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Revealing localized plastic flow in apparent elastic region before yielding in metallic glasses

L. Z. Zhao, R. J. Xue, Y. Z. Li, W. H. Wang, and H. Y. Bai[a)]
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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The microscopically localized flow before yielding in metallic glass (MG) is hard to be detected using conventional mechanical tests due to its extremely slow process with a long time scale and lack of structural information. We present a stress relaxation approach to circumvent the experimental problem and to reveal the evolution of the flow before yielding in MG by detecting the evolution of structural heterogeneity and activation energy barrier spectra of flow units. We report on explicit correlations among dynamical heterogeneities, nanoscale flow units, and yielding, revealing a transition from the microscopically flow to macroscopic yielding in MG. [http://dx.doi.org/10.1063/1.4938567]

I. INTRODUCTION

The common wisdom considers that the flow in a solid occurs only when the external stress reaches a critical value of yield strength. Metallic glasses (MGs) show a large apparent elastic regime (~2%) before yielding and seemingly indicate that only elastic deformation occurs in their nominal elastic regime. However, recent experiments and atomistic simulations clearly show that MGs could flow far below their elastic limit (before yielding) in a manner similar to supercooled liquid at a constant stress at room temperature or at temperature far below glass transition temperature T_g.[1–5] The flow before yielding in MGs is markedly different from the stress-induced instantaneous flow of yield and the subsequent plastic flow[1–5] and induces irreversible structural changes, accompanied by an increase in the stored heat of relaxation (taken to be a measure of structural "defects") and marked mechanical properties change when subsequently tested.[1–5]

However, the extremely slow and nano-scale localized flow is hard to be detected using conventional mechanical tests due to its slowness with a long time scale (the permanent plastic strain is only 2.0×10^{-4} after 5 h compressive creep at 80% of MG yield strength)[1–5] and the lack of structural understanding as deep as that for crystalline solids. It requires high-precision instruments to capture the slow flow at the early stage of yielding, which is a challenge in experiments. As a consequence, there still lacks a quantitative understanding of the extremely slow flowing phenomenon as well as its evolution to the macroscopic flow of yield and its microscopic picture. The flow in MGs may be explained with that glass is a "frozen liquid" with a very high viscosity, and as long as a sufficiently long time is applied, the flow is noticeable even though the applied stress is far below the ordinary elastic limit. However, such a simple answer is not adequate to explain the transition from a slow to an instantaneous flow of yield at certain time.[6] On the other hand, the underlying structural origin of yielding in MG is one of the long-standing issues[7–10] due to the slow flow before yielding is unclear and the lack of key experimental evidence which is able to underpin the mechanisms of the initiation of yield. Therefore, the understanding of the slow flowing phenomena and its structural evolution path before yielding, especially its correlation with mechanical behaviors, is of crucial fundamental and practical importance.

The plastic flow in MG is generally attributed to activated processes that involve the collective motion of atoms,[11–23] which occurs initially in some local regions of flow units with higher potential energy. Stress relaxation is a sensitive and effective instantaneous activation-relaxation technique to qualitatively investigate the activation energy, size, and relaxation time spectra of the flow units as well as their evolution as a function of time, temperature, and stress in MGs.[24–29] In this paper, we apply the activation-relaxation technique to investigate distribution and evolution of energy barriers and relaxation time spectra of the activated flow units in the flowing process before yielding in MGs. The results clearly reveal the slow flow manifested with the activation and evolution process of the flow units and the evolution of structural and dynamic heterogeneities. Plausible correlations among relaxations, evolution of flow units, dynamic and structural heterogeneities, and microscopic flow to macroscopic yield transition of MGs are established and interpreted using the perspective of flow units.

II. EXPERIMENTAL

We selected a prototypical $La_{55}Ni_{15}Al_{20}$ bulk MG as a model system to study the slow flow as well as its evaluation and transition to yield MGs. Rod-shaped samples for uniaxial compression were obtained by suction casting, and the ribbon samples for stress relaxation were prepared by melt spinning. Uniaxial compression tests were performed with an Instron 5869 electromechanical test system at a constant strain rate of 1×10^{-4} s^{-1} at 370 K. The tensile stress relaxation experiments were performed on Dynamic mechanical analyzer (DMA) of TA Q800 Instruments in an argon-flushed atmosphere. To avoid the effect of the physical aging, all the

[a)]Author to whom correspondence should be addressed. Electronic mail: hybai@iphy.ac.cn

samples were previously heated up to the supercooled liquid region (above its T_g) and then cooled down from the supercooled liquid state in the argon atmosphere prior to measurements. The size of the samples for stress relaxation is about 10 mm in length, 30 μm in thickness, and 1.5 mm in wideness. For each relaxation experiment, we applied a constant tensile strain at a strain rate of 1×10^{-4} s^{-1} within the nominal elastic regime, and the strain was measured by the optical encoder in DMA with an accuracy of ~1 nm. The stress decay with the loading time of 30 min at 370 K (far below its $T_g = 476$ K) was recorded. The applied constant strain ranges from 0.1% to 2.0% with an interval of 0.1%. Before the experiment, 3 min delay was applied to allow the samples to equilibrate at the test temperature.

III. RESULTS AND DISCUSSIONS

Figure 1(a) is a typical engineering compression stress-strain curve of the $La_{55}Ni_{20}Al_{25}$ MG at 370 K. The MG shows large apparent elastic regime before yielding of 1.7% (tens times higher than conventional metals and alloys). No shear bands are observed in the MG surface using scanning electron microscopy [see inset of Fig. 1(a)] seemingly indicating an elastic deformation of the MG in the nominal elastic regime. Figure 1(b) shows the stress relaxation spectra

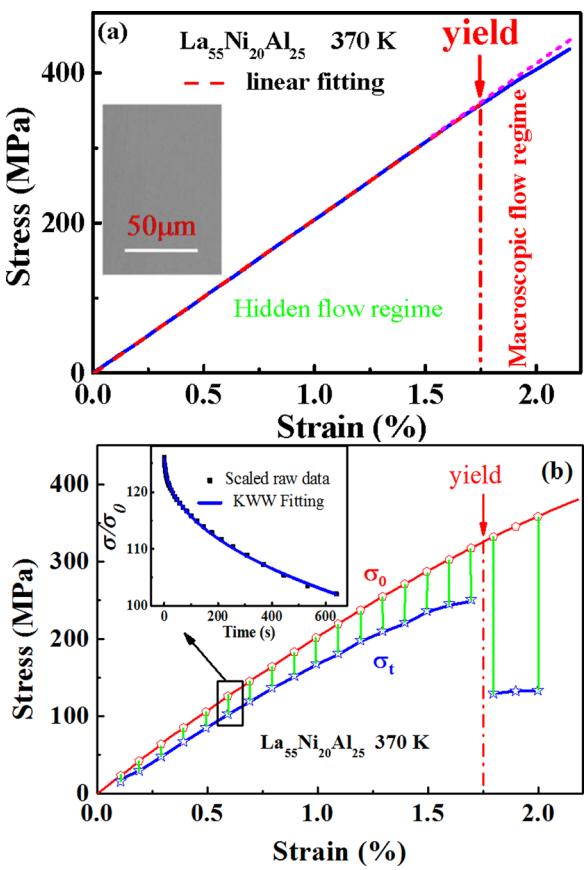

FIG. 1. (a) A typical compression stress-strain curve of $La_{55}Ni_{20}Al_{25}$ MG at 370 K, which shows a slow flow before yielding. The inset is the SEM images of the surface topography of the MG in the elastic region. (b) Stress relaxation spectra (blue line) at the strain range of 0.1%–2.0% with an interval of 0.1%, the initial stress (red open pentagon), and residual stress (blue open stars) trend lines with strain. The inset is a typical stress relaxation curve at the strain of 0.6%.

containing 20 isothermal stress relaxation curves with loading time of 30 min at 370 K. A typical stress relaxation curve measured at an applied constant strain of 0.6% is shown as an inset, where the stress needed to maintain constant strain gradually relaxes with increasing time. We note that after short time loading, only small fraction of reversible flow units with smallest energy barriers and shortest intrinsic relaxation time can be activated, and the residual strain is almost fully recovered after the applied load is removed, and the stress relaxation measurements reflect an anelastic response.[30] However, after enough long time loading in the case of this paper, the irreversible flow units with higher energy barrier and larger intrinsic relaxation time are gradually activated, and the permanent deformation appears and only partial applied strain recovers.[30]

The stress relaxation curve shows non-exponential behavior, which can be described by the Kohlrausch-Williams-Watts (KWW) function of $\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right)^{\beta}$, where τ is the average relaxation time, and β is a non-exponential parameter and $0 < \beta < 1$, which is related to dynamic heterogeneity of the MG.[28–31] The initial stress σ_0 and terminal stress σ_t of each relaxation curve reflect the viscoelastic property of the MG,[31] which are, respectively, enlarged as red and blue open circles in Fig. 1(b). The larger stress drop $\triangle\sigma_0 = \sigma_0 - \sigma_t$ indicates the larger fraction of activated flow units in the MG.[31] We note that the $\triangle\sigma_0$ strongly depends on observation time,[3] and the experimental time of each stress relaxation test is elaborately selected in an order of 10^3 s.[3] With the increase of applied strain, $\triangle\sigma_0$ increases, meaning that more fraction of flow units are activated with increasing applied strain. Before yielding, the increase of $\triangle\sigma_0$ is very slow, while when the applied strain approaches yield (~1.7%), the $\triangle\sigma_0$ increases rapidly due to the occurrence of plastic flow near yield.

Figure 2(a) presents the typical raw data of the stress relaxations under various strains at 370 K. The stress of all the relaxation curves shows a rapidly decrease from initial value and then slows down gradually with increasing time. With increasing strain, the stress relaxation curves shift upward higher stress value. All the curves can be well fitted by the KWW function of $\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right)^{\beta}$, $0 < \beta < 1$. The dispersion (i.e., nonexponentiality) of the relaxation curve is governed by β. The β reflects dynamic heterogeneity of glasses, and the smaller β indicates larger dynamic heterogeneity of a system.[32,33]

Figure 2(b) shows the evolution of the coefficient β obtained from the KWW fitting of stress relaxation curves upon the strain of the MG. Generally, the value of β decreases with increasing applied strain, indicating that the MG becomes more inhomogeneous with increasing applied strain. The strain-dependent β evolution can be divided in three obviously different stages as indicated in Fig. 2(b), which clearly reveals the activation and evolution processes of flow units during the slow flow process before yielding. When the strain is below 0.4%, the value of β rapidly decreases to about 0.5, which is ascribed to be the stochastic activation of isolated flow units, and the activated flow units are reversible and correspond to the so-called β-relaxation.[3] The MG becomes more inhomogeneous with more isolated

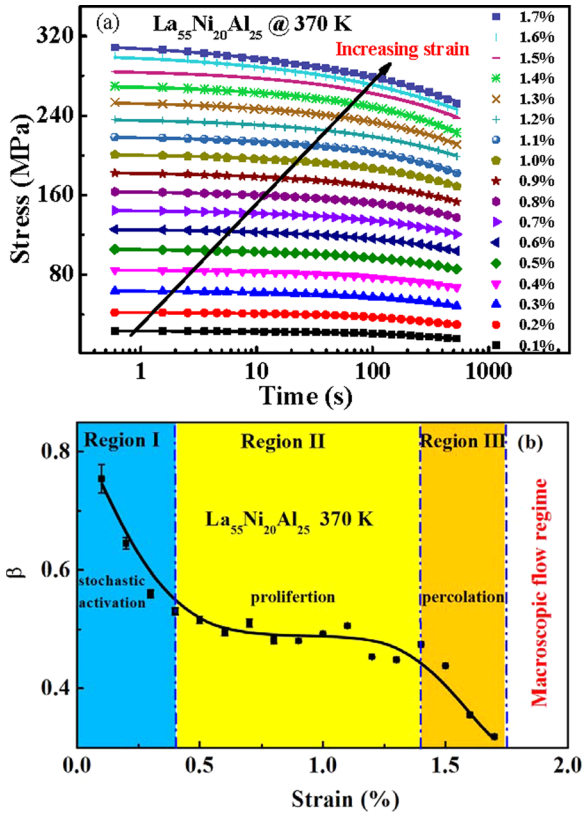

FIG. 2. (a) Stress relaxation and its corresponding KWW fitting curves measured at the strain range of 0.1%–2.0%. (b) Strain dependent of KWW fitting β coefficient of the stress relaxation curves.

flow units activated. The region between 0.4% and 1.4% is the flow units proliferation process, and the β value shows insignificant change as the majority of potential flow units have already been activated in this region, and these activated flow units are extended and start to cooperate with each other, involving in a long time stress relaxation process. When the strain is larger than 1.4% and approaches yield, the β value rapidly decreases to ~0.32. At this stage, high density flow units are coalesced. When the fraction of the flow units reaches a critical value, the flow units percolate and lead to yielding in the MG.[3,27,28] The results clearly exhibit that the flow before yielding is related to the evolution of flow units with applied strain.

The distribution and evolution of activation energy of the activated flow units in MGs can be estimated based on the stress relaxation curves using an activation energy spectrum model:[34] $\Delta\sigma = \int_0^{+\infty} p(E)\theta(E,T,t)dE$, where σ, t, and T are relaxation stress, time, and temperature, respectively; $p(E)$ is the activation energy spectrum of flow units in the range of E to $E+dE$; and $\theta(E,T,t) = 1-\exp(-t/\tau) = 1-\exp[-\upsilon_0 t\exp(E/kT)]$, is the characteristic function, where υ_0 is Debye frequency ($10^{13}\,s^{-1}$).[12] In the frame of step-like approximation,[35,36] $p(E) = -\frac{1}{kT}\frac{d\sigma(t)}{d\ln t}$ and $E = kT\ln(\upsilon_0 t)$.[12] The activation energy spectra of the flow units of the MG at various applied strains are shown in Fig. 3(a). The activation energy spectrum can be fitted by Gaussian stochastic distribution indicating that the statistical energy barrier distribution of the flow units is heterogeneous, and only those flow units with energy barrier $E < E_c$ (the critical value of energy barrier) contribute to the slow flow. The activation energy spectra shift toward the higher value and their full width at half maximum (FWHM) also increases with increasing strain, confirming that more flow units with higher energy barriers are activated at elevated strain. The FWHM of the activation energy spectra and the average energy barrier E_c of flow units are estimated and shown in Fig. 3(b). During the slow flow, both the FWHM and the E_c increase upon increasing strain, implying that the energy barrier distribution of the flow units becomes more dispersive, and more flow units with higher activation energies are engaged into the flow at higher applied strains. The high fraction of liquid-like flow units at higher applied strains makes MG more heterogeneous. Both the change of FWHM

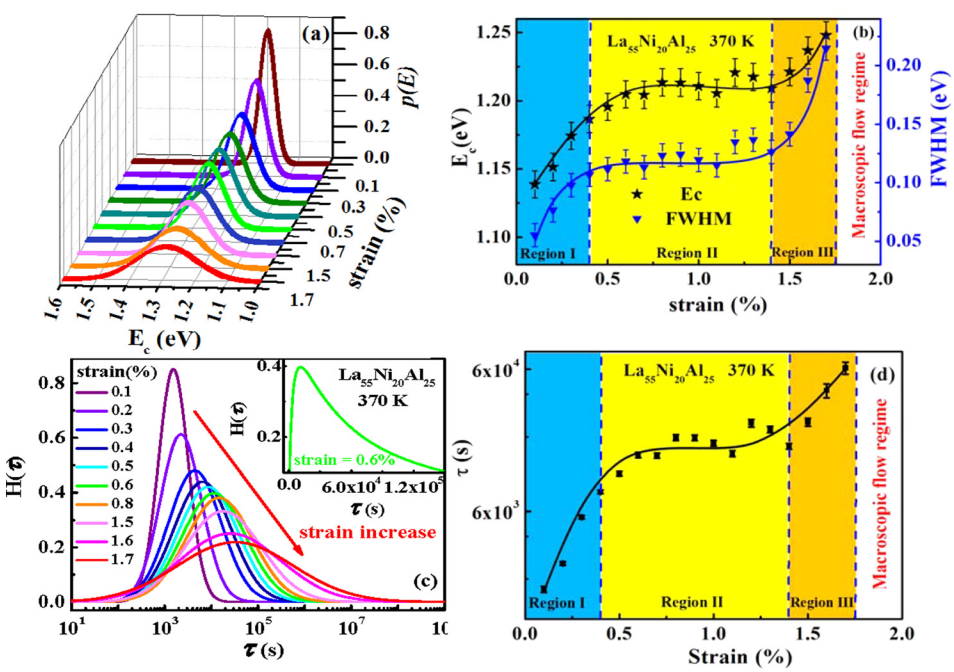

FIG. 3. (a) Strain dependence of activation energy spectra $p(E)$. (b) The variation of FWHM of activation energy spectra and average activation energy upon strain. (c) Strain dependence of relaxation time spectra $H(\tau)$. The inset is an enlarged typical relaxation time curve at the strain of 0.6%. (d) The variation of average relaxation time on strain.

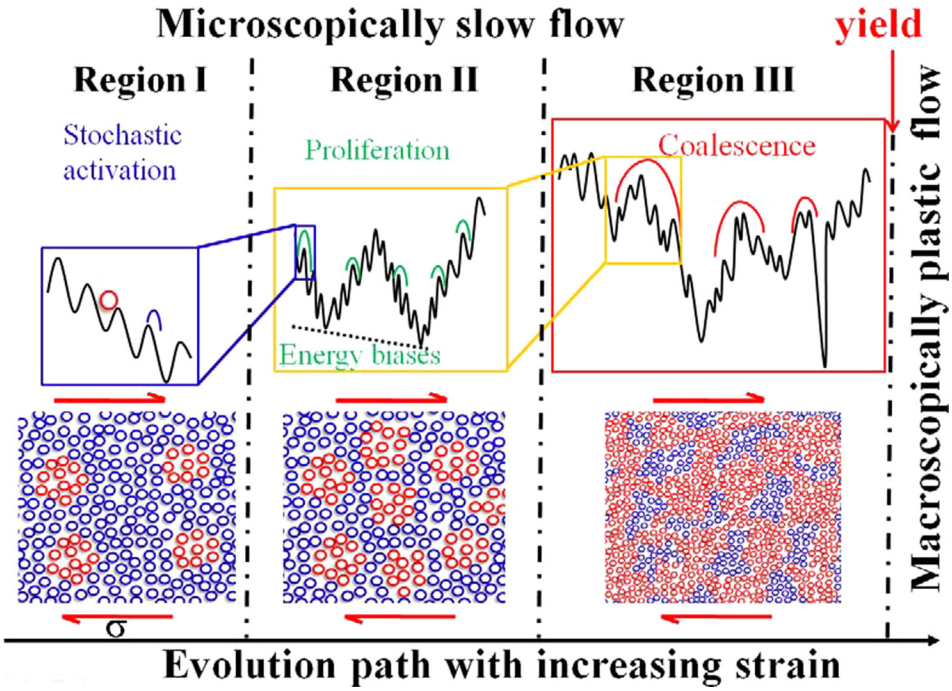

FIG. 4. Evolution path from microscopically slow flow to macroscopically plastic flow with increasing strain. Correlations between evolution of flow units (liquid-like zones) and energy landscape are established during the slow flow to macroscopic flow transition.

and E_c of flow units upon increasing strain can also be separated as three regions, which accords with the change trend of β coefficient during the flow before yielding.

The distribution of intrinsic relaxation time τ of these flow units, which can characterize the dynamic difference of the flow units of MG compared with that of the elastic matrix, can be estimated from the stress relaxations based on the generalized Maxwell model.[28] Assuming a continuum spectrum of relaxation times, the time dependence of $\sigma(t)$ is[37,38] $\sigma(t) = \sigma_R + \int_{-\infty}^{+\infty} H(\ln\tau)e^{-\frac{t}{\tau}}d\ln\tau$, where $H(ln\,\tau)$ is the logarithm distribution function of τ. Considering the fact that the activation energy spectrum in MGs is close to the Gaussian distribution and $\tau = \tau_0 \exp(E_a/KT)$,[33] it is speculated that τ satisfies the lognormal distribution: $H(\ln\tau) = k\exp(-\frac{(\ln\tau - \ln\tau_m)^2}{s^2})$, where τ_m is the most probable relaxation time, s is the width of the τ spectrum, and k is the factor in front of exponential. The associated relaxation time spectra of the flow units in the MG before yielding are obtained and shown in Fig. 3(c). The inset is one enlarged typical relaxation time curve at the strain of 0.6%. We can clearly see that the τ during slow flow satisfies the lognormal distribution. The spectra shift toward higher relaxation time value with increasing strain due to more flow units with higher relaxation time or higher activation energy are activated. The estimated τ of flow units is shown in Fig. 3(d). The τ increases with increasing strains, implying that more flow units are engaged into the relaxation process at higher strains, and the τ change trend during the slow flow can also be separated in three similar stages like that of E_c and β coefficient.

Based on the above results, we attempt to illustrate the extreme slow flow picture before yielding in MGs associated with the evolution of flow units upon applied strain. The picture associated with the energy landscape theory,[39,40] the flow units, and yielding (plastic flow) in MGs is schematically shown in Fig. 4. The flow before yielding relates with three processes: The flow unit activation process, the flow units proliferation process, and the coalescence of the flow units process. Due to the intrinsic structural heterogeneity, there are no equivalent atoms in MG. Atomistic simulations and experimental observations show that the local shear events are located in ~1 nm soft spots, which are related to the range of density and stiffness of nearest-neighbor clusters.[4,5,11–23] Under elastic loading, strains lead to local structural change and enhance the atomic mobility (or decrease the viscosity) by inducing the decrease of energy barriers even well within the nominally elastic regime.[41] When the applied strain is very limited or in the beginning of the elastic region, only little reversible flow units with smallest energy barriers and shortest intrinsic relaxation time can be activated, as illustrated by the high mobility atoms (red balls) embedded in the elastic shell (blue balls) in Fig. 4. The isolated and reversible activation of the potential flow units accommodating the flow during elastic deformation are confined within the elastic matrix and can be regarded as hopping events across inherent structures in the energy landscape as indicated in region I in Fig.4.[3,11,20,41] With increasing applied strain in apparent elastic regime, the flow units with higher energy barrier and larger intrinsic relaxation time are gradually activated, and the concentration of flow units increases, and this leads to the wider flow unit activation energy spectrum and higher density inhomogeneity,[41] corresponding to the flow units proliferation region.

When the applied strain approaches yield, the adjacent weak-bonded regions around flow units are also gradually transformed into a liquid-like state, as the applied strain lowers the energy barrier between adjacent mega-basins in the energy landscape[11,12,15] and the elastic shell of the isolated flow units will collapse and lead to the rapidly increase of the size and fraction of the flow units as illustrated in Fig. 4. When the concentration of the flow units reaches a critical

value, a connectivity percolation of flow units or liquid-like zones occurs corresponding to the coalescence process.[3,6,10] At this stage, the liquid-like flow units lead to localized plastic events and the MG yields, and critical transition from broken-ergodic to ergodic on energy landscape happens. The slow flow transforms into large scale plastic flow of yield. This process is similar to the thermally driven glass to supercooled liquid transition.[41]

IV. CONCLUSION

We demonstrate that the activation and evolution of the flow units by applied strain induce the slow flow before yielding, and the percolation of the flow units at a critical high density leads to the transition from the slow and unnoticeable flow to macroscopic yield. A plausible picture connecting structural heterogeneity, relaxations, flow units, and yielding could provide a general understanding of structural origin and evolution of the extremely slow and unnoticeable flow before yielding in glasses and be helpful for unfolding the mechanism of glassy yield. Bacause MGs are usually used below their T_g, the understanding of the flowing phenomena and the structural evolution path before yielding, and especially its correlation with their mechanical behaviors, is of crucial practical importance for controlling their performances and fabrication.

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