (as-cast state). Clearly, one large overshoot (endothermic heat recovery) in the glass transition region is observed for the annealed sample, which is connected to the recovery enthalpy phenomenon in metallic glasses. The observation is in good agreement with other metallic glasses [48]. As shown in the inset of Fig. 2, XRD spectra confirmed the glass nature of the as-cast and aged samples.

3.2. Stress relaxation in La-based metallic glass

The compressive properties in as-cast and relaxed states were investigated. Two samples of $La_{60}Ni_{15}Al_{25}$ metallic glass were deformed both at a constant temperature of 461 K and with the same strain rate interval ranging from $2.5 × 10^{-4}$ to $5 × 10^{-3} s^{-1}$. Fig. 3(a) shows the typical compressive stress–strain responses during strain rate jump tests at 461 K in the $La_{60}Ni_{15}Al_{25}$ metallic glass. No pronounced stress overshoot is detected in the curves. As in Fig. 3(a), the steady flow stress of the relaxed case is higher than that of the as-cast one, implying that the steady flow stress depends on the initial state at a given strain rate and compressive
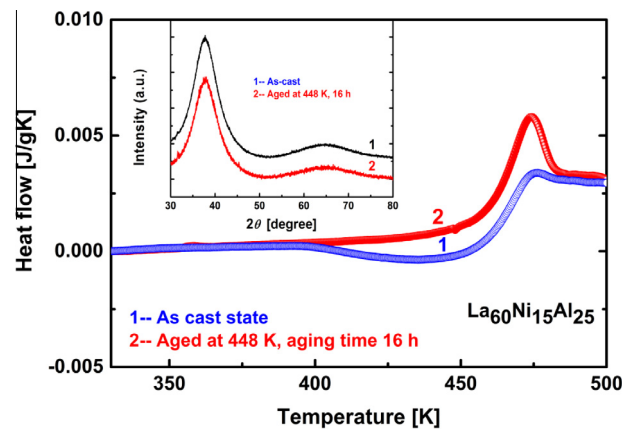

Fig. 1. Temperature dependence of the normalized loss modulus of $La_{60}Ni_{15}Al_{25}$ bulk metallic glass (heating rate: 3 K/min and driving frequency: 3 K/min): (1) As-cast, (2) annealed one (annealing temperature: 448 K and annealing time: 16 h).

Fig. 2. The DSC curves of the $La_{60}Ni_{15}Al_{25}$ BMG in the as-cast state after physical aging at 448 K with aging time of 16 h. Inset shows XRD patterns of the as-cast sample and the aged one.
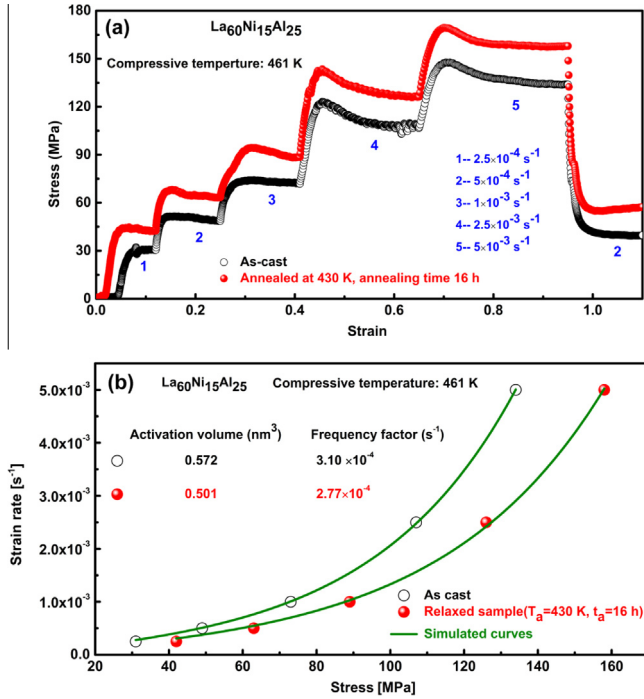
Fig. 3. (a) Typical compressive stress–strain responses of $La_{60}Ni_{15}Al_{25}$ metallic glass during strain rate jump tests ranging from 2.5×10^{-4} to 5×10^{-3} s^{-1} at a given temperature of 461 K for two different states: as-cast, and relaxed one below T_g (annealing temperature T_a = 430 K and annealing time t_a = 16 h). (b)Variation of the steady flow stress with the applied strain rate in the $La_{60}Ni_{15}Al_{25}$ BMG at different states. The solid lines are deduced from the equation $\dot{\varepsilon} = \dot{\varepsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right)$.

temperature. Logically, the shear modulus of the relaxed sample is slightly higher than that of the as-cast one. From the experimental results, Fig. 3(b) displays the variation of the steady flow stress with the applied strain rate in the $La_{60}Ni_{15}Al_{25}$ BMG.

It is well known that free volume among BMGs plays an important role in the mechanical properties. Based on the free volume theory, the strain rate $(\dot{\varepsilon})$ is associated with the applied stress, experimental temperature and free-volume accumulations of the glassy alloys during the compressive tests and takes the form of [22,49,50]:

$$\dot{\varepsilon} = 2c_f v_D \exp\left(-\frac{\Delta G^m}{kT}\right) \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) = \dot{\varepsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right), \quad (1)$$

where v_D is the Debye frequency, ΔG^m is the activation energy, V is the activation volume ($V = v_0\Omega$, v_0 is the characteristic strain, Ω is the volume of flow unit, say, STZ), $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, $\dot{\varepsilon}_0$ is a rate factor and expected to be a constant at a given temperature, T is the temperature and c_f is the concentration of the flow defects.

Eq. (1) can be used to describe the mechanical properties of $La_{60}Ni_{15}Al_{25}$ metallic glass at high temperature where the deformation is homogenous. The activation volume V and the strain rate factor $\dot{\varepsilon}_0$ can be obtained from the Eq. (1). Assuming that the average atomic volume in metallic glass is $\Omega = 0.013$ nm^3, the activation volume during plastic deformation is about 40 atomic volumes (as-cast and relaxed states) around T_g. If the characteristic strain is about 0.1, then the size of the flow unit is approximately 400 atoms. From Fig. 3(b), a decrease of the activation volume can be observed which results from the physical aging below T_g. It is noted that for other rare earth based metallic glasses, the activation volume of $Ce_{65}Cu_{25}Al_{10}$ metallic glass (the activation volume ranges from 0.20 to 0.25 nm^3) is smaller than that of the $La_{60}Ni_{15}Al_{25}$ metallic glass [51]. It can be expected that the atomic

radius of the La is larger than Ce, which maybe induce denser atomic arrangement, and during the plastic deformation, it will trigger the β relaxation. The activation volume could be employed as an indicator to describe the chemical heterogeneity of the glassy materials [21].

Intuitively, this tendency is reasonable since annealing below the glass transition temperature T_g induces a diminution of the Gibbs free energy and a decrease of atomic mobility. In addition, the activation volume could be connected to the microstructure or architecture in glassy materials. In metallic glass it is of interest to observe structural relaxation below T_g which induces the embrittlement phenomenon [52,53]. The experiments have shown that many polymers present higher activation volume than metallic glasses during the deformation process [54]. Benefiting from the chemical heterogeneity of the side group and the chain backbone in macromolecules, local motion in polymers is easier than in glassy alloys.

The plastic deformation of metallic glass is usually heterogeneous and related to formation of the localized shear bands at low temperature, followed by the propagation of these shear bands [55,56]. On the other hand, homogeneous deformation takes place at a higher temperature in metallic glasses (typically for $T > 0.8T_g$). In such cases, the glassy alloys always exhibit pronounced plasticity [57]. Brittleness increases by increasing of the strain rate during deformation. In the case of homogenous deformation, it is generally accepted that a transition from a Newtonian to non-Newtonian viscous flow occurs and this transition shows a strong dependence on temperature and strain rate [57]. During the homogenous deformation, the non-Newtonian viscous flow in amorphous alloys is generally accompanied by the existence of an overshoot phenomenon in the stress–strain curve [48]. The variation of the steady-state flow with the strain rate of $La_{60}Ni_{15}Al_{25}$ metallic glass at different testing temperatures is given in Fig. 4. Strain rate sensitivity reflects the rheological regime, which is defined as $m = \frac{\partial \log \sigma_{flow}}{\partial \log \dot{\varepsilon}}$ [30]. When the parameter m is close to unity, the deformation process corresponds to the Newtonian viscous flow. The strain rate sensitivity m remains nearly constant at low temperature, $m = 0.11$ at 423 K, which reflects a typical non-Newtonian behavior. In contrast, when the compressive temperature increases to 473 K (the temperature above T_g), m tends to be unity, indicating a Newtonian viscous flow phenomenon.

In the compressive tests, based on Eq. (1), the viscosity of the glassy materials can be expressed by following equation [58]:

$$\eta = \frac{\sigma}{3\dot{\varepsilon}} = \frac{\sigma}{3\dot{\varepsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right)} \quad (2)$$
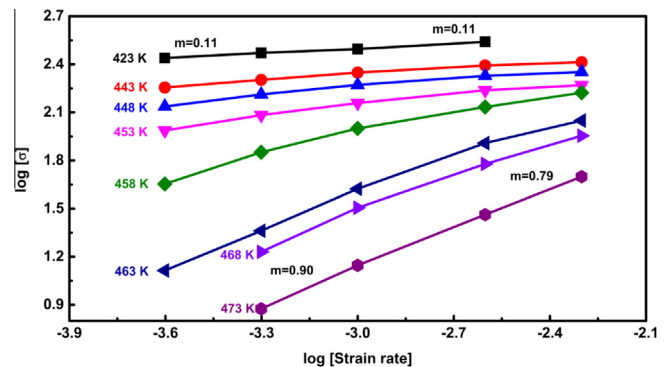

Fig. 4. Variation of the steady-state flow with strain rate in the $La_{60}Ni_{15}Al_{25}$ metallic glass at different compressive temperatures.

which assumes that the concentration of flow defects c_f corresponds to the equilibrium value in the Newtonian domain. At low stress, the Newtonian viscosity η_N can be written as follow [59]:

$$\eta_N = \frac{2\sqrt{3}kT}{3\dot{\varepsilon}_0 V} \qquad (3)$$

From Eqs. (2) and (3), a master curve can be obtained by a horizontal shift to the reference temperature, which is 448 K in the current study. According to the theoretical approach in the previous study, the master curve of the normalized viscosity η/η_N can be approximated by the stretched exponential function [60]:

$$\frac{\eta}{\eta_N} = 1 - \exp\left(-\left(\frac{B}{\dot{\varepsilon}^{\beta_{KWW}}}\right)\right) \qquad (4)$$

where B and β_{KWW} are fitting parameters. B is a constant and β_{KWW} is linked to the slope of the non-Newtonian viscosity. The master curve of the normalized viscosity η/η_N of the La$_{60}$Ni$_{15}$Al$_{25}$ metallic glass at a reference temperature of 448 K is shown in Fig. 5. This curve can be well fitted by the Eq. (4). $\beta_{KWW} = 0.80$ is a typical value of La$_{60}$Ni$_{15}$Al$_{25}$ metallic glass, which exhibits reasonable accuracy compared with previous literature [61–63]. This result highlights the fact that the β relaxation has no clear effect on viscous flow since the master curve is not modified by the proximity of the secondary relaxation temperature.

In order to investigate the stress relaxation kinetics of La$_{60}$Ni$_{15}$Al$_{25}$ metallic glass, compressive tests were carried out at 423 K and 443 K at a constant strain 2.5×10^{-4} s^{-1} (The compressive temperature below T_g). The crosshead was stopped for different strain values, the samples were relaxed for sufficient time to get an equilibrium relaxed stress value and then the compression experiment was restarted. The process was repeated 5 times to study the compressive stress relaxation kinetics of the La-based bulk metallic glass. Fig. 6 shows stress–strain compression and relaxation curves of La$_{60}$Ni$_{15}$Al$_{25}$ BMG at two given temperatures (423 K and 443 K, respectively). Remarkable stress overshoots were observed under the current compressive conditions, which imply a non-Newtonian behavior. A comparison of a simple stress–strain curve and a stress–strain/relaxation curve at 423 K with the same constant stain rate is presented in Fig. 6(a). The magnitude of the overshoot decreases progressively, but the flow stress appears nearly unaffected by the prior history. Therefore relaxation could affect the three components of the deformation: elastic, visco-elastic and viscoplastic in a different way.

The stress relaxation can be described as a function of time by the empirical stretched exponential or Kohlrausch–Williams–Watts (KWW) model [64]:

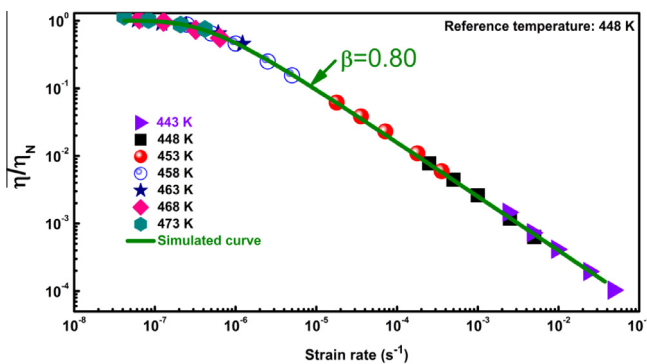$$\sigma(t) - \sigma(t \to \infty) = A\{\exp[-(t_a/\tau)^{\beta_{KWW}}]\} \qquad (5)$$

Fig. 5. Master curve of the normalized viscosity η/η_N of La$_{60}$Ni$_{15}$Al$_{25}$ metallic glass (as-cast state) at a reference temperature of 448 K. The solid line is deduced from Eq. (4). It can be found that the kinetic parameter $\beta_{KWW} = 0.80$.
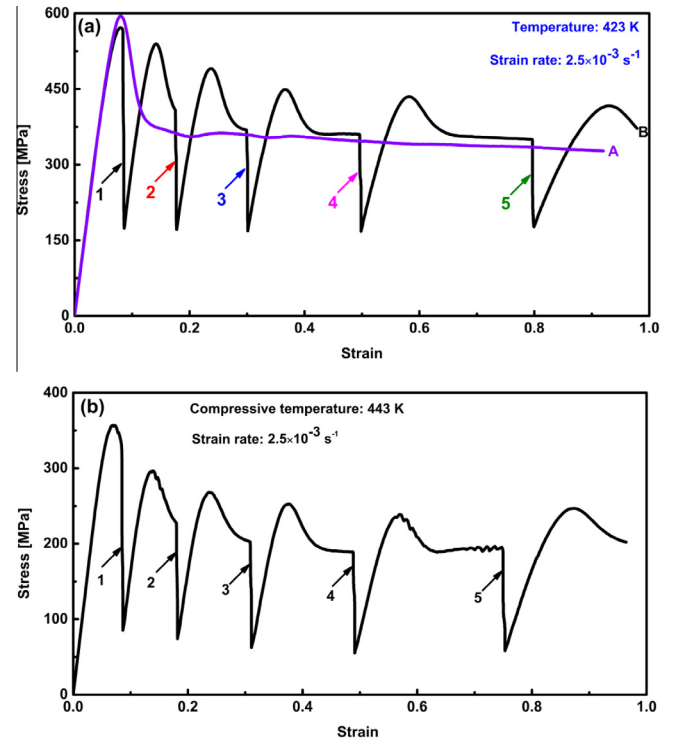

Fig. 6. (a) True stress versus true strain (curve A) and stress relaxation (curve B) at a strain rate of 2.5×10^{-3} s^{-1} for a given temperature 423 K in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG. (b)Stress relaxation curves at a strain rate of 2.5×10^{-3} s^{-1} for a given temperature 443 K in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG.

where A is the maximum magnitude of the relaxation process. The parameter Δ can then be defined, which varies during compressive tests experiments:

$$\Delta = \frac{\sigma(t) - \sigma(t \to \infty)}{\sigma(t = 0) - \sigma(t \to \infty)} \qquad (6)$$

Fig. 7 displays the variation of stress with the annealing time at a constant strain rate 2.5×10^{-3} s^{-1} for a given temperature 423 K in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG. It is observed that all the stress relaxation curves tend to reach a new equilibrium state. Furthermore, some interesting information can be obtained from Fig. 7: (i) The compressive stress between the first run (stage 1) and the last run (stage 5) reaches the same value after decay time; i.e., the viscoplastic component is always the same. (ii) The stress relaxation
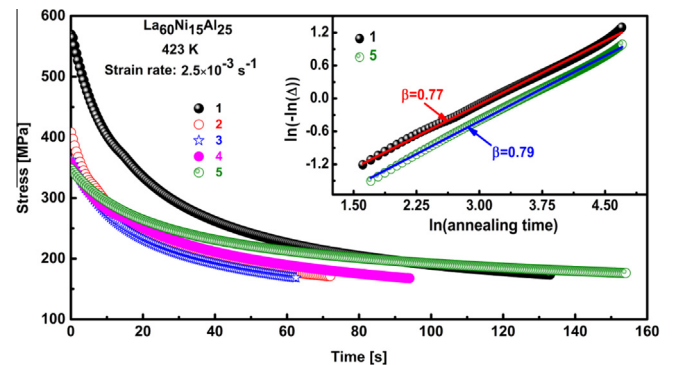

Fig. 7. Relaxation of the stress versus time at a constant strain of 2.5×10^{-3} s^{-1} at 423 K in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG at various stages. The inset is a double logarithmic plot of variation of the parameter Δ versus the logarithm of the annealing time in La$_{60}$Ni$_{15}$Al$_{25}$ BMG (For stage 1 and stage 5, the values of the parameter β_{KWW} fitted by the Eq. (5) are 0.77 and 0.79, respectively). Annealing temperature $T_a = 423$ K.

kinetics parameter β_{KWW} can be calculated by Eq. (5), where the values of the parameter β_{KWW} fitted by the Eq. (5) are 0.77 and 0.79, respectively. These suggest that the compressive stress relaxation kinetics in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG remains independent of the previous stress-relaxation history below T_g. Comparing creep and stress relaxation behavior in the polymer (i.e. metallocene-prepared linear low density polyethylene, m-LLDPE), indicates that the β_{KWW} value (ranges from 0.16 to 0.26) is less than that in metallic glasses [65], which suggests that the polymers are of broader distribution of relaxation time.

To further illustrate the stress relaxation kinetics of the La-based BMG, a compressive relaxation strain–stress experiment was performed at higher temperature (T_a = 443 K). Fig. 8 presents the stress relaxation behavior in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG for different temperatures (423 K and 443 K) at a constant strain rate 2.5×10^{-3} s^{-1} at stage 5. Obviously, the compelling experimental evidence of the compressive stress exhibits temperature sensitivity. However, the stress relaxation kinetics parameter β_{KWW} is nearly constant, as shown in Fig. 8. In light of this scenario, the compressive stress relaxation kinetics parameter remains temperature independent in the La-based BMG below T_g.

The stress relaxation of the metallic glasses was frequently studied by tensile or compressive tests [17–19]. To further understand the mechanical properties of the La$_{60}$Ni$_{15}$Al$_{25}$ BMG, we also characterized the stress relaxation by the DMA. Fig. 9 shows the storage (G') and loss (G'') shear modulus as a function of the annealing time at 433 K. An increase of the storage modulus G' (∼5%) and a decrease of the loss modulus G'' during the stress relaxation were observed.

For a glassy material during the physical aging, there exists non-exponential behavior. In the framework of the evolution of the loss modulus G'', the characteristic time τ_{aging} can be expressed as [66,67]:

$$G''(t_{aging}) = A \exp\left[-\left(\frac{t_{aging}}{\tau_{aging}}\right)^{\beta_{aging}}\right] + G''(t_{aging} \to \infty) \quad (7)$$

where A (=$G''(t_{aging} = 0) - G''(t_{aging} \to \infty)$) is the change of the loss modulus G'' during the stress relaxation in the DMA experiments. The parameter β_{aging} represents the stretch exponent, which ranges from 0 to 1; β_{aging} in the stress relaxation mode is smaller than β_{KWW} obtained by the isothermal route for glassy materials [66,68].

After investigating the stress relaxation around T_g, it is interesting to study the stress relaxation around the β relaxation temperature. The stress relaxation behavior of the La$_{60}$Ni$_{15}$Al$_{25}$ BMG as a function of time at 393 K is shown in Fig. 10. It indicates that the parameter β_{KWW} is strongly dependent on the mechanical relaxation processes of stress relaxation (the kinetic parameter
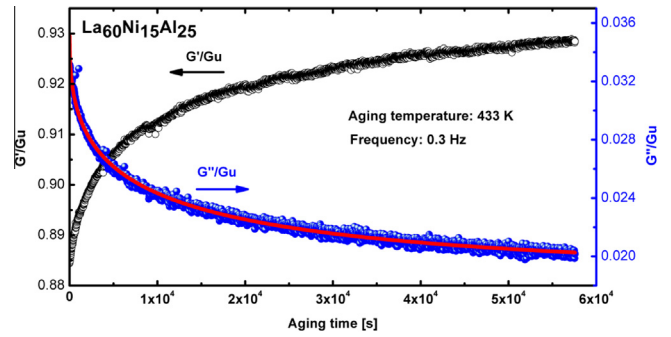

Fig. 9. Storage modulus G' and loss factor G'' in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG versus annealing time. Annealing temperature T_a = 433 K (frequency is 0.3 Hz). The solid curve is fitted by Eq. (7) and the best fitting parameters are as follows: A = 0.0166, τ_{aging} = 8980 ± 2 s, β_{aging} = 0.435 ± 0.01 and $G''(t_{aging} \to \infty)$ = 0.0185.
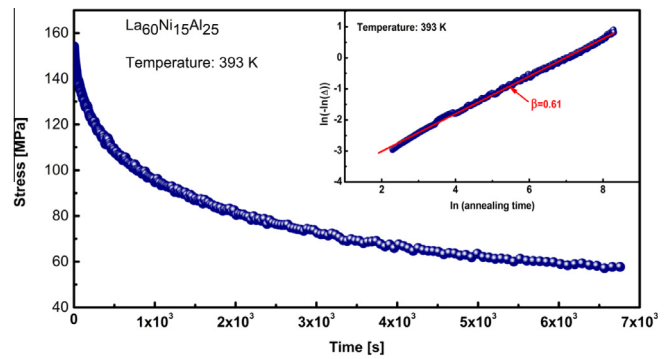

Fig. 10. Stress relaxation behavior as a function of time at 393 K in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG. The inset is the kinetic parameter β_{KWW} = 0.61.

β_{KWW} = 0.61 is shown in the inset of the Fig. 10). As proposed by Wang et al. [69], the kinetic parameter β_{KWW} is linked to the dynamic heterogeneity. When the temperature is below the β relaxation peak, the parameter β_{KWW} is smaller, it is noted that β_{KWW} increases dramatically when the temperature surpasses the glass transition temperature. The β relaxation in metallic glasses is related to reversible displacement of the "defects" (i.e. flow units, quasi-point defects) [41–44]. When the stress relaxation was performed around the β relaxation temperature, only minor parts of the atoms were moved. On the other hand, when the temperature is above T_g, the α relaxation has been activated, which corresponds to the cooperative motions of the atoms. In this sense, it can be concluded that the lower β_{KWW} around the β relaxation is ascribed to reversible "defects".

4. Conclusion

The deformation behavior and stress relaxation in a La$_{60}$Ni$_{15}$Al$_{25}$ bulk metallic glass have been investigated by a series of mechanical experiments. The secondary relaxation shows strong effects on the plasticity of amorphous materials such as polymers, in order to investigate the influence of the secondary relaxation to the mechanical behavior, experiments were performed in a broad range of temperatures and strain rates. The experimental results have been discussed in the framework of physical models. A good agreement is achieved between theoretical model and experimental data. The high value of the activation volume observed in the La$_{60}$Ni$_{15}$Al$_{25}$ bulk metallic glass could be linked to the existence of a secondary structural relaxation process. The mechanical behavior of this bulk metallic glass is not affected by the existence of a secondary relaxation process, while the high value of the activation
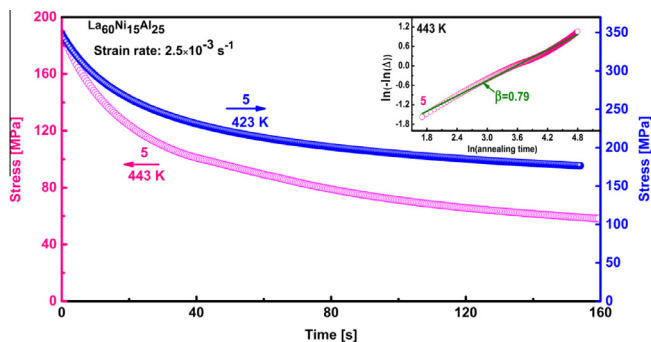

Fig. 8. Various stress relaxation behavior as a function of time for different temperatures (423 K and 443 K, respectively) at a strain rate 2.5×10^{-3} s^{-1} in the La$_{60}$Ni$_{15}$Al$_{25}$ BMG. The inset is the kinetic parameter β_{KWW} = 0.79 at stage 5 (compressive temperature 443 K).

volume suggests the existence of a specific atomic arrangement. The stretch exponent parameter β_{KWW} is strongly dependent on the β relaxation in the $La_{60}Ni_{15}Al_{25}$ bulk metallic glass. The parameter β_{KWW} is smaller when temperature belows the β relaxation. When stress relaxation occurs around the domain of α relaxation, the value of β_{KWW} increases drastically. The compressive stress relaxation confirmed that the β_{KWW} could be used as an indicator of the chemical heterogeneity for the glassy materials.

Acknowledgements

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