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Correlation between strain rate sensitivity and $\alpha$ relaxation of metallic glasses

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An inherent correlation between the strain rate sensitivity and $\alpha$ relaxation of metallic glasses (MGs) is observed. This correlation can be attributed to the secondary term which incorporates the nonaffine displacements of atoms in the analytical expression of the elastic modulus of amorphous solids. The observed correlation supports the proposition that stress and temperature play equivalent role in the glass transition of MGs. Besides, an ideal liquid state of MGs is observed in the supercooled liquid region when they are deformed below a critical loading rate. This observation would benefit the application of MGs in the fabrication of micro parts for MEMS (Micro Electro-Mechanical Systems).

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I. INTRODUCTION

Compared to crystal alloys,$^1$ the deformation mechanism of metallic glasses (MGs) is far from being well understood.$^2$ This fact is mostly due to the lack of clearly defined periodic atomic structures in amorphous materials.$^3$ Nowadays, it is prevalent to describe the plastic deformation of crystal materials as thermally activated movements of crystal defects, like dislocation, twinning, and grain boundary etc.$^4$ The strain rate sensitivity index $m = \partial \ln \tau / \partial \ln \dot{\gamma}$ is related to the type of defects which is involved in deformation, where $\tau$ is flow stress and $\dot{\gamma}$ is shear strain rate. This is because of the relation between the strain rate sensitivity index $m$ and the activation volume$^5$ $\Delta V$ which is required for the thermally activated movements of crystal defects in deformation: $\Delta V = kT \tau m$, where $k$ is Boltzmann constant; $T$ is temperature. Since different crystal defects are of different activation volumes,$^6$ the strain rate sensitivity index $m$ actually reflects the underlying atomistic mechanism of deformation. From this aspect of view, although MGs do not contain crystal defects, their strain rate sensitivity in plastic deformation could also be useful to understanding their atomistic deformation mechanisms.$^7$ Recently, in spite that controversy on the understanding of the strain rate sensitivity of MGs observed in nanoindentation exists,$^8$ nanoindentation$^9,10,11$ remains an effective technique for studying the strain rate sensitivity of the plastic deformation of MGs, for its high resolution in the measurement of indentation depth and the confined deformation mode in indentation which effectively prevents shear fracture from happening.

On the other hand, since MGs do not contain crystal defects, structural relaxation$^{12}$ which can be viewed as viscous atomic rearrangements is proposed to be crucial in the deformation of MGs.$^{13}$ Specifically, the main $\alpha$ relaxation is related to the macroscopic homologous flow of MGs.$^{14}$ The secondary relaxation (or $\beta$ relaxation), also known as Johari-Goldstein relaxation, is related to the elementary flow unit of MGs due to the consistent activation energy required for the two processes.$^{15}$ The main $\alpha$ relaxation can be envisioned as the percolation of the Johari-Goldstein relaxation.$^{13}$ Therefore, the plastic deformation of MGs can be understood as the movements of...
Johari-Goldstein relaxation events,\textsuperscript{16} like the fact that the deformation of crystal alloys can be understood as the movements of crystal defects. Usually, the structural relaxation of MGs is characterized by dynamic mechanical analysis (DMA),\textsuperscript{17} where the storage modulus spectrum and loss modulus spectrum of MGs in temperature domain can be obtained at different sweep frequencies. The structural relaxation spectrum shows different internal friction peaks which correspond to different relaxation processes,\textsuperscript{18} for instance, the main $\alpha$ relaxation, the $\beta$ relaxation,\textsuperscript{19} and the unusual fast $\beta$ relaxation\textsuperscript{20} The structural relaxation spectrum depends intimately on the sweep frequency used in DMA, indicating the frequency dependence of the structural relaxation of MGs. For the crucial relationship between structural relaxation and deformation of MGs, the frequency dependence of the structural relaxation of MGs is also very important to understanding the deformation mechanism of MGs.\textsuperscript{21}

Since Johari-Goldstein relaxation is related to the elementary flow unit of MGs, in this work, we choose 3 typical MG systems which exhibit different Johari-Goldstein relaxation characteristics, namely, a La-based (La) MG (La$_{62}$Al$_{14}$Ag$_{2}$Sb$_{3}$Ni$_{10.83}$Co$_{10.83}$) showing pronounced Johari-Goldstein relaxation,\textsuperscript{22} a Pd-based (Pd) MG (Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$) showing less-pronounced Johari-Goldstein relaxation,\textsuperscript{18} and a Zr-based (Zr) MG (Zr$_{41.2}$Ti$_{13.8}$Cu$_{10}$Ni$_{12.8}$Be$_{22.5}$, Vit1) showing no pronounced Johari-Goldstein relaxation,\textsuperscript{23} to systematically investigate the strain rate sensitivity and structural relaxation of MGs and to explore the deformation mechanism of MGs.

II. EXPERIMENTAL

Alloy sheets of the 3 MGs of a size of 2 mm$\times$30 mm$\times$40 mm are prepared from pre-melted master alloys by copper mould casting under Ti-gettered Ar atmosphere. The amorphous structure of the prepared sheets is examined via X-ray Diffraction (XRD) and differential scanning calorimeter (DSC). The samples for nanoindentation were polished to mirror finish before experiments. Nanoindentation is conducted on an MTS Nano Indenter XP$^{\text{TM}}$ with a Berkovich diamond tip. Load control mode and a group of loading rates $P$: 0.33mN/s, 1.32mN/s, 13.2mN/s, and 70mN/s are selected. DMA is conducted on a TA DMA Q800 instrument equipped with a single cantilever clip. Specimens of 0.8 mm$\times$2 mm$\times$35 mm in size for DMA are prepared via electrical discharging machining. Temperature sweeps are performed at a series of loading frequencies: 0.05, 0.2, 1, 5, and 20 Hz. The heating rate and the applied dynamic strain are $q = 3$ K/s and $\varepsilon_0 = 0.03\%$, respectively.

III. RESULTS

In Fig. 1, the open circles show the indentation depth ($h$)-dependent nominal strain rate $\dot{\varepsilon} = \frac{1}{h} \cdot \frac{dh}{dt}$ of the 3 MGs at different loading rates in nanoindentation. The nominal strain rate $\dot{\varepsilon} = \frac{1}{h} \cdot \frac{dh}{dt}$ is directly derived from the time-displacement curve in each test.\textsuperscript{24} The solid rhombuses show the equivalent strain rate $\dot{\varepsilon} = P/2P$ in nanoindentation.\textsuperscript{7} It can be seen that $\dot{\varepsilon} = P/2P$ matches with $\dot{\varepsilon} = \frac{1}{h} \cdot \frac{dh}{dt}$ at loading rates of 0.33 mN/s and 1.32 mN/s. At loading rates of 13.2 mN/s and 70mN/s, a deviation between $\dot{\varepsilon} = P/2P$ and $\dot{\varepsilon} = \frac{1}{h} \cdot \frac{dh}{dt}$, which is similar for different MGs can be observed at low indentation depth, indicating the transient response in the initial stage of nanoindentation at high loading rates. In both cases, with increasing indentation depth, a well determined strain rate value both with $\dot{\varepsilon} = P/2P$ and with $\dot{\varepsilon} = \frac{1}{h} \cdot \frac{dh}{dt}$ can be achieved at the rear part of the curve. This well determined strain rate is in favor of studying the strain rate sensitivity of MGs in nanoindentation.\textsuperscript{7}

Fig. 2(a) shows the strain rate-dependent hardness of the 3 MGs together with the results reported previously.\textsuperscript{7} It can be seen that the strain rate sensitivities of hardness of the 3MGs are similar to the previously reported results. Fig. 2(b) shows the strain rate-dependent reduced modulus of the 3 MGs. In this work, the Pd MG exhibits a strain rate sensitivity index of hardness $m_H = \frac{\partial \lg H}{\partial \lg \dot{\varepsilon}} = -0.0013$ and a strain rate sensitivity index of reduced modulus $(E)$ $m_E = \frac{\partial \lg E}{\partial \lg \dot{\varepsilon}} = -0.0027$, while the La MG shows a larger $m_H = 0.075$ and a larger $m_E = 0.024$. The Zr MG shows a value of $m_H = 0.0090$ and a value of $m_E = 0.0032$. Unlike the characteristic of Johari-Goldstein relaxation of the 3 MGs, where La MG shows pronounced Johari-Goldstein.
relaxation, Pd MG shows less pronounced Johari-Goldstein relaxation, and Zr MG shows no pronounced Johari-Goldstein relaxation, it can be found in the strain rate sensitivity of the 3 MGs that La MG shows prominent strain rate sensitivity, Zr MG shows less prominent strain rate sensitivity, and Pd MG shows little (nearly 0) strain rate sensitivity. The mechanism of the negative strain rate sensitivity of Pd MG, i.e. strain rate softening, has already been addressed in MGs.\\25,26\\

Fig. 3 shows the normalized storage modulus $E'/E'_0$ and normalized loss modulus $E''/E''_{peak}$ of the La (a), Pd (b), and Zr (c) MGs at different frequency, where $E'_0$ is the initial storage modulus at room temperature and $E''_{peak}$ is the peak value of the loss modulus. The storage modulus $E'$ and the loss modulus $E''$ are the real part and the imagine part of the complex modulus: $E^* = E' + iE''$, as $E' = |E^*| \cdot \cos \delta$ and $E'' = |E^*| \cdot \sin \delta$, where $\delta$ is the phase difference between the applied periodical strain $\epsilon$ and the stress response $\sigma$.\\17\\ $E'$ and $E''$ indicate the solid-like (i.e. elastic) part and

FIG. 1. Nominal strain rate of La (a), Pd (b) and Zr (c) MGs in nanoindentation under different loading rate.
FIG. 2. Strain rate-dependent properties of La, Zr and Pd MGs: hardness together with the results reported in Ref. 7 (a), reduced modulus (b).

liquid-like (i.e., viscous) part of the mechanical response of MGs, respectively. The peaks emerge on the spectrum of $E''/E'_{\text{peak}}$ representing different relaxation processes (i.e., $\alpha$ or $\beta$ relaxation, as indicated in the panel) are identical to those previously reported for the 3 MGs, indicating their different characteristics of Johari-Goldstein relaxation (or $\beta$ relaxation). Moreover, distinct frequency-dependent $\alpha$ relaxation of the 3 MGs can be observed. Especially, it is noted that a region in which both $E'$ and $E''$ equal 0 MPa can be found on the spectrums obtained below a critical loading frequency $f_c$. For the relation: $\cos^2 \delta + \sin^2 \delta = 1$, it can be inferred that in the region where $E' = 0$ MPa and $E'' = 0$ MPa indicating $|E^*| = 0$ MPa, MGs transit in to an ideal liquid state for the vanishing deformation resistance as $|E^*| = 0$ MPa at the corresponding loading frequency. As shown in Fig. 3, $f_c$ is different for the 3 MGs. For Pd MG in Fig. 3(b), a $f_c = 5$ Hz can be identified, because that as the frequency increases to 20 Hz, $E''$ clearly deviates from 0 MPa, though $E'$ is almost 0 MPa. For Zr MG in Fig. 3(c), $f_c$ can be identified as 0.2 Hz. For La MG in Fig. 3(a), actually, both $E'$ and $E''$ cannot reach 0 MPa even at $f = 0.05$ Hz. Due to the inferior limit of frequency of the DMA instrument, tests with lower frequency are unavailable. This observation of $f_c$ would benefit finding perfect MGs for the fabrication of micro parts of MEMS (Micro Electro-Mechanical Systems) and provide optimized temperature and loading rate for designing the manufacturing process, as a vanishing deformation resistance enhances the microformability.

It is unexpected to see the splitting of the peak of $E''$ at $f < 0.2$ Hz which suggests the complex heterogeneous dynamics of La MG in supercooled liquid state. Fig. 3(d) shows the frequency (ln $f$) vs. $(1000/T_p)$ plot of the 3 MGs, where $T_p$ is the temperature where $E''$ peaks. The activation energy $\Delta \zeta$ for the structural relaxation of the 3 MGs can be estimated by fitting the plot linearly, as shown in Fig. 3(d). The values of $\Delta \zeta$ are comparable to previous works.

To characterize the frequency dependence of $E^* = E' + iE''$, Fig. 4(a) and 4(b) show the peak loss modulus $E''_{\text{peak}}$ and the normalized relaxed storage modulus during glass transition $\epsilon_r = \frac{E''_{\text{peak}}}{E'}$. 

![Diagram](image_url)
FIG. 3. The normalized storage modulus $E'_{\alpha}/E'_0$ and normalized loss modulus $E''_{\alpha}/E''_{\text{peak}}$ of La (a), Pd (b) and Zr (c) MGs measured at different frequency, and (d) the frequency $(\ln f)$ vs. peak temperature $(1000/T)$ plot of the 3 MGs, in which the temperature is where the loss modulus peaks. $E'_0$ is the initial storage modulus at room temperature and $E''_{\text{peak}}$ is the peak value of the loss modulus. The dashed arrow indicates the variation of $E'_{\alpha}$ the storage modulus after glass transition at different frequency.

where $E'_{\alpha}$ is the storage modulus after glass transition as indicated by the dashed arrows in Fig. 3, $e_0$ reflects the vanish of the stiffness of MG during the glass transition. The frequency dependence of the structural relaxation of the 3 MGs, i.e., $m_S = \partial \ln e_0 / \partial \ln f$ of the normalized relaxed storage modulus $e_0$, and $m_L = \partial \ln E''_{\text{peak}} / \partial \ln f$ of the peak loss modulus $E''_{\text{peak}}$, are determined. It is found that $m_S = 0.19$ and $m_L = 0.21$ for La MG, $m_S = 0.039$ and $m_L = 0.19$ for Zr MG, and $m_S = 0.0043$ and $m_L = 0.012$ for Pd MG. Similar to the strain rate sensitivity of the 3 MGs where La MG shows prominent strain rate sensitivity, Zr MG shows less prominent strain rate sensitivity, and Pd MG shows little strain rate sensitivity, the frequency-dependent $E^* = E' + iE''$ of the 3 MGs indicates that La MG shows prominent frequency dependence, Zr MG shows less prominent frequency dependence, and Pd MG shows little frequency dependence. Especially, a linear correlation between $m_S$ and $m_E$ of the 3 MGs is shown in the inset of Fig. 4(b). Thus, the results in Fig. 2 and Fig. 4 suggest an inherent correlation between strain rate sensitivity and structural relaxation of MGs.

IV. DISCUSSION

It is noted that the strain rate in DMA can be estimated as $\dot{e} = 4f \cdot \varepsilon_0$, where $\varepsilon_0 = 0.03\%$ is the amplitude of the applied periodic strain, corresponding to a range of strain rates from $6 \times 10^{-5}s^{-1}$ to $2.4 \times 10^{-2}s^{-1}$, and overlaps with the strain rates in nanoindentation as estimated in Fig. 2. Based on this overlap, noticing the strain rate sensitivity $m_H$ and $m_E$, and the frequency dependence $m_L$ and $m_S$ of the 3 MGs as shown in Fig. 5, it can be seen that La MG shows prominent strain rate sensitivity and prominent frequency dependence, Zr MG shows less prominent strain rate sensitivity and less prominent frequency dependence, and Pd MG shows little strain rate sensitivity and little frequency dependence. These results (see also the linear correlation between $m_S$ and $m_E$ as shown in the inset of Fig. 4(b)) suggest an inherent correlation between the strain rate sensitivity and the frequency dependence of $\alpha$ relaxation of metallic glasses, rather than a correlation between the strain rate sensitivity and the characteristic of Johari-Goldstein relaxation of the 3 MGs. It is also
FIG. 4. The peak loss modulus $E''_{\text{peak}}$ (a) and normalized relaxed storage modulus $e_r$ (b) of La, Zr and Pd MGs at different frequency. Inset shows the relation between strain rate sensitivity $m_E$ and frequency dependence $m_S$.

It is important to see that in Fig. 3(b), especially on the storage modulus spectrum, the frequency dependence of Johari-Goldstein relaxation of Pd MG is clearly more prominent than the frequency dependence of the $\alpha$ relaxation of Pd MG. Recalling the nearly 0 strain rate sensitivity of Pd MG, this phenomenon again evidences the observed inherent correlation between strain rate sensitivity and $\alpha$ relaxation of MGs, instead of a correlation between strain rate sensitivity and Johari-Goldstein relaxation.

Because that the relation between structural relaxation and deformation of MGs is explained in Part I, thus, to interpret the observed correlation between strain rate sensitivity and $\alpha$ relaxation, it

FIG. 5. The strain rate sensitivity $m_H$ and $m_E$, and the frequency dependence $m_L$ and $m_S$ of 3 metallic glasses (MGs).
is important to understand the origin of the strain rate sensitivity of MGs. The origin of the strain rate sensitivity of the plastic deformation of MGs can be understood based on the yield mechanism of MGs. The yield of MGs has been depicted as a critical condition when the activation rate of the elementary flow units satisfies the external strain rate.\textsuperscript{28} The activation of flow unit is a local thermal-assisted and stress-driven nonaffine rearrangement process among a cluster of atoms.\textsuperscript{29} In transition state theory, the activation rate of elementary flow units reads: \( w = w_0 \exp \left( -\frac{W_f}{kT} \right) \), where \( w_0 \) is an attempting frequency, \( W_f \) is the activation energy. The critical activation rate at the yield point reads: \( w_c = C \dot{\varepsilon} \), where \( C \) is a constant; \( \dot{\varepsilon} \) is the strain rate. With increasing strain rates, the critical activation rate of flow units \( w_c \) at the yield point increases concomitantly. High strain rate would lead to high critical activation rate of flow units, namely lower activation energy \( W_f \). Because \( W_f \) is determined by the flow stress, this explains the origin of the strain rate sensitivity in the plastic deformation of MGs. Hence, the strain rate-dependent hardness and reduced modulus in Fig. 2 actually indicate the strain rate-dependent activation of flow units in MGs. For the intimate relationship between flow units and structural relaxation,\textsuperscript{13} it is reasonable that the strain rate sensitivity of MGs should correlate with the strain rate sensitivity of structural relaxation. As stated above, the strain rate in DMA can be estimated as \( \dot{\varepsilon} = 4f \cdot \dot{\varepsilon}_0 \). The strain rate sensitivity of structural relaxation is actually the frequency dependence of structural relaxation. Therefore, as shown in Fig. 5 and the inset of Fig. 4(b), an inherent correlation between the strain rate sensitivity and structural relaxation of MGs can be found.

Since the activation rate of flow units satisfies the strain rate at the yield point, i.e., the elastic modulus equals 0 MPa at the yield point,\textsuperscript{30} the yield of MGs can also be understood as the vanishing process of elastic modulus upon increasing external stress. It is well known that the modulus of amorphous solids is composed by the primary Born-Huang term which is rate irrelevant and a secondary correction term which arises from the nonaffine displacements of atoms and is closely related to external loading rate.\textsuperscript{30–32} Therefore, the strain rate sensitivity can be attributed to the secondary correction term of the elastic modulus of amorphous solids. Because of the fact that the nonaffine displacements of atoms in space-time,\textsuperscript{33} constitute the flow units and structural relaxation of MGs, they consequently determine the correlation between strain rate sensitivity of MGs and the frequency dependence of structural relaxation.

On the other hand, it is important to note that \( E'' \) and \( \varepsilon_r \) in structural relaxation indicate the thermally activated glass transition (i.e., \( \alpha \) relaxation) of MGs in the temperature sweep in DMA. As suggested previously,\textsuperscript{34,35} a stress-temperature scale exists on the phase diagram of viscosity in the glass transition of metallic glasses. The stress-temperature scale suggests that stress and temperature play equivalent role in the glass transition of MGs, i.e., both heating and loading can lead to glass transition (i.e., \( \alpha \) relaxation). The yield of MGs, i.e., the vanishing of elastic modulus in loading, is actually a stress-driven glass transition process or a stress-driven \( \alpha \) relaxation process. This stress-driven \( \alpha \) relaxation process is equivalent to the vanishing of storage modulus in heating (i.e., a thermal \( \alpha \) relaxation process). Thus, the strain rate-dependent flow correlates with the frequency-dependent \( \alpha \) relaxation, and the strain rate sensitivity correlates with the frequency dependence of \( \alpha \) relaxation. Hence, the observed correlation between strain rate sensitivity and \( \alpha \) relaxation supports the stress-temperature scale in the glass transition of MGs from the angle of rate sensitivity and improves the current understanding on the \( \alpha \) relaxation of MGs. Our results also indicate that the \( \alpha \) relaxation, i.e., the percolation of Johari-Goldstein relaxation, rather than the Johari-Goldstein relaxation itself is related to the strain rate sensitivity. This would be a salient feature of the plastic deformation of MGs.

V. CONCLUSIONS

In summary, the strain rate sensitivity in nanoindentation and the frequency-dependent structural relaxation in dynamic mechanical analysis of Zr (Zr\textsubscript{41.2}Ti\textsubscript{13.8}Cu\textsubscript{19}Ni\textsubscript{12.3}B\textsubscript{2}25, Vit1), La (La\textsubscript{62}Al\textsubscript{14}Ag\textsubscript{2.3}Ni\textsubscript{10.83}Co\textsubscript{10.83}), and Pd (Pd\textsubscript{40}Cu\textsubscript{38}Ni\textsubscript{12}P\textsubscript{20}) metallic glasses are investigated to show an inherent correlation between the strain rate sensitivity and the \( \alpha \) relaxation of metallic glasses. The inherent correlation supports the stress-temperature scale in the glass transition of metallic...
glasses and advances the current knowledge on the $\alpha$ relaxation of metallic glasses. Besides, the complex modulus equaling 0 MPa suggests an ideal liquid state of metallic glasses in the supercooled liquid region when they are deformed below a critical loading rate, which would benefit the application of metallic glasses in the fabrication of micro parts for MEMS (Micro Electro-Mechanical Systems).

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