Identifying the high entropy characteristic in La-based metallic glasses

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Abstract: High temperature deformation was probed in a La-based high entropy metallic glass with an evident slow β relaxation. The correlation between high configurational entropy and high temperature deformation mechanism was analyzed. On the one hand, by increasing the strain rate, the degree of deviation from Newtonian behavior in high entropy metallic glasses is lower than that of conventional metallic glasses, which is ascribed to the high configurational entropy. On the other hand, high configurational entropy leads to a decrease of activation volume in high temperature deformation of metallic glasses. Identifying the influence of high configurational entropy on the deformation mechanism paves the way for further understanding of the mechanical behavior of metallic glasses.

Keywords: High entropy metallic glass; Slow β relaxation; High temperature deformation; Free volume model

30 Metallic glasses (MGs) are metallic alloys in which long-range ordered atomic
31 structure is absent ¹⁻³. High entropy alloys (HEAs) are defined as multicomponent
32 alloys containing at least five elements with equiatomic or near-equiatomic ratio
33 between 5 and 35 at.% ^{4,5}. Combining the amorphous structure of MGs and the **high**
34 **configurational entropy** of HEAs, high entropy metallic glasses (HE-MGs) have
35 attracted intensive attention in recent years benefiting from their superior mechanical
36 properties, excellent glass-forming ability and unique properties ⁶⁻⁸. It is significant to
37 investigate the performance of HE-MGs, which could be new candidates to be applied
38 as structural and engineering materials.

39 The plastic deformation mechanism of MGs can be classified into two types:
40 inhomogeneous deformation and homogeneous deformation ⁹. In general, deformation
41 mode of MGs is inhomogeneous at high strain rates and/or low temperature, this mode
42 is characterized by the initiation and propagation of shear bands ¹⁰. On the contrary,
43 homogeneous deformation of MGs takes place at high temperatures (i.e., $T > 0.8 T_g$,
44 where T_g is the glass transition temperature) and/or low strain rates ¹¹. In the
45 homogeneous mode, MGs display remarkable plasticity and show a smooth transition
46 from Newtonian- (i.e., viscosity independent on strain rate) to non-Newtonian flow (i.e.,
47 viscosity dependent on strain rate). This phenomenon has been verified in typical MGs
48 (e.g., Pd-, Cu-, Zr-based MGs) ^{12,13}. In addition, previous reports have clarified that this
49 transition is attributed to an introduction of structural defects induced by external stress
50 ¹². Currently, there is an active discussion relative to the correlation between
51 microscopic deformation mechanisms and relaxation behaviors in glassy solids ¹⁴⁻¹⁶.
52 There are two relaxation processes in glassy solids: the slow β relaxation, correlated to
53 local atomic jumps, and the main α relaxation, which is related to large-scale atomic
54 rearrangements ^{17,18}. Significantly, the slow β relaxation is closely correlated to the
55 plasticity of MGs, i.e., the activation energy of slow β relaxation E_β is approximately
56 equal to the energy barrier of shear transformation zones (STZs) W_{STZ} ¹⁹.

57 HEAs display four core features: (1) **high configurational entropy** effects, (2)

sluggish diffusion, (3) severe lattice distortion and (4) cocktail effects²⁰. However, whether these effects still exist in HE-MGs is still under discussion. Recent investigations have reported great advances in the influence of **high configurational entropy** on the thermodynamics and kinetics of HE-MGs²¹⁻²⁴. Benefiting from the sluggish diffusion, the atomic rearrangements of HE-MGs are remarkably hindered²⁵. Moreover, the **high configurational entropy** and the sluggish diffusion improve the structural instability, which results in intensifying the intrinsic ductility²⁴. Unfortunately, the deformation mechanism, dynamic relaxation behavior, structural and dynamic heterogeneities and their correlations with **high configurational entropy** have yet to be clarified. In particular, to what extent the characteristics of HEAs stimulate the plastic deformation mechanism is still unclear. In the current work, La₃₀Ce₃₀Ni₁₀Al₂₀Co₁₀ HE-MG was chosen as model alloy to investigate the high temperature plastic deformation mechanism from a novel perspective, considering the **high configurational entropy** of HE-MGs. The results obtained could offer an ingenious understanding of the apparent features of the **high configurational entropy** effect.

A master alloy ingot with a nominal chemical composition of La₃₀Ce₃₀Ni₁₀Al₂₀Co₁₀ (at.%) was prepared by arc-melting in a titanium-gettered high purity atmosphere. The ingot was re-melted at least five times to ensure the chemical homogeneity. Ribbons with a cross section of 0.02 mm×1.2 mm were prepared by the melt spinning technique. The dynamic mechanical properties of the model glass were characterized in a commercial dynamic mechanical analyzer (DMA, TA instruments Q800) in tension film mode. The strain response $\varepsilon = \varepsilon_0 \cos(2\pi ft + \delta)$ of the viscous-elastic material to a sinusoidal stress $\sigma = \sigma_0 \cos(2\pi ft)$ was obtained, where f is the driving frequency and δ the phase lag. The complex Young's modulus can be expressed as $E = \sigma/\varepsilon = E' + iE''$, where E' is the storage modulus while E'' is the loss modulus. The internal friction (also called loss factor) correlated to the molecules/atoms mobility of glassy solids is defined as $\tan\delta = E''/E'$. High temperature deformation tests of model alloys were conducted in the DMA at various temperatures with strain rate ranges from $1 \times 10^{-4} \text{ s}^{-1}$ to 1.25×10^{-3}

86 s^{-1} .

87 Fig. 1 (a) displays the temperature dependence of the normalized storage modulus
88 E'/E_u and loss modulus E''/E_u of $La_{30}Ce_{30}Ni_{10}Al_{20}Co_{10}$ HE-MG (driving frequency is
89 3 Hz and heating rate is 3 K/min). E_u is the value of the storage modulus at ambient
90 temperature. One can see that $La_{30}Ce_{30}Ni_{10}Al_{20}Co_{10}$ HE-MG exhibits a pronounced
91 slow β relaxation peak and a main α relaxation peak. The results also show that the
92 temperature span of slow β relaxation is wider than that of α relaxation. Fig. 1 (b) shows
93 the normalized loss modulus E''/E''_{max} versus the normalized temperature T/T_α in typical
94 La-based MGs, where E''_{max} is the maximum value of loss modulus while T_α is the α
95 relaxation peak temperature. The interplay between chemical composition and
96 diffusion of the smallest atoms of MGs have a crucial influence on the slow β relaxation
97 process^{26,27}. As a consequence, the intensity of slow β relaxation varies in La-based
98 MGs.

99

100 Fig.1 (a) Dependence of normalized storage modulus E'/E_u and loss modulus E''/E_u of
101 $La_{30}Ce_{30}Ni_{10}Al_{20}Co_{10}$ HE-MG on temperature. E_u is the value of storage modulus at
102 ambient temperature. (b) Normalized loss modulus E''/E''_{max} in typical La-based MGs
103 as function of normalized temperature T/T_α . E''_{max} is the maximum of the loss modulus

and T_α is the α relaxation peak temperature.

Strain rate jump tests is an effective method to probe the high temperature deformation behavior of MGs²⁸. Fig. 2(a) displays uniaxial, tensile true stress–strain responses during a strain rate jump test at a given temperature of 440 K and strain rates ranging from $1 \times 10^{-4} \text{ s}^{-1}$ to $1.25 \times 10^{-3} \text{ s}^{-1}$. The true stress increases sharply with the increase of the strain, then, it gradually decreases after reaching a peak value, and finally equilibrates at a stable value. This mechanical behavior can be well described by the free volume model proposed by Spaepen et al²⁹. The stress overshoot is attributed to the creation of free volume by plastic deformation³⁰.

Based on a series of strain rate jumps, the variation of apparent viscosity with both strain rate and temperature could be readily computed as: $\eta = \sigma(T)/3\dot{\epsilon}$, where $\dot{\epsilon}$ is the strain rate and $\sigma(T)$ is the corresponding steady state flow stress. Fig. 2(b) shows the apparent viscosity as a function of strain rate at various temperatures. The viscosity-strain rate curves of $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG show the main characteristics of amorphous systems, in which viscosity increases as strain rate decreases and approaches the Newtonian regime. Taking into account that an obvious transition from non-Newtonian to Newtonian flow is hardly observed in such a relatively narrow strain rate window (the lower the strain rate, the longer the isothermal time required, and the more difficult it is for the sample to remain amorphous), at the highest temperature of 453 K, an approximate Newtonian behavior with small strain rate dependence on viscosity could be observed.

Referring to a previous theoretical approach, the evolution of normalized viscosity η/η_N with strain rate can be described by the Kohlrausch-Williams-Watts (KWW) stretched exponential equation³¹:

$$\frac{\eta}{\eta_N} = \left\{ 1 - \exp \left[- \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_{KWW}} \right)^{\beta_{KWW}} \right] \right\} \quad (1)$$

Where η_N is the Newtonian viscosity, γ is a fitting parameter related to the critical transition strain rate and β_{KWW} is the stretching exponent determining the slope of the non-Newtonian viscosity as a function of strain rate. Generally, the value of β_{KWW} is in the range from 0 to 1. One can obtain the master curve of normalized viscosity η/η_N by horizontal shift of the data obtained at different temperatures. As illustrated by Fig. 2(c), a master curve of normalized viscosity at the reference temperature $T_{ref} = 440 \text{ K}$ was obtained. The horizontal shift leads to a fairly good agreement with the experimental

data. The value of β_{KWW} for $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG is equal to 0.58. The values of β_{KWW} in some HE-MGs and MGs are displayed in Fig. 2(d) (experimental results of other MGs were obtained from literature^{12,13,31-36}). One can see that the value of β_{KWW} in HE-MGs is approximately equal to 0.6 while that of MGs ranges from 0.7 to 0.9. Therefore, the value of β_{KWW} in HE-MGs is significantly lower than the average value found in MGs. It is reasonable to conclude that the degree of deviation from the Newtonian behavior in this HE-MGs is lower in most MGs, which may be due to the high configurational entropy effect on viscous flow.

In addition to strain rate jumps, stress relaxation and creep are also powerful methods to explore the anelastic deformation and structural/dynamic heterogeneity of MGs³⁷. The mechanical response of HE-MGs under constant stress (creep) or strain (stress relaxation) could be well described by various relaxation events³⁸⁻⁴⁰. And the evolution of these relaxation events includes various characteristic relaxation times and activation barriers. The width of such distribution of characteristic relaxation times can be assessed by the value of the exponent β_{KWW} ³⁷. In other words, the exponent β_{KWW} is an indicator of the structural/dynamic heterogeneity of HE-MGs. A larger β_{KWW} corresponds to less heterogeneity. The stretched exponential relaxation has been explained by two limiting scenarios: one is the “homogeneous”, all of the particles in the system relax identically but by an intrinsically nonexponential process; the other is the “heterogeneous”, the superposition of different simple exponential relaxations with different relaxation times⁴¹. It is worth mentioning that MGs exhibit various values of β_{KWW} under the different mechanical simulations, which provides a novel insight into exploring the evolution of structural/dynamic heterogeneity.

Fig.2 (a) Typical true stress-true strain curve of $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG during tensile strain rate jump tests at 440 K. The strain rates range from 1×10^{-4} to 1.25×10^{-3} ; (b) Viscosity as a function of strain rate at various temperatures; (c) Master curve of normalized viscosity η/η_N and the fitting curve using Eq. (1), the reference temperature is 440 K; (d) KWW parameter β_{KWW} of the normalized viscosity master curve for typical MGs and for HE-MGs.

Transition state theory, which is extensively used to describe the correlation between steady state flow stress and strain rate, was proposed by Turnbull and extended by Spaepen in the framework of the free volume model²⁹. Under the situation of uniaxial tension, the transition from non-Newtonian flow to Newtonian flow in typical MGs can be described as²⁹:

$$\dot{\epsilon} = 2c_f \vartheta_D \exp\left(\frac{-\Delta G}{kT}\right) \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) = \dot{\epsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) \quad (2)$$

where c_f is the concentration of activated defects, ϑ_D is the Debye frequency of 10^{13} s^{-1} , ΔG is the apparent activation energy, V is the apparent characteristic activation volume, and $\dot{\epsilon}_0$ is the temperature-dependent rate factor. Fig. 3(a) displays the steady state flow stress versus strain rate, the solid curves correspond to Eq. (2) with the values of activation volume V fitted from the data at various temperatures. The activation volume was about 0.19 nm^3 at 440 K, while it increased to 0.53 nm^3 at 453 K, this change reflects a drastic uptrend with temperature. As seen in Fig. 2(b), the viscosity decreases as the test temperature increases, introducing a higher flow capacity and a

larger activation volume at higher temperatures. The above outcomes are consistent with those in various MGs^{12,13}. Considering an average atomic volume of $\Omega_f = 0.013 \text{ nm}^3$, the activation volume during plastic deformation of the $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG corresponds to about 20~42 atoms³³.

Previous literature has reported the effects of substituting one element by another with a near-equal atomic radius (such as the substitution of Co by Ni)^{7,42}. Such substitution introduces a noteworthy influence on the **configurational entropy**, which provides a novel insight into exploring the effect of **configurational entropy** on high temperature deformation of MGs. We selected three MGs with different **configurational entropy**, i.e., $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$, $\text{La}_{30}\text{Ce}_{30}\text{Al}_{15}\text{Co}_{25}$ and $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG, to clarify the correlation between **configurational entropy** and activation volume. The **configurational entropy** S_c of MGs could be directly estimated as $S_c = -R \sum_{j=1}^n x_j \ln(x_j)$. One can obtain that the configurational entropy is $0.94 R$, $1.35 R$, and $1.50 R$ for $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$, $\text{La}_{30}\text{Ce}_{30}\text{Al}_{15}\text{Co}_{25}$, and $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$, respectively. Fig. 3(b) shows the evolution of activation volume V as a function of normalized temperature T/T_α . Interestingly, the activation volume of the La-based HE-MG is significantly smaller than that of the other La-based MGs. It should be pointed out that a smaller activation volume corresponds to less atoms contributing to plastic deformation. It is reasonable to speculate that **high configurational entropy** promotes small activation volume. In parallel, the Gibbs free energy plays a key role as driving force to activate the atomic rearrangements²⁹. The introduction of **high configurational entropy** reduces the Gibbs free energy, which confirms the correspondence between **high configurational entropy** and small activation volume⁴³.

Fig.3 (a) Variation of the strain rate with the steady stress in La₃₀Ce₃₀Ni₁₀Al₂₀Co₁₀ HE-MG and the fitting curves using Eq. (2); (b) Normalized temperature dependence of activation volume in La₆₀Ni₁₅Al₂₅ MG, La₃₀Ce₃₀Al₁₅Co₂₅ MG and La₃₀Ce₃₀Ni₁₀Al₂₀Co₁₀ HE-MG.

From the perspective of potential energy landscape, the slow β relaxation is associated with atomic transition processes between subbasins⁴⁴. In addition, the slow β relaxation is the trigger to activate the plastic strain during the plastic deformation⁴⁵. Assuming that the applied stress slopes the potential energy landscape, resulting in a lower potential barrier for the transition to a stable configuration, with the increase of the stress more atoms trapped in the basins can be activated by thermal and mechanical stimulation thus triggering the plastic deformation.

It is well known that La- and Ce-based MGs display a distinct peak of slow β relaxation while CuZr-based MGs exhibit a weaker slow β relaxation, the latter observed as an “excess wing”¹. The activation volume of high temperature deformation in CuZr-based MGs has been reported to range from 0.15 nm³ to 0.35 nm³⁴⁶. Significantly, the activation volumes and the concentration of flow defects of La-based MGs in the current work are higher than the ones found in CuZr-based MGs. In the

literature, MGs have been modelled as constituted by soft “liquid-like” and hard “solid-like” regions⁴⁷. The soft “liquid-like” regions, where the deformation units are easier to activate, possess low density, low elastic modulus and high atomic mobility associated with high flow capacity. It is well accepted that the slow β relaxation, originated from the string-like atoms movement in “soft” regions, is closely associated with the structural heterogeneity^{1,2,27,48}. Therefore, more atoms may be involved in response to thermal or mechanical stimulations and contribute to the plastic deformation in MGs with obvious slow β relaxation. **It is then reasonable that MGs possessing apparent slow β relaxation show higher activation volumes, which is in good agreement with the experimental results.** Fig. 4 is a schematic diagram of activation volumes in MGs and HE-MGs showing a pronounced slow β relaxation. **From the results shown in this work, less atoms are activated in $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG.** Nevertheless, knowledge of the distribution of deformation units (liquid-like regions) is absent, which makes difficult to establish the correlation between structural heterogeneity and **high configurational entropy**.

Fig.4 Schematic diagram of activation volumes in MGs and HE-MGs with a pronounced β relaxation.

In summary, the high temperature deformation behavior and the effect of **high configurational entropy** on the high temperature deformation mechanism of $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG were discussed in the framework of the free volume model. The main results are summarized as follows:

- **$\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG with a pronounced slow β relaxation is a suitable candidate to elucidate the effects of both high configurational entropy and slow β relaxation on the mechanical behavior of MGs.**

- **Different from conventional La-based MGs, a weaker deviation from Newtonian**

behavior is found in the HE-MG, which can be ascribed to higher configurational entropy.

- Compared with conventional La-based MGs, in $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ HE-MG the high configurational entropy is related to a small activation volume of the high temperature deformation behavior.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (NSFC) (Grant No. 51971178) and Natural Science Basic Research Plan for Distinguished Young Scholars in Shaanxi Province (Grant No. 2021JC-12). E. Pineda and D. Crespo acknowledge financial support from MICINN (grant FIS2017-82625-P) and Generalitat de Catalunya (grant 2017SGR0042). The investigation of Y. J. Duan is sponsored by Innovation Foundation for Doctor Dissertation of Northwestern Polytechnical University (No. CX202031). The investigation of L.T. Zhang is sponsored by Innovation Foundation for Doctor Dissertation of Northwestern Polytechnical University (No. CX2021015).

Data availability statement

The data that supports the findings of this study are available within the article.

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