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Relating activation of shear transformation zones to β relaxations in metallic glasses

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The mechanisms of plastic deformation of glassy solids and structural origin of β relaxation are two fundamental issues. We provide compelling experimental evidence that the activation of shear transformation zones (STZs) and β relaxations in metallic glasses are directly related, and the activation energy of the β relaxation and the potential-energy barriers of STZs are nearly equivalent. Our results suggest an intrinsic correlation among potential STZs, β relaxation, and the inhomogeneous atomic structure of metallic glasses, which has implications for understanding the deformation mechanism and structural origin of β relaxation in glasses.

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Plastic deformation of metallic glasses (MGs) far below glass transition temperature T_g is a long-standing issue.[1–4] Microscopically, MGs are proposed to deform by plastic rearrangements of atomic regions involving tens of atoms termed shear transformation zones (STZs),[3,4] and a consequence of formations and self-organizations of STZs that induce macroscopical shear banding of MGs. As recognized by Johari *et al.*,[5] the relaxation of supercooled liquids and glasses are governed by two main processes: a fast process, that is the β relaxation which is a locally initiated and reversible process, and a slow process, termed the α process, which is a large-scale irreversible rearrangement of the material. The β relaxation, which is an Arrhenius process,[5–7] persists from supercooled liquid regime to glassy states, and is separated from the non-Arrhenius α relaxation at a crossover temperature.[5–7] It has been proved to be an intrinsic and universal feature of glasses but poorly understood.[5,6] Usually, it is related to localized motions with cooperative nature, a reminiscent of STZs in MGs. From the theory of potential-energy landscape (PEL),[7,8] the β relaxations were identified as hopping events across subbasins within an inherent megabasin (inherent structure) while α relaxations entail escape from one megabasin and eventually jump into another (e.g., see Fig. 1 in Ref. 8). Experimentally, the activation energy of the β relaxations, E_β, can be determined by dielectric spectroscopy,[6] differential scanning calorimeter,[9] and by dynamic mechanical spectroscopy (DMS).[10] Since MGs are good conductors, dielectric method that commonly used in nonmetallic glasses is not feasible. The DMS, which is widely used in field of polymer glasses,[6] has been employed for studying the β relaxation in MGs.[10]

Based on the PEL theory and the Frenkel's analysis of shear strengths in dislocation free solids, Johnson *et al.*[11] proposed a cooperative shear model (CSM) to understand the deformation mechanisms and rheological properties of MGs.[11,12] The CSM gives rise to functional relations between viscosity and shear modulus (e.g., see Ref. 12 for a review). According to the CSM, activation of isolated STZs confined within elastic matrix could be associated with the β relaxation.[13] However, the validity of this correlation, which is the fundamental conceptual standpoint of CSM,[11,13] remains unclear, mainly due to the unclearness of the nature and the origins of the β relaxation and how the events of STZs relate to the β relaxation.

In this Rapid Communication, we provide experimental evidence showing a close link between the β relaxations and events of STZs. We show that the activation energy of the β relaxation and the potential-energy barriers of STZs are nearly equivalent. Based on the observation, we attempt to understand the fundamental issues of plastic deformation and relaxations in metallic glasses through correlating the flow resistance of STZs and β relaxation to common microstructural origin.

Dynamic mechanical measurements were performed on MGs listed in Table SIII in supplementary material[14] using TA2980 DMS by the single-cantilever bending method at a heating rate of 3 K/min, with varied testing frequency f. As a typical example, Fig. 1(a) shows the loss modulus E'' of a $La_{55}Al_{15}Ni_{10}Cu_{10}Co_{10}$ MG between 300 and 500 K with f range of 0.1–8 Hz. Both the loss modulus as a function of temperature for different frequencies and the loss modulus as a function of frequency at different temperatures can be used to characterize the relaxation in glasses.[10,15] In addition to the α relaxation peaks around T_g ($\sim$446 K), broad humps around 320–400 K can also be observed, which were identified as the β relaxations.[10] The E_β was estimated by plotting $\log(f)$ versus $1000/T_p$ (Arrhenius plot), where T_p is the peak temperature of the hump, as shown in the inset of Fig. 1(a), which determines $E_\beta \approx 89 \pm 6$ kJ/mol for $La_{55}Al_{15}Ni_{10}Cu_{10}Co_{10}$ MG (for the details of the determination of E_β, see method section in online supplementary material[14]). Table SIII (Ref. 14) summarizes the values of E_β and T_g determined from our DMS measurements for various MGs and available data collected from literatures,[14] which covers more than 20 individuals from ten typical metallic glass systems. Figure 1(b) shows the plot of E_β against RT_g of the

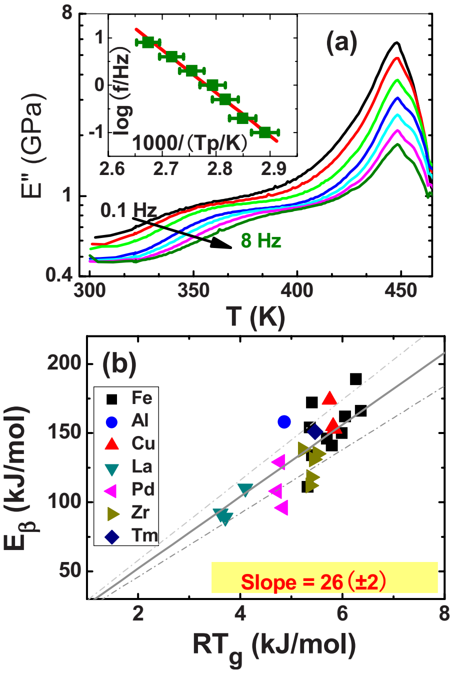

FIG. 1. (Color online) (a) The temperature dependence of the loss modulus E'' for a $La_{55}Al_{15}Ni_{10}Cu_{10}Co_{10}$ MG, measured with f (from top to bottom, indicated by the arrow) 0.1, 0.2, 0.5, 1, 2, 4, and 8 Hz, at the heating rate of 3 K/min. The inset plots $\log(f)$ vs $1000/T_p$, where T_p is peak temperature of the β-relaxation hump. (b) Relationship between activation energy of β-relaxation E_β and RT_g for metallic glasses listed in Table SIII (Ref. 14). The solid line is a least-squares linear fit.

data. An approximately linear relationship of $E_\beta \approx 26(\pm 2)RT_g$ can be obtained (R is the gas constant). The similar empirical relationship between E_β and T_g in the form of $E_\beta \approx 24RT_g$ has also been found to exist in nonmetallic glasses,[15] which agrees well with that in metallic glasses.[9,10] The results indicate that E_β scales with T_g, the characteristic temperature of α transition, which confirms the proposed "β-relaxation to α-relaxation" self-similar organization of PELs.[13] In nonmetallic glasses, the results that E_β scales with T_g were discussed on the basis of model coupling theory (e.g., see Ref. 15 for details).

The potential-energy barrier for an unsheared STZ can be estimated using the CSM model as[11] $W=(8/\pi^2)G\gamma_c^2\zeta\Omega$, where, G the shear modulus, Ω the average volume of an STZ, $\gamma_c \approx 0.027$ the average elastic limit, and $\zeta \approx 3$ a correction factor arising from the matrix confinement of a "stressed" STZ.[13] Assuming n atoms take part in an isolated STZ event, let $\Omega = nC_fV_a$, where $V_a = M/(\rho N_0)$ the atomic volume, N_0 Avogadro's number, ρ density, M molar mass, and $C_f \geq 1$ is a free volume parameter. Events of STZs are triggered around the free volume sites,[3,4] where atomic packing is not as close as that of the surroundings, consequently, $\Omega = nV_a$ from random dense packing model should be revised to incorporate a factor C_f.[4] As suggested by Falk *et al.*,[4] $C_f \sim 1.1$. The n is estimated to be about ~ 200 on the basis of theoretical analysis of Johnson *et al.*[11,12] ($\sim$100–300), nanoindentation experiments on MGs of Pan *et al.*[16] ($\sim$100–600 in MGs), simulated results of Mayr[17] ($\sim$140 in a simulated CuTi metallic glass) and Falk *et al.*[4] ($\sim$10–20 in a simulated two-dimensional glass with Lennard-Jones potential), bubble raft experiment of Argon[3] ($\sim$10–20), and the experimental results in a colloidal glass of Schall *et al.*[18] ($\sim$25). Considering the different interaction potentials, $n \sim 200$ is a reasonable order of magnitude in MGs. The molar potential-energy barrier for an unsheared STZ is $W_{STZ} = N_0W = (8/\pi^2)nG\gamma_c^2\zeta C_fV_m$, where $V_m = N_0V_a$ is the molar volume. Taking account $C_f \sim 1.1$ and $n \sim 200$, we get $W_{STZ} \approx 0.39GV_m$. The W_{STZ} ($\sim$100–200 kJ/mol) we estimated from CSM is roughly consistent with the simulation results of Mayr's[17] (0.35 eV $\approx$ 34 kJ/mol for a CuTi metallic glass), and the nanoindentation experiments[16] which give $W_{STZ} \sim 150$–500 kJ/mol. Our estimation is also consistent with the experimental results in colloid glass.[18] The comparisons indicate that our estimation on W_{STZ} is acceptable. The relevant data of G, V_a, and GV_m and estimated W_{STZ} for more than 40 different MGs are presented in Table SIV (see supplementary material[14]). We note that the potential energy W_{STZ} of an STZ can be estimated by the relationship $W_{STZ} \propto G^*nV_a$, which is key point of the most STZ models not only for CSM,[3,4] and our extraction of the STZ energy is not CSM specific.

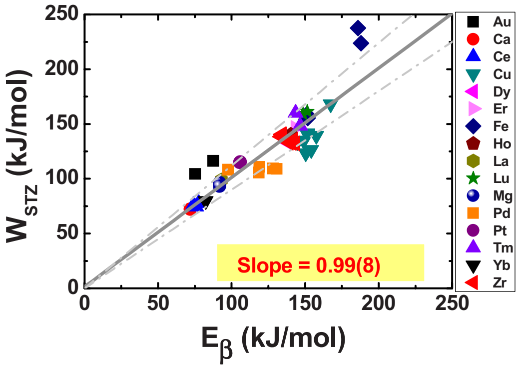

FIG. 2. (Color online) Relationship between activation energy of β-relaxation E_β and energy barriers of STZs W_{STZ}.

Figure 2 shows a plot of the W_{STZ} versus the E_β (estimated as $E_\beta \approx 26RT_g$) for the MGs listed in Table SIV.[14] The data reveals nearly a one-to-one correspondence between E_β and W_{STZ} that extends over a broad range. A least-squares linear fit gives a correlation coefficient about 0.90, suggesting a clear correlation between W_{STZ} and E_β. Interestingly, the fitted line roughly passes though the point of origin (see Fig. 2) with a slope of $k = 0.99 \pm 0.08$, an evidence of $E_\beta \approx W_{STZ}$. This linear relationship is further verified to hold in individual systems of MGs based on such as Cu-, Fe-, and rare-earth-based MGs (see Fig. S4 in online supplementary material[14]). Since α relaxation is a non-Arrhenius process and is frozen below T_g, the apparent activation energy of α transition is highly temperature dependent and much larger than E_β and W_{STZ}. Therefore, the above results confirm that activation of STZs and the β relaxations are directly correlated. We note that the GV_m (correlated with $W_{STZ} \approx 0.39GV_m$) and RT_g ($E_\beta \approx 26RT_g$) are correlated for various MGs (see Fig. S5 in online supplementary material). This recognized generalized correlation in essence is a manifestation of the relationship between activation of STZs and β

relaxation. As GV_m is a measurement of the energy barrier of STZs and RT_g measures the activation energy of the β relaxation, one can readily use GV_m and RT_g, which can be easily measured, to characterize the events of STZs and the β relaxations in MGs, respectively.

It is believed that the β relaxation relates to the dynamical heterogeneity in glasses but its structural origin is rather vague.[5–10] On the other hand, there is general consensus that the potential STZs are nucleated around the sites of free volumes,[1–4] where the atomic packing is relatively loose ($C_f > 1$). This picture is validated by the experimental observations that some MGs consist of the weakly bonded regions (or soft regions) and strongly bonded regions (or hard regions)[19–22] and such heterogeneous structure benefits the plastic deformation of the metallic glasses.[20,21] Based on the correlation between STZs and β relaxations via their activation energies, the origin of β relaxation could be understood from the microstructural characteristic of MGs which is inhomogeneous on the atomic scale and comprises closely packed and loosely packed regions.[19–22] The β relaxations, similar to the events of potential STZs, take place in the loosely packed regions where the local translational atomic motions can be readily activated, compared with that in closely packed regions. We therefore speculate that the structural heterogeneity is the common structural origin of events of STZs and the β relaxations. The β relaxation in MGs then corresponds to a process involving "thermal-driven events of STZs," i.e., a group of atoms within loosely packed regions undergo an inelastic distortion from one configuration to another, crossing an energy barrier, and consequently, $E_\beta \approx W_{\mathrm{STZ}}$. For β relaxation, the driving force is essentially obtained from the thermal fluctuations, and there is no directional flow and the process is reversible due to the confinements of the surrounding closely packed regions. In contrast, the directional flow events of STZs are induced by external shear stress.

The fact that the events of STZs are directly related to the β relaxations in MGs could provide insights for understanding the deformation mechanisms and plasticity/ductility of MGs. The heterogeneous microstructures may be much different for MGs with different behavior of β relaxation. For a system with pronounced β relaxation and larger Poisson's ratio, ν,[6,23] it shows marked structural heterogeneity,[22] which comprises more loosely packed regions for triggering the β relaxations and the activation of STZs. This further implies that the MGs with lower E_β and W_{STZ} have good ductility. Based on the well-established correlation of Poisson ratio with plasticity,[24] the MG with pronounced β relaxation is expected to have lower W_{STZ} and E_β and better plasticity. To check this speculation, we further investigate how the global ductility of MGs depends on the energy barriers of STZs. Figure 3 shows a plot of the W_{STZ} against ν [which is taken as a ductility indicator of MGs (Ref. 24)] for various MGs listed in Table SIV.[14] One can see that, over a broad range, the MGs such as Au-, Pt-, and Zr-based systems with lower W_{STZ} tend to have larger ν, and better plasticity. This relationship also stands well in individual systems of MGs such as Cu-, Fe-, and some late rare-earth-based MGs. The exceptions found in systems of MGs based on Ca, Ce, Yb, and Mg, as boxed in Fig. 3, might be due to the low T_g (near or even lower than room temperature, at which MGs are fabricated and kept) and/or low oxidation resistance of these MGs, for which the processes such as physical aging, and oxide deterioration are involved, which drastically change the organizations of PELs.[7,8] We note that our estimation of W_{STZ} does not consider the correction factor ζ which is v dependent.[25] Since ζ represents a "dynamical confinements to an STZ from the surrounding materials,"[13,25] our estimation of $W_{\mathrm{STZ}} \sim 0.39 GV_m$, in essence, highlights the importance of the "plastic core" of a potential STZ.[13] As ζ correlates v reversely,[25] the two factors of the plastic core $G\Omega$ and matrix confinement ζ can be analyzed independently. Nevertheless, the correlation between ductility and W_{STZ} for a wide variety of "unrelaxed" MGs suggests that the structural heterogeneity favors the activation of STZs and plasticity of MGs (i.e., lower W_{STZ} favors better plasticity in MGs). The results have implications for the design of ductile metallic glasses.

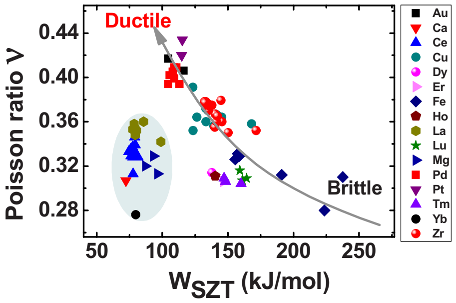

FIG. 3. (Color online) Relationship between W_{STZ} and ν for MGs listed in Table SIV (Ref. 14). Solid curve with arrow is drawn for guiding eyes. MGs based on La, Ca, Mg, Ce, and Yb are boxed by shallow circle.

In a broad class of polymer glasses, it is widely recognized the β relaxations affect mechanical properties.[26–31] For instance, in many polymer glasses, the transition from ductile to brittle occurs at the characteristic temperature of the β relaxations,[26–29] and transitions of impact toughness yield strength and failure modes were also often correlated with β relaxations.[26] Moreover, polymers with pronounced β relaxations often possess good ductility and vice versa.[26,28] It was alleged that the cooperative motions of molecular segments responsible for β relaxation act as "molecular lubricants" that prevents localized deformation and retards the nucleation of crazing.[28] The effect of these motions was considered to reduce the resistance for polymer chains to slide relative to one another when external stress is applied (i.e., lowering the energy barriers to chain slippage).[28] However, exceptions to these were also often observed[27,28] which make the correlation between mechanical properties and β relaxation remains inconclusive. Some theories,[29–31] such as Eyring's model,[29] have been proposed to relate molecular motions to mechanical properties. However, these models are unable to account for all the experiments results,[32] and the correlation between mechanical properties to β relaxation is still an open question. This might be due to the complicated structures (which consisting primarily of chains units) and dynamics of glassy polymers, and the modes of molecular motions responsible for β relaxations could vary from one type of polymer glass to another.[27,28] Metallic glass is the relative simple glass with atoms or atomic clusters as its structural units.[33] Its structure is close to dense random packing of spheres without the complex intramolecular effect, rotational degree of freedom, or angle jump in polymer glasses. Metallic glasses offer a model for verifying the correlation between relaxation and plasticity and how universal it is in various glasses. The similar connection between mechanical properties and β relaxation in metallic glasses provides a direct evidence for understanding the universal link between them and demonstrates a connection of the underlying physics for quite different classes of glass formers.[34]

In summary, by identifying the equivalence of activation energy of β relaxation and the potential-energy barrier of STZs, we propose that the events of STZs and β relaxations are directly related due to their common microstructural origin. The β relaxation, which is regarded as a thermal-driven process of events of STZs, and intrinsic plasticity in metallic glasses are suggested to correlate with the structural heterogeneity of metallic glasses.

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