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# Ultrasonic-promoted defect activation and structural rejuvenation in a La-based metallic glass

C.C. Yuan<sup>a,\*</sup>, Z.W. Lv<sup>a</sup>, X. Li<sup>b</sup>, C.M. Pang<sup>a</sup>, R. Liu<sup>a</sup>, C. Yang<sup>b</sup>, J. Ma<sup>b</sup>, W.W. Zhu<sup>a</sup>, B. Huang<sup>c</sup>, H.B. Ke<sup>d</sup>

<sup>a</sup> School of Materials Science and Engineering, Jiangsu Key Laboratory for Advanced Metallic Materials, Southeast University, Nanjing, 211189, PR China

<sup>b</sup> Shenzhen Key Laboratory of High Performance Nontraditional Manufacturing, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen,

518060, PR China

<sup>c</sup> Institute of Materials, School of Materials Science and Engineering, Shanghai University, Shanghai, 200444, PR China

<sup>d</sup> Songshan Lake Materials Laboratory, Dongguan, 523808, PR China

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#### ABSTRACT

Ultrasonic-assistant rejuvenation in a La-based metallic glass was demonstrated by means of nanoindentation for the first time. A more pronounced nanoindentation creep behavior along with mechanical softening was detected. It is proposed to be associated with the activation of flow defects with long characteristic relaxation time at a low loading rate and short characteristic relaxation time at a high loading rate during anelastic deformation process based on the Maxwell-Voigt model. Such rejuvenation behavior also leads to an unstable plastic flow and a relatively low energy barrier for atomic diffusion during the fast growth process of crystalline phases accompanied with the reduced glass transition and crystallization temperatures. Our studies might provide insights into the microscopic deformation mechanism of glassy materials, which could help in seeking the novel applications of amorphous alloys such as ultrasonic-assistant cold joining or molding.

#### Author contributions

**C.C. Yuan:** Conceptualization, Investigation, Writing - Original Draft, Writing - Review & Editing, Project administration, Funding acquisition, Supervision.

Z. W. Lv: Methodology, Data Curation, Visualization, Investigation. X. Li: Methodology, Investigation.

A. Li. Methodology, investigation.

- C.M. Pang: Software, Data Curation, Investigation.
- **R. Liu:** Software, Investigation.
- C. Yang: Methodology.
- J. Ma: Conceptualization, Writing Review & Editing.
- W.W. Zhu: Methodology, Writing Review & Editing.
- B. Huang: Writing -Review & Editing.
- H. B. Ke: Writing -Review & Editing.

#### 1. Introduction

Rejuvenation, known as the reverse process of physical aging, has been investigated for decades in glassy materials, e.g., molecular and

polymeric glasses, stemming from the relaxation kinetics of their nonequilibrium glassy state [1]. The stress [2–4] or thermal [5] excitation such as pressurization [2] or cryothermal [5] cycling can simulate the structural rejuvenation accompanied by local atomic rearrangement, which is closely related to the improved mechanical performance of metallic glasses (MGs), i.e., greater strength, stiffness, ductility or plasticity [2-6]. Periodic deformation with ultrasonic frequency is proposed that can induce a rejuvenated state in MGs via directly injecting high energy into the glassy matrix [7], which effectively tunes the thermophysical and chemical properties of MGs. Ultrasonic annealing at a temperature far away from the glass transition temperature  $T_g$  accelerates atomic jumps associated with the Jahari-Goldstin (slow  $\beta$ -) relaxation, which initiates crystallization in weakly bonded regions even at a low temperature [8]. The thermoplastic formability of MGs can be enhanced by ultrasonic vibration via lowering resistant stress approaching the supercooled liquid region [9]. The formation of atomic bonding between the ultrathin surface layer during ultrasonic vibration enables the cold joining of MGs via the fast surface dynamics near the bonding interface [10,11]. Besides, the high energy injected into MGs by

\* Corresponding author. School of Materials Science and Engineering, Jiangsu Key Laboratory for Advanced Metallic Materials, Southeast University, Nanjing, 211189, PR China.

E-mail address: yuanchenchenneu@hotmail.com (C.C. Yuan).

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ultrasonic vibration can improve the catalytic performance by introducing residual stress and meanwhile reducing the activation energy of degradation via enhancing the potential energy of amorphous/metastable state in a very short time [12].

Despite the important role of ultrasonic treatment on the novel industrial applications of MGs, the underlying rejuvenation mechanism has not been fully revealed. It is proposed that local structural rejuvenation at the surface of MGs arises from the increase of the vibration amplitude of atoms due to the resonance actuation, which is correlated to the activation of slow  $\beta$ -relaxation. This process links to the evolution of loose-packing regions accompanied with the decrease of elastic modulus (E) [7,8]. However, recent molecular dynamics simulation suggests that the strain field of the string-like atomic motions originating from the slow  $\beta$ -relaxation intends to induce accelerated aging rather than rejuvenation, while the activation of  $\alpha$ -relaxation demonstrated by nanoscale flow defects is attributed to structural rejuvenation under oscillating shear vibration [13]. It arouses an interesting question that what is the role of slow  $\beta$ -relaxation on the structural rejuvenation that induced by ultrasonic vibration. More specifically, how defects activation is affected by the structural rearrangement during ultrasonic treatment process?

La-based MG processes the obvious slow  $\beta$ -relaxation along with the distinguishing intrinsic structural heterogeneity at the as-cast state [14]. Compared to Pd- [15], Zr (Cu) - [16-18], Ti- [19], Fe (Co) - [20-23], and U-based [24] MGs, La-based MGs have a relatively low glass transition temperature  $T_g$  (~400–500 K) that is close to the room temperature (i.e., ~298 K). It allows the slow  $\beta$ -relaxation as demonstrated by locally confined or caged dynamics defects (i.e., flow defects) be excited easily at ambient temperature in La-based MGs. Thus, a La-based MG with a nominal composition of La55Al25Ni5Cu10Co5 was chosen here as a prototype to detect the defect activation and the associated rejuvenation mechanism under ultrasonic vibration. Nanoindentation is sensitive to the mechanical response at the microscopic scale even when the sample deforms at a low strain amplitude like mechanical vibration [25]. It can be utilized to trace the defect activation during nanoindentation creep deformation process under the frame of Maxwell-Voigt model [26,27]. Therefore, the mechanical properties such as hardness (H), E as well as the creep behavior of the La-based MG before and after ultrasonic vibration were investigated in light of nanoindentation. The nanoindentation creep behaviors of Pd- [15], Zr (Cu) - [16,18], Fe (Co) -[20–23], and U-based [24] MGs that have higher  $T_g$  (~550–700 K) are also included for comparison to unravel the microscopic deformation mechanism in ultrasonic-vibrated MGs.

Based on the nanoindentation technique, a structural rejuvenation under ultrasonic treatment is found in the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG. After ultrasonic vibration with the exciting energy of 30 J, the as-cast Labased MG sample converts into a high-energy softening state along with a pronounced creep deformation as well as the reduced H and E, which has not been found in our previous studied Zr-based MG that even treated with a higher vibration energy of 140 J [18]. Such transition observed in the La-based MG is mainly attributed to the generation of excess free volume under the high-frequency cyclic loading. It is closely bound up with the activation of flow defects based on the Maxwell-Voigt model. We found that the flow defects with short relaxation time at a low loading rate are associated with the phonon softening accompanied with the decrease of E, while the flow defects with long relaxation time at a low loading rate will lead to the unstable plastic flow of the La-based MG along with the pronounced creep deformation. This work may help in understanding the structural evolution in disordered materials during ultrasonic-assistant plastic flow and unrevealing the underlying rejuvenation mechanism from the perspective of the mechanical response at the microscale.

#### 2. Experimental

The alloy with a nominal composition of La55Al25Ni5Cu10Co5 was

prepared by arc melting mixtures of pure La (99.5 at. %), Al (99.996 at. %), Ni (99.95 at. %), Cu (99.999 at. %), Co (99.95 at. %) in a high-purity argon atmosphere (>99.99 at. %). The obtained alloy ingot was coppermold casted into the cylindrical rods with a diameter of  $\sim 2$  mm, then cut into small pieces with a length of  $\sim 2$  mm before the ultrasonic treatment. The mechanical vibration at the ultrasound frequency of 20,000 Hz was conducted on BRANSON 2000X ea/ae with the exciting energy of 30 J under the trigger force of 22 N, which has been widely used in metal micro-forming process and can result in the structural rearrangement in a very short time (even less than 1 s) [9-12]. Fig. 1 (a) shows the schematics of the ultrasonic vibration system. After putting the as-cast La55Al25Ni5Cu10Co5 rod into the stoke bin, the sonotrode starts to pound on the specimen with a fixed frequency of 20,000 Hz, see Fig. 1 (b). Both the top and bottom sides were polished before further thermal and mechanical property measurements. The thermodynamic properties of samples were examined by differential scanning calorimeter (DSC, NETZSCH 404 F3) at heating rates ranging from 5 to 40 K/min. The glassy nature of samples was checked by X-ray diffraction (XRD, Bruker D8 Discover diffractometer) with Cu  $K_{\alpha}$  radiation. A NanoTest Vantage (Micro Materials Ltd) was adopted for nanoindentation measurements at room temperature by using a standard Berkovich diamond indenter with the load and displacement resolutions of about 750 nN and 0.3 nm, respectively. One side of specimens was mechanically polished to mirror finish before nanoindentation tests. A standard fused silica sample was utilized for the machine compliance calibration via the transducer-tip configuration and the tip area functional calibration before each indentation experiment. post-indentation drift calibration method was conducted for the thermal drift correction, see details in ref 23. Atomic force microscope (AFM, Veeco Dimension ICON) was performed to collect the surface morphology around the indents based on Tapping mode.

#### 3. Results and discussion

#### 3.1. Thermodynamic property

The DSC profile in Fig. 2 presents a tunable thermophysical property under the high-frequency mechanical vibration. A clear glass transition feature following by crystallization event(s) is demonstrated by DSC traces at a heating rate of 20 K/min. The glass transition temperature  $T_g$ , crystallization temperature  $T_x$ , the supercooled liquid region  $\Delta T_x = (T_x - T_g)$ , the onset melting temperature  $T_m$ , and the liquidus temperature  $T_1$ are listed in Table 1. It can be seen that  $T_g$  slightly decreases from 458 to 454 K after ultrasonic vibration. Meanwhile,  $T_x$  is also reduced from 525 to 520 K, which makes the derived  $\Delta T_x$  almost unchanged of about 67–66 K.  $T_m$  and  $T_1$  almost keep constant of 668–669 and 712 K, respectively.

The inset in Fig. 2 presents the magnified view of the thermal traces near  $T_g$ , giving the amount of the exothermic heat  $\Delta H_{\rm rel} = \int (dQ/dt)dT$  [28] as listed in Table 1. Rather than an annealing process [29], the



**Fig. 1.** (a) Schematic illustration of the contact ultrasonic vibration system. (b) The sketches of ultrasonic vibration processes before and after treatment.



**Fig. 2.** DSC curves of the as-cast and 30 J samples at a heating rate of 20 K/min represent the structural rearrangement during vibration. The inset shows enthalpy recovery measurements.

obvious increase of  $\Delta H_{\rm rel}$  from 0.553 to 0.685 kJ/mol upon ultrasonic vibration is found. The excess free volume ( $\Delta \nu$ ) is in direct proportion to the recovery enthalpy  $\Delta H_{\rm rel}$  [30]. It implies that about 24% more excess free volumes are generated in the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG as a result of the local dilatation effect induced by the high-frequency mechanical vibration. This phenomenon suggests that the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG undergoing ultrasonic vibration will go through a structural rejuvenation [7] instead of structural aging under cyclic loading [31], where the glass changes from a metastable as-quenched state into a rejuvenated high-energy state.

#### 3.2. Nanoindentation creep behaviors

Fig. 3 shows the room-temperature nanoindentation behavior of the  $La_{55}Al_{25}Ni_5Cu_{10}Co_5$  MG at different energy states (denoted as the as-cast and 30 J samples). The samples are firstly loaded by nanoindentation along the mechanical vibration direction (see Fig. 1 (b)) to a limit of 50 mN at a constant loading rate of 0.5, 1, 5, 10, 50, and 100 mN/s, then held for a period of 100 s and unloaded at the same rate as the loading rate. The typical load-displacement curves at the loading rate ranging from 0.5 to 100 mN/s with a load limit of 50 mN are displayed in Fig. 3 (a) and (b). A notable serrated plastic flow as indicated by the pop-in on *P*-*h* curves (marked by the black arrow) can be observed during the initial loading stage at loading rates lower than 10 mN/s, which implies

### Table 1 Thermodynamic and dynamic properties of the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG after ultrasonic vibration with the energy of 30 J. The data of the as-cast sample is included for comparison.

	<i>T</i> <sub>g</sub> (K)	<i>T</i> <sub>x</sub> (K)	$\Delta T_{\rm x}$ (K)	<i>T</i> <sub>m</sub> (K)	$T_{1}(K)$	$\Delta H_{\rm rel}$ . (kJ/mol)	$\Delta H_{\rm cry}$ . (kJ/mol)	$E_{\rm g}$ (kJ/mol)	$E_{\rm x}$ (kJ/mol)	$E_{\rm p}$ (kJ/mol)	т
As-cast 30J	458 454	525 520	67 66	669 668	712 712	0.553 0.685	4.626 4.114	$\begin{array}{c} 140\pm10\\ 208\pm13 \end{array}$	$\begin{array}{c} 122\pm11\\ 181\pm34 \end{array}$	$\begin{array}{c} 131\pm 46\\ 108\pm 39 \end{array}$	$\begin{array}{c} 16\pm1\\ 24\pm1 \end{array}$



**Fig. 3.** Creep behaviors of the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG before and after ultrasonic vibration with the energy of 30 J measured at room temperature under the loading rates ranging from 0.5 to 100 mN/s. Load - displacement curves under different loading rates: (a) as-cast and (b) 30 J. The curves in (a) and (b) offset from the origin for clear viewing. **The** creep displacement during the load holding period: (c) as-cast and (d) 30 J.

the formation of shear band during nanoindentation. A transition from serrated to non-serrated flow is identified at a higher loading rate [32, 33].

Fig. 3 (c) and (d) display the creep displacement and strain rate curves during a constant load holding period. After rapidly increasing with the holding time during the first stage of the load holding period, the strain exhibits a relatively steady-state behavior. Consistent with the observation in Pd- [15], Zr (Cu) - [16,18], Fe (Co) - [20,22], U-based [24] MGs, the magnitude of creep deformation increases obviously with elevated loading rates, exhibiting a high degree of the loading rate sensitivity. With increasing loading rates from 0.5 to 100 mN/s, the maximum creep displacement during the load holding period increases from less than 10 to more than 60 nm. Compared with the as-cast sample, the 30 J sample exhibits a more pronounced creep deformation with much deeper penetration depth. The maximum creep displacement abruptly increases from 50 nm of the as-cast sample to 66 nm of the 30 J sample.

#### 3.3. Mechanical softening demonstrated by H and reduced modulus $E_r$

The pronounced creep behavior of the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG after ultrasonic vibration agrees well with the ultrasonic-induced mechanical softening as demonstrated by the evident reduction of both H and  $E_r$ . The H and  $E_r$  of as-cast and ultrasonic-vibrated La-based samples derived from nanoindentation (see details in ref. 15) are listed in Table 2. The  $E_r$ and H measured at the very low and high loading rate such as 0.5 and 100 mN/s that exhibit large standard errors (more than 10%) are excluded from the comparison. It is clear that after the high-frequency mechanical vibration with an energy of 30 J,  $E_r$  is sharply reduced by about more than 20%. For instance,  $E_r$  of the sample decreases from 56.2  $\pm$  0.3 to 43  $\pm$  1 GPa after ultrasonic vibration at the loading rate of 5 mN/s. Likewise, the H decreases from 3.07  $\pm$  0.02 GPa of the as-cast sample to 2.80  $\pm$  0.01 GPa of the 30 J sample at a loading rate of 5 mN/s. With increasing loading rates from 1 to 50 mN/s, both  $E_r$  and H almost keep constant, which confirms that these two parameters are independent on the loading rates [26].

#### 3.4. AFM analysis on the local plastic deformation

The local plastic deformation of the as-cast and 30 J samples during nanoindentation is further characterized by using AFM. Fig. 4 shows AFM images around indents. It is found that a batch of partial circular patterned shear bands appears in the pile-up region around indents. This well coincides with the report of Li [34] and Liu [35] et al., illustrating that a shear-deformation mode is dominant during nanoindentation. Particularly in the 30 J sample, multiple shear bands with a large in-between distance are found that appear around the indent, see Fig. 4 (a) and (b), which indicates that the rejuvenated 30 J sample exhibits more pronounced shear deformation than the as-cast sample. This is in line with the notable serration during the initial loading period in Fig. 3 (a) and (b).

The pronouncedly localized deformation during nanoindentation

#### Table 2

Hardness *H* and the reduced modulus  $E_r$  of the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG after ultrasonic vibration with the energy of 30 J measured at different loading rates. The data of the as-cast sample is included for comparison.

H (GPa)		E <sub>r</sub> (GPa)		
As-cast	30 J	As-cast	30 J	
$1.73\pm0.77$	$\textbf{2.86} \pm \textbf{0.03}$	$\textbf{42.8} \pm \textbf{8.8}$	$\textbf{44.9} \pm \textbf{0.7}$	
$\textbf{3.09} \pm \textbf{0.02}$	$\textbf{2.81} \pm \textbf{0.01}$	$56.6 \pm 0.2$	$\textbf{43.7} \pm \textbf{0.9}$	
$\textbf{3.07} \pm \textbf{0.02}$	$\textbf{2.80} \pm \textbf{0.01}$	$\textbf{56.2} \pm \textbf{0.3}$	$\textbf{43.1} \pm \textbf{1.0}$	
$\textbf{3.07} \pm \textbf{0.04}$	$\textbf{2.89} \pm \textbf{0.08}$	$55.9 \pm 0.3$	$\textbf{43.6} \pm \textbf{1.3}$	
$\textbf{2.91} \pm \textbf{0.08}$	$\textbf{2.80} \pm \textbf{0.07}$	$\textbf{57.4} \pm \textbf{0.7}$	$\textbf{45.7} \pm \textbf{1.4}$	
$\textbf{2.50} \pm \textbf{0.22}$	$2.59\pm0.06$	$\textbf{57.0} \pm \textbf{2.9}$	$\textbf{46.5} \pm \textbf{0.8}$	
	$\label{eq:GPa} \begin{array}{c} H \mbox{ (GPa)} \\ \hline As\mbox{-}cast \\ \hline 1.73 \pm 0.77 \\ 3.09 \pm 0.02 \\ 3.07 \pm 0.02 \\ 3.07 \pm 0.04 \\ 2.91 \pm 0.08 \\ 2.50 \pm 0.22 \end{array}$	$\begin{tabular}{ c c c c } \hline $H$ (GPa) & $$$ & $$ & $$ & $$ & $$ & $$ & $$ &$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

can be further quantified by the pile-up around indents. Herein, we evaluate the pile-up digitally by using topographic profiles, see Fig. 4 (c) and (d). For the as-cast sample, the maximum height of the pile-up is 128 nm at a loading rate of 5 mN/s, which is more than 30% higher than 96 nm of the 30 J sample. It rapidly climbs up to 205 nm at the loading rate of 100 mN/s for the as-cast sample. The lower pile-up of the 30 J sample at a wider region around the indent indicates more homogeneous plastic flow [15,18] when the sample transforms from low-energy to high-energy state, which is consistent with the large plasticity of the ultrasonic-vibrated sample [6].

Meanwhile, the much deeper penetration depth in the as-cast sample, especially at a higher loading rate of 100 mN/s, is observed from the topographic profile of indenters, see Fig. 4 (c). It increases dramatically from 439 to 585 nm with increasing loading rates from 0.5 to 100 mN/s. The deeper penetration depth along with higher pile-up implies a more localized plastic deformation in the as-cased La-based MG sample. This phenomenon is also found in other as-cast MGs such as Pd- [15], Zr- [18, 36] and Fe-based [22] MGs, which is mainly attributed to the structural heterogeneity induced by the fast copper-mold cooling process in as-quenched MGs. Compared with the as-caset sample, the maximum penetration depth for the sample with the vibration energy of 30 J fluctuates more obviously from 50 to 400 nm. It indicates that the 30 J sample under a high-energy glassy state exhibits a quite unstable plastic flow behavior.

#### 3.5. Stress exponent n

The stress exponent *n* as an indicator of time-dependent creep deformation mechanism can be derived according to the empirical power-law relationship between the strain rate  $\dot{\epsilon}$  and the stress  $\sigma$  [37]:

$$\dot{\varepsilon} = k\sigma^n$$
 (1)

where *k* is a temperature dependence constant,  $\dot{\varepsilon} = \dot{h}/h$ ,  $\sigma = P/24.5h^2$ , *P* the applied load on the sample, *h* the instantaneous indenter displacement that can be expressed by the empirical equation  $h(t) = h_0 + a(t-t_0)^b + kt$  proposed by Li and Ngan [38],  $t_0$ ,  $h_0$ , *a*, *b*, and *k* fitting constants. It is noticed in Fig. 5 (a) that the creep displacement is described well by this empirical equation. The corresponding fitting parameters  $h_0$ , *a*, *b*, *k*, are listed in the inset table of Fig. 5 (a).  $h_0$  that represents the initial displacement before creep deformation shows a much larger value of 947 nm for the sample mechanically vibrated with the applied energy of 30 J than 877 nm of the as-cast sample, displaying a more arresting deformation capacity.

The typical  $\ln \dot{e} \cdot \ln \sigma$  curves under the loading rate of 5 mN/s for the as-cast and 30 J samples are plotted in Fig. 5 (b), where the stress exponent *n* can be derived by the slope of:

$$n = \partial \ln \dot{\varepsilon} / \partial \ln \sigma \tag{2}$$

As shown in Fig. 5 (b), *n* becomes a constant value towards the end of the holding period for the power-law creep, demonstrating a steady-state creep behavior. The average value of *n* estimated from five measurements with a standard error at different loading rates is plotted in Fig. 5 (c). The data at the loading rate of 0.5 mN/s that exhibit a large standard error are excluded from the comparison. With increasing loading rates from 1 to 100 mN/s, the *n* decreases gradually from  $15 \pm 2$  to  $13 \pm 1$  and  $11 \pm 2$  to  $4 \pm 0.3$  for the as-cast and 30 J samples, respectively. It is in good agreement with the creep behavior of Fe- and CoFe-based MGs [21,22] that *n* is reduced upon the ascending load rate. After vibration with the energy of 30 J, the sample shows an obviously low value of *n*, consistent with its notable mechanical softening phenomenon.

Compared with MGs with much higher  $T_g$ , e.g., Fe- and CoFe-based MGs [21,22], the value of n in MGs with the relatively low  $T_g$ , e.g., La- and Zr-based [18] MGs, is less sensitive to the loading rate. For instance, n of Fe-based MGs varies from close to 30 to less than 5 with



**Fig. 4.** AFM images  $(10 \ \mu m \times 10 \ \mu m)$  of indents for the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG samples before and after ultrasonic vibration with the energy of 30 J under the room-temperature nanoindentation at a loading rate of 5 mN/s: (a) as-cast and (b) 30 J. The colored height information around the triangular indents reveals both large material pileup at the perimeter of the indent and overlapping layers of severely displaced materials. The cross-sectional profiles of the indents along the orange line of (a) and (b): (c) as-cast and (d) 30 J, showing the surface uplift above the reference surface.

increasing loading rates from 1 to 100 mN/s [21]. While as shown in our previous work, the Zr-based MG displays a constant value of n about 12 that is irrelated to the loading rates after ultrasonic vibration. Slightly different from the Zr-based MG, n of the 30 J La-based sample varies from 11 to 4 when the loading rates change from 1 to 100 mN/s, which may be due to its unstable plastic flow as shown by AFM images.

## 3.6. Defects activation based on relaxation time spectrum in the frame of Maxwell-Voigt model

The creep displacement of a viscoelastic material like MGs intends to obey the Maxwell-Voigt law [39]. As illustrated in Fig. 6 (a), Kelvin units and Maxwell units interact mutually. Here,  $\varepsilon$  is the total strain,  $\varepsilon_{\rm Ms}$  the strain of the Maxwell spring,  $\varepsilon_{\rm Md}$  the strain of the Maxwell dashpot, and  $\varepsilon_{\rm Ki}$  the strain of the *i*-th Kelvin unit. The total displacement can be expressed as:

$$h = h_0 + \sum_{i=1}^n h_i \left( 1 - e^{-t/\tau_i} \right) + t / \mu_0$$
(3)

where  $h_i$  is *i*-th indentation displacement,  $\tau_i$  the characteristic relaxation time for the activation of the *i*-th anelastic Kelvin dashpot, and  $\mu_0$  viscosity constant of Maxwell dashpot. The displacement during the creeping process, thereby, can be divided into two stages: the primary anelastic stage and the secondary viscoplastic stage, see Fig. 5 (b) and (c). In the primary stage, the stress increases promptly along with a drop of strain rate, while in the secondary stage, the strain rate changes into a constant and relatively low value.

As shown in Fig. 6 (d), the typical displacement-time (*h*-*t*) curve of the as-cast sample at a loading rate of 5 mN/s can be fitted well by two Kelvin units (n = 2) with a Maxwell unit connected in series [40]:

$$h = h_1 \left( 1 - e^{-t/\tau_1} \right) + h_2 \left( 1 - e^{-t/\tau_2} \right) + t / \mu_0$$
(4)

where the initial displacement  $h_0$  as well as the initial time in equation (3) is set to 0,  $h_1$ ,  $\tau_1$ , and  $h_2$ ,  $\tau_2$  are the displacement and characteristic relaxation time of first and second Kelvin units, respectively, standing for the first elastic creep stage.  $t/\mu_0$  represents the secondary viscous creep stage. It can be seen that the correlation coefficient  $R^2$  is more than 0.99. The fitting parameters for the typical creep curves at different loading rates are listed in Table 3.

With increasing loading rate from 0.5 to 100 mN/s,  $\mu_0^{-1}$  of as-cast and 30 J samples increase from 0.04  $\pm$  0.03 to 0.20  $\pm$  0.01 and 0.15

 $\pm$  0.01 to 0.39  $\pm$  0.01, respectively. Compared with the as-cast sample,  $\mu_0$  that represents the viscosity coefficient of the Maxwell dashpot remarkably decreases after ultrasonic vibration at the energy of 30 J, demonstrating more significant viscous plastic flow of the 30 J sample during the viscoplastic deformation stage. Both the  $h_1$  and  $h_2$  increase obviously with increasing loading rates, along with the shift of  $\tau_1$  and  $\tau_2$ toward the long-time region. It indicates that the primary elastic stage highly relies on the loading rates. In order to analyze two separate anelastic deformation processes concretely, the relaxation time spectra are calculated by using the equation [41]:

$$L(\tau) = \left[\sum_{i=1}^{n} \left(1 + \frac{t}{\tau_i}\right) \frac{h_i}{\tau_i} e^{-t/\tau_i}\right] \frac{A_0}{P_0 h_{in}} t|_{t=2\tau}$$
(5)

where *L* is the spectrum intensity,  $A_0/P_0$  the inverse of the hardness *H* and  $h_{\rm in}$  the maximum indentation depth. The derived relaxation spectra of the as-cast and 30 J samples with two separate relaxation peaks are displayed in Fig. 7 (a) and (b). The data at the relatively low loading rate such as 0.5 mN/s that exhibit a large standard error for the *H*, *E*<sub>r</sub>, and *n* are eliminated from the comparison.

It is found that with increasing loading rates from 1 to 100 mN/s, both the intensity and relaxation time of the first and second peaks alter remarkably. The intensity of both first and second peaks in relaxation



**Fig. 5.** (a) Typical experimental and fitted room-temperature creep curves of the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG before and after ultrasonic vibration at a loading rate of 5 mN/s and **the peak load of** 50 mN by using the empirical equation  $h(t) = h_0 + a(t - t_0)^b + kt$ . The inset table in (a) shows the corresponding fitting parameter  $h_0$ , a, b and k. (b) The Iné-In  $\sigma$  plot, accordingly. (c) **Steady-state stress exponent**, n, of the as-cast and 30 J samples as a function of indentation loading rates. The solid lines in (c) are guides for the eyes.

spectra increases steeply with increasing loading rates, see Fig. 7 (a) and (b). As mentioned by Castellero et al. [26], each anelastic deformation process that derived from nanoindentation creep curves, is associated with the localized shear transformation involving the rearrangement of small atomic clusters, which corresponds to the activation of flow defects with different relaxation time. Two anelastic components as marked as two peaks in relaxation spectra actually correspond to the activation of flow defects with two different kinds of sizes, i.e., small defects with short characteristic relaxation time and large defects with large characteristic relaxation time [26]. The intensity of each peak is in proportion to the number of flow defects activated during the anelastic deformation process. The increase of the peak intensity with loading rates implies more flow defects intend to be activated at a higher loading rate. It is in coincidence with the observation in Pd-, Zr-, CoFe-, and U-based MGs [15,18,22,24], illustrating a stress-induced defect activation mechanism in MGs. On the other hand, the evident increase of the characteristic relaxation time  $\tau_1$  and  $\tau_2$  with elevated loading rates as listed in Table 3 is also displayed in Fig. 7 (a) and (b). Based on the core-shell model [42], the defects with more free volume are able to dissipate the stress that concentrates around the elastic matrix through a structural rearrangement with a longer relaxation time than that of the elastic matrix during the inelastic deformation of MGs [43]. The increase of  $\tau_1$  and  $\tau_2$  suggests that the flow defects with enlarged size are more likely to be activated at a higher loading rate during the anelastic deformation process.

Compared with the as-cast sample, the first peak in the relaxation spectra of the 30 J sample is more sensitive to the loading rates. The dramatic increase of the intensity of the first peak for the 30 J sample, particularly at a higher loading rate of 50 and 100 mN/s is shown in Fig. 7 (b). To clarify the effect of ultrasonic vibration on the defect activation during anelastic deformation process, the relaxation spectra of as-cast and 30 J sample are compared at different loading rates. Fig. 7 (c) shows the corresponding relaxation spectra at a loading rate of 5 mN/s. The intensity of the second peak in relaxation spectra of the 30 J sample is a factor of two higher than that of as-cast samples. It indicates that flow defects with longer characteristic relaxation time are more likely to be activated at a low loading rate after ultrasonic vibration. When the loading rates increase up to more than 50 mN/s, the flow defects with shorter characteristic relaxation time as demonstrated by the first relaxation peak are prone to be activated after ultrasonic vibration, see Fig. 7 (d). The dominant role of flow defects with shorter characteristic relaxation time at a high load rate during anelastic deformation process has also been found in the case of the ultrasonicvibrated Pd40Cu30P20Ni10 MGs [15], which is proposed to be associated with the soft transverse acoustic process accompanied with the obvious decrease of E [15,44]. It promotes more homogenous plastic deformation in the Pd-based MG as demonstrated by the fixed maximum penetration depth that independent on the loading rate. Unlike the Pd-based MG, an unstable plastic flow as indicated by the large fluctuation in the maximum penetration depth, especially at a low loading rate, is observed in the ultrasonic-vibrated La-based MG. It might be ascribed to the activation of flow defects with long characteristic relaxation time at a low loading rate in the 30 J sample, as shown in Fig. 7 (c). These large defects intend to embed in the weakly bonded region of the glassy matrix, which are thermally unstable and easily activated as a consequence of structural rejuvenation and annihilated during the relaxation process [26]. The appearance of these large defects might lead to some open-volume regions percolated with each other, which eventually gives rise to shear softening accompanied with a pronounced and unstable creep behavior in the ultrasonic-vibrated La-based MG.

# 3.7. The activation energy for glass transition, the nucleation, and growth of crystals

It has been reported that the ultrasonic treatment not only assists



**Fig. 6.** Illustration of the modeling analysis on the nanoindentation creep test: (a) the viscoelastic model used for analyzing the creep process; (b) the division of the creep process into three different parts; (c) the schematic diagram of the *h*-*t* curve during the load holding stage. (d) Experimental and fitted room-temperature creep curves of the typical as-cast  $La_{55}Al_{25}Ni_5Cu_{10}Co_5$  MG sample at a loading rate of 5 mN/s and the peak load of 50 mN by using Maxwell-Voigt model.

Table 3 The fitting parameters of the creep curves of the  $La_{55}Al_{25}Ni_5Cu_{10}Co_5$  MG before and after ultrasonic vibration with the energy of 30 J based on the Maxwell-Voigt model.

	Loading rate (mN·s <sup><math>-1</math></sup> )	<i>h</i> <sub>1</sub> (nm)	$\tau_1(s)$	<i>h</i> <sub>2</sub> (nm)	$\tau_2(s)$	$\mu_0^{-1} \text{ (nm s}^{-1}\text{)}$
As-cast	0.5	$4.1\pm0.3$	$1.9\pm0.3$	$10\pm4$	$44\pm16$	$\textbf{0.04} \pm \textbf{0.03}$
	1	$5.3\pm0.3$	$1.0\pm0.2$	$7.3\pm0.3$	$17\pm2$	$0.15\pm0.01$
	5	$7.4\pm0.4$	$0.9\pm0.1$	$8.2\pm0.3$	$13\pm1$	$0.21\pm0.01$
	10	$\textbf{8.8}\pm\textbf{0.3}$	$1.2\pm0.1$	$16\pm2$	$32\pm4$	$0.15\pm0.02$
	50	$11.1\pm0.3$	$1.1\pm0.1$	$15.5\pm0.7$	$24\pm2$	$0.17\pm0.01$
	100	$10.3\pm0.2$	$0.6\pm0.1$	$20.1\pm0.6$	$25\pm1$	$0.20\pm0.01$
30 J	0.5	$3.3\pm0.4$	$1.7\pm0.4$	$5.4\pm0.3$	$15\pm2$	$0.15\pm0.01$
	1	$5.9\pm0.3$	$0.9\pm0.1$	$9.6\pm0.3$	$16\pm1$	$0.24\pm0.01$
	5	$6.9\pm0.3$	$1.0\pm0.1$	$13.1\pm0.3$	$17\pm1$	$0.28\pm0.01$
	10	$8.1\pm0.3$	$0.6\pm0.1$	$15.0\pm0.3$	$15\pm1$	$0.34\pm0.01$
	50	$12.1\pm0.4$	$1.4\pm0.1$	$15.8\pm0.6$	$21\pm2$	$0.34\pm0.01$
	100	$12.4\pm0.3$	$1.0\pm0.1$	$15.6\pm0.5$	$22\pm1$	$\textbf{0.39} \pm \textbf{0.01}$

shear deformation [45], but also has high impact on the crystallization behavior of MGs [8]. Therefore, the activation energy  $E_c$  for atomic diffusion of MGs during glass transition ( $E_g$ ) or crystallization ( $E_x$  and  $E_p$ ) is derived in virtue of the characteristic temperature *T*, i.e.,  $T_g$ ,  $T_x$ , and the peak crystallization temperature  $T_p$  [46]:

$$\ln\left(\frac{T^2}{\theta}\right) = \frac{E_{\rm c}}{RT} + \ln\left(\frac{E_{\rm c}}{k_0R}\right) \tag{6}$$

where  $\theta$  is the heating rate, *R* the gas constant, and  $k_0$  the frequency factor (i.e.,  $k_g$  at  $T_g$ ,  $k_x$  at  $T_x$ , and  $k_p$  at  $T_x$ ). The DSC traces of the as-cast and 30 J samples with heating rates ranging from 5 to 40 K/min are displayed in Fig. 8 (a) and (b). Fig. 8 (c) and (d) gives the corresponding Kissinger plots (ln ( $T^2/\theta$ ) - 1000/T). According to the slope  $E_c/R$  of Kissinger plots, we can access to the activation energies,  $E_g$ ,  $E_x$ , and  $E_p$ . The values of  $E_g$  are 140 and 208 kJ/mol for the as-cast and 30 J samples, respectively. It is found that  $E_g$  of the 30 J sample is almost twice of the as-cast sample. This means that the energy barrier for atomic diffusion in the supercooled liquid region intends to be enhanced by ultrasonic vibration in the La-based MG. The structural rearrangement aroused by ultrasonic vibration also effectively improves the activation energy for nucleation,  $E_x$ . The value of  $E_x$  increases from 122 kJ/mol of the as-cast sample to 181 kJ/mol of the 30 J sample. The increase of the energy barrier for the nucleation illuminates that the incubation time of crystal nucleus is extended under ultrasonic vibration. On the other hand, the activation energy for the growth of crystalline phases,  $E_{\rm p}$  is reduced by about 64% after ultrasonic vibration, which is 131 kJ/mol of the as-cast sample and 108 kJ/mol of the 30 J sample. It results in a low energy barrier for atomic diffusion during the fast crystallization process. This phenomenon is in well agreement with the reduction of the crystallization enthalpy  $\Delta H_x$  from 4.624 to 3.824 J/mol after ultrasonic vibration (see in Table 1), which may be attributed to the stress-induced structural rejuvenation as discussed in section 3.1. along with fast atomic diffusion [7,36]. It is also the underlying reason for the ultrasound-accelerated crystallization events as reported in fragile MGs at the temperature far away from  $T_g$  [8].

Based on  $E_g$ , the fragility parameter m [47] can be derived as well:



**Fig. 7.** The relaxation spectra of the  $La_{55}Al_{25}Ni_5Cu_{10}Co_5$  MG before and after ultrasonic vibration with the energy of 30 J **on the anelastic part of their** room-temperature **creep curves at the different loading rate and the peak load of** 50 mN: (a) as-cast and (b) 30 J. The relaxation spectra of the as-cast and 30 J samples at the loading rate of 5 mN/s (c) and 50 mN/s (d).

$$m = \frac{dlog\eta(T)}{d(T_g/T)}\Big|_{T=T_g} = \frac{E_g}{\ln 10 RT_g}$$
(7)

where  $\eta(T) = \eta_0 \exp(E/k_B T)$ ,  $\eta_0$  the viscosity at the high-temperature limit and  $k_B$  Boltzmann's constant. As shown in Table 1, the calculated value of *m* is  $16 \pm 1$  for the as-cast sample. It increases to  $24 \pm 1$ after ultrasonic vibration, demonstrating more fragile dynamic behavior approaching supercooled liquid regime. Such change in fragility is similar to that observed in the Zr-based MG [18], but much more obvious in case of the La-based MG. In fact, the fragility *m* correlates with the slow  $\beta$ -relaxation at the glassy state [48]. The glass-forming liquid with higher fragility normally shows more pronounced slow  $\beta$ -relaxation due to the high dynamical heterogeneity in supercooled liquids and structural heterogeneity in glassy solids [49,50]. More fragile viscous flow in the ultrasonic-vibrated La-based MG sample indicates that the structural heterogeneity induced by the high-frequency mechanical vibration leads to the more pronounced slow  $\beta$ -relaxation as a result of the defect activation. This is in coincidence with the work of Wang. et al. that the ultrasonic-assistant structural rejuvenation and local density fluctuation are associated with the process of the slow  $\beta$ -relaxation [7]. The pronounced slow  $\beta$ -relaxation has been reported that closely relates to the global plasticity of La-based MGs [51], which can impactfully alter the plastic flow behavior of MGs [50]. Therefore, we propose that the excellent plastic flow behavior as demonstrated by the large creep deformation after ultrasonic treatment in the studied La-based MG is actually attributed to the slow  $\beta$ -relaxation at ambient temperature associated with the activation of flow defects, which may be one of dominant factors that promotes the ultrasonic-assistant cold joining or molding of bulk MGs with large size besides the fast surface dynamics of glassy materials on a small scale, such as amorphous thin films [11,52,53]. On the other hand, the percolated open-volume

regions induced by the activation of large defects would accelerate the  $\alpha$ -relaxation process at the same time, which might relate to the slightly decrease of  $T_g$  after ultrasonic vibration. It is coincident with the more obvious viscoplastic deformation at the secondary creep stage of the 30 J sample.

#### 4. Conclusion

In summary, the microscopic mechanical behaviors of the as-cast and ultrasonic-vibrated La55Al25Ni5Cu10Co5 MGs were investigated by means of nanoindentation. The mechanical softening along with structural rejuvenation was found after ultrasonic treatment, which is associated with the defect activation in the frame of Maxwell-Voigt model. At a low loading rate, the flow defects with long characteristic relaxation time intend to be activated under ultrasonic vibration, which can result in the large creep displacement along with an unstable plastic flow. With increasing loading rate up to 50 mN/s, the flow defects with short characteristic relaxation time are more likely to be activated, which prone to involve in the soft transverse acoustic phonon process accompanied with the dramatic reduction of  $E_r$  in the ultrasonic-vibrated Labased MG. A more fragile dynamic behavior as demonstrated by the notable increase of *m* implies that the pronounced plastic flow induced by ultrasonic vibration is closely related to the activation of slow  $\beta$ -relaxation. Our work provides a clear picture of the ultrasonicpromoted structural transition in a La-based MG from the as-quenched metastable state into a rejuvenated high-energy state in virtue of the microscopic mechanical response, which has not been noticed in both Zr- and Pd-based MGs with higher Tg and even higher ultrasonicvibrated energy [15,18]. Such ultrasonic-assistant rejuvenation behavior also lowers the energy barrier for atomic diffusion during crystallization and slightly reduces  $T_g$  and  $T_x$  of the La-based MG. This



**Fig. 8.** DSC traces of the La<sub>55</sub>Al<sub>25</sub>Ni<sub>5</sub>Cu<sub>10</sub>Co<sub>5</sub> MG before and after ultrasonic vibration with the energy of 30 J at heating rates ranging from 5 to 40 K/min: (a) as-cast and (b) 30 J. Kissinger plots, the calculated the activation energies relative to  $T_g$ ,  $T_x$ , and  $T_p$ , and the fragility parameter *m*: (c) as-cast and (d) 30 J.

study may help us reveal the defect activation mechanism of MGs as well as other disordered materials under ultrasonic vibration, which might shed new light on understanding the microscopic deformation mechanism of glassy materials and further promote their advanced industrial applications based on the cold working methods with low in production cost.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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