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Communication: Non-monotonic evolution of dynamical heterogeneity in unfreezing process of metallic glasses

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The relaxation dynamics in unfreezing process of metallic glasses is investigated by the activation-relaxation technique. A non-monotonic dynamical microstructural heterogeneities evolution with temperature is discovered, which confirms and supplies more features to flow units concept of glasses. A flow unit perspective is proposed to microscopically describe this non-monotonic evolution of the dynamical heterogeneities as well as its relationship with the deformation mode development of metallic glasses. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4927701]

Glass is formed by cooling the liquid fast enough to a certain point when the liquid is too viscous to flow on the available observation time scale.[1–5] Such a liquid-glass transition, which has received a huge attention of the research community in decades, is a dynamic freezing process.[2,4,6,7] The diversity and complexity of the relaxation dynamics of the viscous liquids are remarkably reflected by the many temperature critical points at which the supercooled liquids show crossover events,[8–10] including alpha-beta relaxation splitting,[3,11] breaking down of Stokes-Einstein relation,[12,13] appearing of dynamics heterogeneity,[1,12] mode-coupling crossover,[14] etc. Both experimental and numerical efforts have been devoted to uncover the details of the complex dynamics evolution of the freezing process of liquids from their high temperature flowing state down to the rigid solid state.[7,15] However, the dynamics of the reverse unfreezing process has been paid much less attention due to the difficulties caused by off-equilibrium nature of glasses[8] and relative lack of effective approaches to the studies of this process. The fully revealing of the glass unfreezing dynamics evolution is necessary not only for the future theory but also for the wide application of glasses. Argon had early realized the transition between different deformation modes of metallic glasses (MGs) during temperature rising.[16] Lu *et al.* revealed that the deformation mode of MGs would change from shear localization region to non-Newtonian region and in the end to homogeneous Newtonian flow region with increasing temperature.[17]

Metallic glasses, whose structure is close to a dense random packing of spheres without the complex intramolecular effect, rotational degree of freedom, or angle jump in molecular and network glass formers, have been in the focus of research advancing our understanding of liquids and of structural glasses in general.[18–21] Stress relaxation with the instantaneous activation-relaxation technique is an effective approach for investigating the deformation carriers of dislocation or grain boundary in crystal materials and the relaxation dynamics in materials by the perturbative activation.[22–24] Previous loading relaxation experiments conducted on MGs revealed some important characteristics of deformation kinetics within the supercooled liquid region and around their glass transition temperatures T_g.[25] However, up to now, little work has been done on the dynamical heterogeneity evolution during unfreezing process covering a wide temperature range, and the microstructural mechanism of these different deformation modes and their transitions remain unclear.

Here, we apply stress relaxation method to study the dynamics evolution of metallic glasses during the unfreezing glass-liquid process. It is found that in the temperature induced glass to liquid transition process, the heterogeneity evolution is non-monotonic, which can be well understood using the flow unit perspective. Particularly, the key role of the interaction between flow units is revealed. This finding might provide a clearer microstructural picture to the deformation mode as well as their development with temperature in MGs and may give useful insights into the transition between glasses and viscous liquids.

$Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ (Vit1b) MG with excellent glass forming ability and highly thermal stability was used in the experiments. Glassy ribbons with a thickness about 0.02 mm and width about 1.2 mm were produced by the melt-spinning method in an argon atmosphere. A TA Q800 dynamic mechanical analyzer (DMA) was employed to do the tensile stress relaxation measurements. To make sure that all the samples have the same initial state and avoiding the physical ageing effect, prior to the measurements, all the samples were heated up to 631 K (10 K above their $T_g \sim 621$ K, which was determined by the differential scanning calorimetry (DSC) method at a heating rate 20 K/min), kept isothermal for 3 min, and then cooled down with the same cooling rates in the argon atmosphere. A time-temperature-superposition test mode was used in our stress relaxation measurements, in which at each temperature, a constant strain 0.4% was loaded on the sample for 30 min after an initial 3 min equilibration.

A typical loading process of a constant strain ε of Vit1b ($T_g = 621$ K) metallic glass and the corresponding stress response $\sigma(t)$ at temperature 553 K are shown in Fig. 1(a). Initially, the stress $\sigma(t)$ rapidly decreases and then slows down gradually. Qualitatively, this stress relieving process is caused by the accumulation of local visco-plastic

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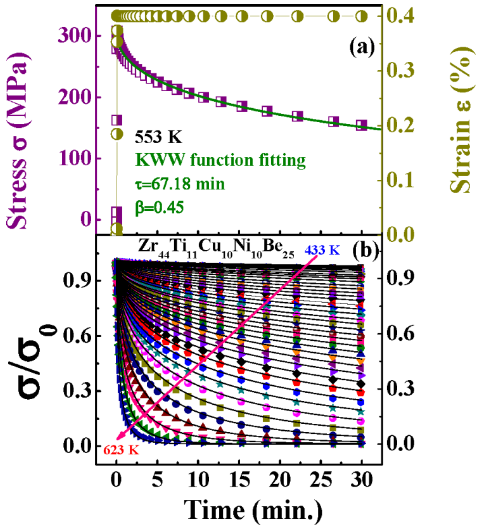

FIG. 1. (a) A typical experimental loading process of a constant strain $\varepsilon = 0.4\%$ to $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ MG and the corresponding stress response σ at temperature 553 K. The stress relaxation data are well fitted by KWW function (solid line), with parameters $\tau = 67.18$ min and $\beta = 0.45$. (b) Stress relaxation data (symbols) at every 5 K from 433 to 623 K and the corresponding fitting curves (solid lines) of KWW function.

deformations or flow events.[26] The stress relaxation data can be well fitted by the Kohlrausch-Williams-Watts (KWW) function $\sigma = \sigma_0 \exp[-(t/\tau)^{\beta}]$ $(0 < \beta < 1)$, where τ is the characteristic relaxation time and β is non-dimensional relaxation parameter. Since the stress relaxation is based on the activation of the relaxation units similar to the creep experiments, the good fitting of stretched-exponential function indicates that the stress relaxation process is highly heterogeneous on microscopic scale.[27,28] This agrees well with the concept of structural and dynamical heterogeneities and some widely used structural models in which the MGs consist of tightly bonded regions (also called solid-like regions) and loosely bonded regions (or liquid-like regions).[29,30] The liquid-like sites are presumed to first accommodate the external stress and are responsible for the viscoelastic flow of the glass.[30,31]

To study the evolution of the heterogeneities during the glass to liquid transition, the stress relaxation in a wide temperature range from 433 K to 623 K (slightly higher than T_g) was investigated and shown in Fig. 1(b). For comparison, all the data are normalized by their initial stress σ_0. In principle, the properties of glasses are measurement time dependent,[25,32] and the definition of liquid-like and solid-like also depends on observing time.[7] To exclude the effect of the experimental time scale on the relaxations of different temperatures, the time duration of each stress relaxation measurement is fixed to the same value of 30 min. Qualitatively, the increasing temperature leads to an increment of relaxation rate, indicating easier activation events at higher temperatures. In the flow unit perspective, this can be understood as that higher temperature activates and transforms more volume fraction of metallic glass into liquid-like regions, as a result, the glass goes quicker inelastic deformation. The best KWW function fitting curves are also given in Fig. 1(b) as solid lines.

Figure 2(a) shows the variation of fitting parameters with temperature, including the apparent characteristic relaxation time τ and non-exponential index β. The rapid decrease of τ,

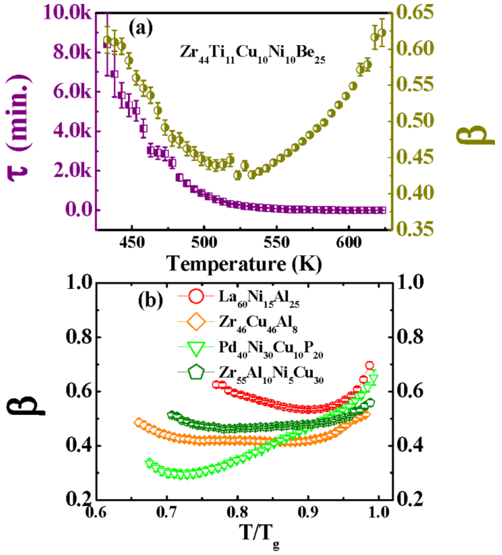

FIG. 2. (a) The variation of the best KWW function fitting parameters of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ MG with temperature. (b) The fitting parameters β of a few other typical metallic glasses.

which is the description of relaxation rate, indicates the easier activation of flow units at higher temperatures in MG, which agrees with the general understanding of the unfreezing process. With temperature gradually going up, more regions are transformed into liquid-like regions and in the end, the system becomes a completely flowing liquid state. Surprisingly, when temperature rises, the value of β first decreases and reaches the lowest value, after then it turns to increase on the contrary, showing a valley shape curve. To confirm the universality of this β changing trend, we measured the stress relaxation of a few other metallic glasses including Zr-based, Pd-based, and La-based MGs at various temperatures. The results in Fig. 2(b) clearly show that all these MGs manifest the same behavior, although the transition temperature and the shape of the curves appear somewhat different.

The question is then raised, what is the microstructural mechanism determining this β appearance? According to activation energy spectrum model,[33] the variation of relaxing stress σ with time t at temperature T can be expressed by an integral equation, $\sigma(t)/\sigma(0) = \int_0^{+\infty} P(E)\exp(-t/\tau)\,dE = \int_0^{+\infty} P(E)\exp[-t\upsilon_0/\exp(E/k_BT)]dE$, where $P(E)$ is the probability distribution of the activation energy of all the activation process involved. The υ_0 is an effective attempt frequency in the order of the Debye frequency, and k_B is the Boltzmann constant. A Gaussian form spectrum of activation energy distribution, which has been confirmed to be able to effectively depict the distribution of flow units and the heterogeneous glass dynamics,[22,34] was taken here for further analysis. With the assumptions, the $P(E)$ of all the temperatures were obtained, and the representative ones are shown in Fig. 3(a) as insets.

We highlight the variation of full width at half maximum (FWHM) of the activation energy spectra as shown in Fig. 3(a). The FWHM can be directly connected to the dynamics heterogeneity, and the larger FWHM implies a wider distribution of the activation energy distribution, meaning higher structural and dynamics heterogeneities in a MG. Remarkably, the

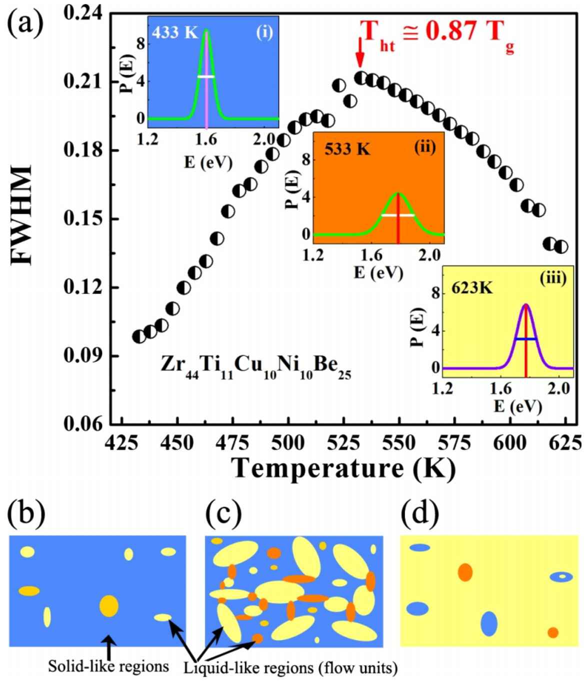

FIG. 3. (a) The variation of full width at half maximum (FWHM) of activation energy spectra with temperature. Insets (i)–(iii) show the activation energy spectra P(E) of Vit1b at three representative temperatures. (b)–(d) Schematic illustration of the evolution of flow units with temperature. Different colors are used to represent the different flow units.

evolution of the FWHM is also non-monotonic. During the temperature rising, it first increases but turns down subsequently, confirming that during the glasses unfreezing process, statistical energy barrier distribution of the relaxation units first becomes more dispersive. When temperature increases further, specifically higher than $0.87T_g$ in the glassy alloy, the distribution tends to converge. The heterogeneity transition temperature point, T_{ht}, as indicated in Fig. 3(a), is the crossover or transition point of the non-monotonic behavior of the evolution of the dynamics heterogeneity. The insets in Fig. 3(a) show the typical shapes of activation energy spectrum from low to high temperatures, exhibiting the development of the non-monotonic distribution behavior.

The non-monotonic behavior of the evolution of the dynamics heterogeneity and the heterogeneity transition temperature point can be understood from the structural flow defects or flow units point of view.[30] Recent simulations and experiments showed that liquid-like regions with viscoelastic behavior act as the flow units in MGs.[35,36] The liquid-like sites in glass even were directly imaged by the aberration-corrected transmission electron microscopy.[29] These flow units can accommodate the external stress or temperature by relaxing or flowing.[22,30,31] In low temperatures, the MG mainly consists of the elastic matrix, in which few flow units are distributed dispersedly. These flow units are in the isolated state embedded in the elastic matrix and do not interact with each other, as schematically shown in Fig. 3(b). These flow units have narrowly distributed activation energy spectrum. With the elevation of temperature, some elastic matrix zones tend to soften and transform into liquid-like zones with viscous features, and these newly activated flow units with higher characteristic activation energy also engage into stress relaxation process and lead to the more heterogeneous metallic glasses. The higher fraction of the flow units induce the quicker stress relaxation as observed. When T approaches T_{ht}, more potential flow units are activated as schematically shown in Fig. 3(c). One important qualitative change happens here is the interaction between the flow units, and the flow units of interaction zones are emphasized by orange color in the figure. Because of the intimate interaction among the flow units, they tend to take action cooperatively during the stress relaxation process. Further rising of temperature to near T_g, abundant liquid-like flow units are dominant in the glasses and lead to the quick softening and collapse of the remaining solid like regions, resulting in rapid increase of the relaxation rate. In contrast to the distribution of flow units in the solid-like matrix in low temperature state, in this case, the elastic solid-like regions are distributed in the matrix of viscous supercooled liquids, as schematically shown in Fig. 3(d). Consequently, the metallic glasses eventually unfreeze into the totally viscous liquids state with Newtonian flow behaviors. The β value of the alloy increases and alloy becomes homogeneous again, which accords with our observed non-monotonic growth of relaxation dynamics heterogeneity. The dynamical mechanical spectroscopy (DMS) of the MG (not shown) also shows that, near the T_{ht}, α-process begins to contribute to the relaxation. This confirms our view point that around this temperature, microscopically flow units tend to interact with each other and extended cooperative flowing regions were formed.

This non-monotonic dynamical and microstructural heterogeneities evolution associated with the evolution of flow units during unfreezing process is useful for understanding the general deformation behaviors development with temperature. The most fundamental element in the deformation map of MGs is the transition from inhomogeneous deformation to homogeneous steady-state flow.[37] At different deformation rates, the transition happens at different temperatures. Since the observing time in our stress relaxation experiment is 30 min, the corresponding strain rate is about $5.6 \times 10^{-4}\ \mathrm{s}^{-1}$. The deformation mode transition temperature, defined as T_{dt} in this paper, of typical MGs at a strain rate $5 \times 10^{-4}\ \mathrm{s}^{-1}$ is measured,

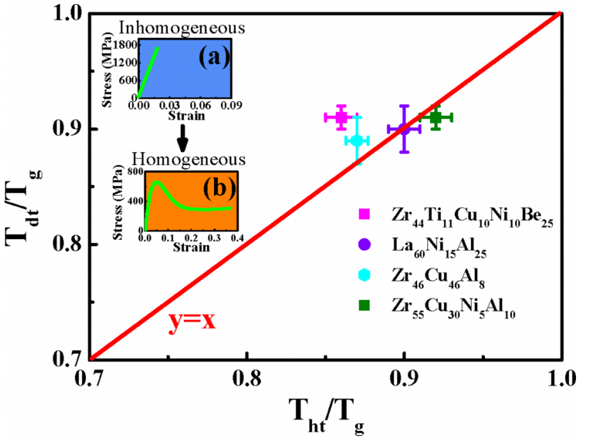

FIG. 4. Comparison between the deformation mode transition temperature T_{dt}/T_g and the heterogeneity transition temperature T_{ht}/T_g of a few typical metallic glasses. Insets (a) and (b) show the representative stress-strain curves of the metallic glasses, exhibiting the deformation mode transition with temperature from inhomogeneous deformation to homogeneous flow.

and the T_{dt}/T_g against T_{ht}/T_g is shown in Fig. 4. The data reveal a good correspondence between the deformation mode transition temperature T_{dt} and the heterogeneity transition temperature point T_{ht}, indicating $T_{dt} \approx T_{ht}$. This implies the structure evolution features underlying the different deformation modes in different temperatures. At low temperatures, the few and highly dispersive flow units lead to a highly localized strain in few shear bands,[38] and the strain softening or thermal softening effect causes the catastrophic failure along a dominant shear band of MGs. The typical stress-strain curve for this inhomogeneous deformation of MGs[17] is also given in inset (a) of Fig. 4. When the temperature is high enough, the gradually formed abundant flow units begin to interact with each other and take action cooperatively. This cooperative kinetics turns the deformation mode into homogeneous flow, as that shown in inset (b) of Fig. 4.

In summary, a non-monotonic heterogeneity evolution of the relaxation dynamics and its intimate relation to the deformation mode in metallic glasses are discovered. The micro-scale highly heterogeneous picture of glasses with solid-like regions and liquid-like regions and their development with temperature can be used to understand this non-monotonic behavior and the general deformation behaviors. Our work may provide some new insights into the transition between glasses and viscous liquids, especially the important role played by flow units.

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