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Citation: Applied Physics Letters **106**, 031908 (2015); doi: 10.1063/1.4906603
View online: http://dx.doi.org/10.1063/1.4906603
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/106/3?ver=pdfcov
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Dynamic correlation between the flow units of supercooled metallic liquid

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(Received 27 December 2014; accepted 14 January 2015; published online 23 January 2015)

In contrast to the nano-sized shear bands in metallic glasses at room temperature, a millimeter-sized shear band is observed in the flow of supercooled metallic liquid. To understand the precipitation of the observed millimeter-sized shear band, an empirical approach to characterize the dynamic correlation between the flow units is proposed based on the transient mechanical response in the flow of supercooled metallic liquid. The characterized dynamic correlation well reproduces the staged-feature of the Van Hove's self-correlation function and explains the precipitation of shear band. Besides, for the dominant dynamic correlation approaching the glass transition temperature T_g, glass transition is suggested to be more than *frozen*. *© 2015 AIP Publishing LLC.*
[http://dx.doi.org/10.1063/1.4906603]

Since viscosity, the resistance of flow, is intimately related to glass transition,[1] the flow of glass is thought of as the entrance to the physics beneath the sluggish glassy dynamics.[2,3] Metallic glasses[4] are expected to exhibit appreciable flow[5] for the non-oriented and non-saturated character of metallic bonds and to be an ideal research subject. In the flow of metallic glass, the precipitation of sharp nano-sized shear band is of special eccentricity due to its limited scale in thickness, which is usually of several tens of nanometers,[6] regardless of loading rate. It is unlikely that the adiabatic shear effect commonly observed in high rate deformation of crystal alloys is the main cause,[6] because adiabatic shear band could be hundreds of micrometers in thickness,[7] 3 orders of magnitude larger than its counterpart in metallic glasses, at least. Not specific to metallic glasses, in granular materials and colloids, where shear bands are frequently seen, the shear banding thickness is observed to be universally of about ten particle diameters suggesting a universal structure origin.[8–10] Thereby, the shear banding process would be a key to the entrance.

In the flow theory of glasses, a core-shell concept of elementary flow unit has been proposed[11–13] based on the dynamic heterogeneity[14,15] of glasses, i.e., coexistence of liquid-like and solid-like regions, which develops as the liquid being cooled toward and below glass transition.[3] The core (liquid-like region, or envisaged as the sites of higher free volume concentration) affords structure rearrangement in flow and the shell (solid-like region), acting as elastic matrix to carry external load and on which the internal Eshelby stress develops, mediates the correlation between the activations of individual flow units.[16] Although significances of the dynamic correlation, which works as the correlation between individual flow units in shear banding, has been recognized,[17–19] an effective characterization on the spatial and temporal scales of this effect remains elusive.[14] In addition, for the extremely fast nucleation and propagation of shear band in metallic glasses,[20] it is difficult to investigate the shear banding process at room temperature.

In this letter, for the millimeter-sized shear band observed in the flow of supercooled metallic liquid and the homological structure of glasses and supercooled liquids, to understand the precipitation of shear band and its relevance to the dynamic correlation between the flow units, an empirical approach to characterize the dynamic correlation is proposed based on the transient mechanical response in the flow of supercooled metallic liquid. Besides, based on the characterized dynamic correlation approaching T_g, glass transition is implied to be more than *frozen*.[21,22]

Rods of 3 mm in diameter of bulk metallic glasses $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ (at. %, Vit106a) of which the thermal properties have been thoroughly studied[23,24] were prepared, and cylindrical specimens of aspect ratio[25] 1:1 were carefully machined to ensure the two ends being parallel. The high temperature compressive stress-strain (SS) curves were obtained above $T_{g\text{-}end} = 703$ K (the end of glass transition temperature) with a Zwick/Roell mechanical testing system equipped with an air furnace. The morphology of the samples after deformation is characterized by Quanta-200 SEM. The test temperature was selected to be 703 K, 713 K, 723 K, and 733 K. Compression tests at strain rates from $10^{-3}\,s^{-1}$ to $10^{0}\,s^{-1}$ were carefully selected to guarantee the endurance of the test less than 300 s.[23,24] The samples after deformation were also examined by thermal analysis and X-ray diffraction to maintain the amorphous state. More details of the experimental procedure can be found elsewhere.[26]

Fig. 1 shows the morphologies of the supercooled metallic liquids before (a) and after compression (b)–(d). The cast fins formed due to the gap between the two copper half-molds serves as a clear indicator of the deformation mode, where both homogeneous deformation Fig. 1(b) and brittle fracture (usually seen in the compression test at room temperature) Fig. 1(c) can be observed. In contrast to the nano-sized shear band commonly observed at room temperature, at 723 K and a strain rate $\dot{\varepsilon}$ of $5\,s^{-1}$, a shear band of millimeter in thickness which is judged by the distortion deformation of

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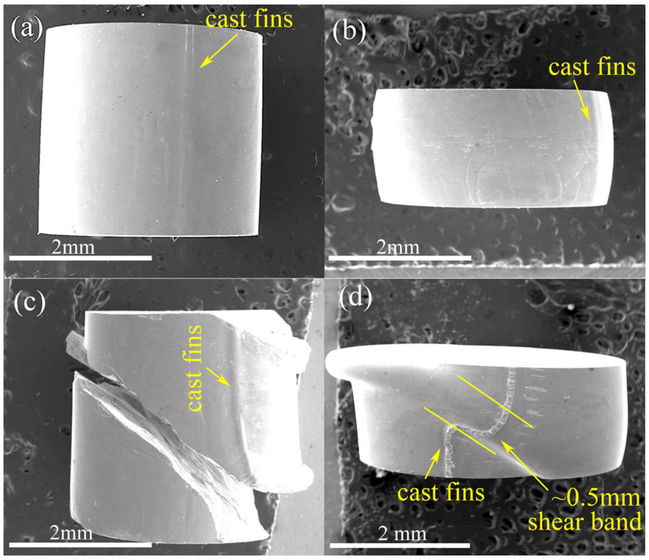

FIG. 1. The morphology of supercooled metallic liquid before and after compression test: (a) before deformation, (b) homogeneous deformation, (c) shear localized fracture, and (d) shear band of millimeter in thickness at 723 K and a strain rate of 5 s^{-1}.

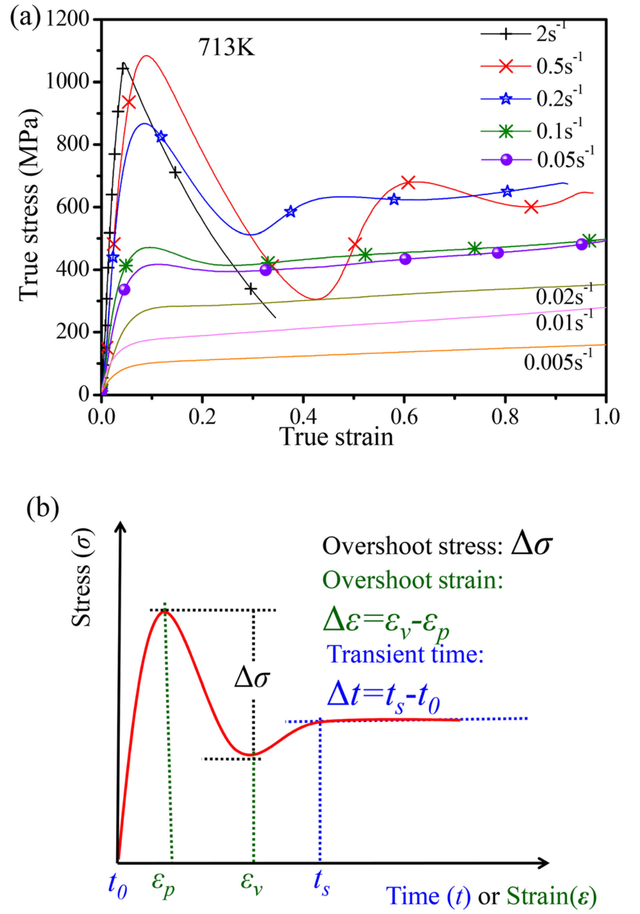

FIG. 2. Characterization of dynamic correlation: (a) Typical SS curves of supercooled metallic liquid, the ones with stress overshoot are focused on; (b) schematic illustration of determining the transient time Δt and the overshoot strain $\Delta\varepsilon$.

the cast fins, as shown in Fig. 1(d), seems meaningful, for the homological structure of supercooled liquids and glasses and the significance of dynamic correlation which works as correlation between individual flow units in shear banding. In the flow of supercooled metallic liquid, the spatial and temporal correlation between flow units proves to be of special importance by the presence of oscillated SS response,[26] which reflects the microscopic activation behavior of individual flow unit on macroscopic scale. More recently, it has also been revealed within a flow units-based constitutive model that the stress overshoot and the post-yielding flow of metallic glasses are closely determined by the dynamic operations of flow units and the free volume dynamics, respectively.[27] Based on these results, an experimental characterization on the dynamic correlation between flow units is provided to understand the precipitation of the observed millimeter-sized shear band.

A group of SS curves of supercooled metallic liquids is shown in Fig. 2(a). It can be seen that at strain rate $\dot{\varepsilon}$ above 0.05 s^{-1}, a stress overshoot, i.e., the stress decreases after yielding and reaches a plateau, emerges on the SS curves. Before localized fracture sets in at $\dot{\varepsilon} = 2\,s^{-1}$, the width of stress overshoot increases with strain rate. At $\dot{\varepsilon}$ below 0.02 s^{-1}, the SS response of which the stress increases monotonously to a plateau without a stress overshoot usually with the viscosity almost being a constant is considered as Newtonian mode flow,[28] i.e., *the system remains in the meta-equilibrium supercooled state*, indicating the well coupled temporal and spatial correlation in flow. To explore the origin of shear banding, we mainly focus on the shear thinning regime with a stress overshoot where the supercooled liquid evolves out of its initial configuration.[16] Therefore, the characterization of correlation can be justified as follows. Macroscopically, the sample before flow is in an initial meta-equilibrium state, and the flow state with the stress being a constant can be considered as a final steady state under the exerted external stimulus, i.e., flow rate. In turn, the SS response is the output signal of the system in the transition from its initial state to the final flow state which is determined together by the flow rate and the Maxwell relaxation time,[29,30] as the post-yielding flow strongly depend on the relaxation dynamics of free volume of metallic glasses, i.e., the diffusion, creation, and annihilation of free volume.[27] Microscopically, taking a flow unit as an example, its activation will exert a back stress on surrounding elastic matrix. Upon yielding (as the stress climbing over the peak stress of the overshoot), the correlation between flow units mediated by the back stress is assumed to assemble the cooperative activation and percolation of flow units to afford the exerted flow state accompanying the breakdown of back stress along the downward side of the stress overshoot,[16] as supported by the conclusion that stress overshoot is closely determined by the dynamic operations of flow units.[27] Accordingly, as shown in Fig. 2(b), a transient time Δt is defined as the time required for the flow stress to reach a constant, which is assumed to be an index of the transition time from the initial meta-equilibrium state to the final percolated state, i.e., the temporal correlation between flow units. On the other hand, for the stress overshoot reveals the breakdown of the back stress[16] and also for the increasing overshoot strain $\Delta\varepsilon$ and overshoot stress $\Delta\sigma$ with $\dot{\varepsilon}$, $\Delta\varepsilon$ is assumed to be an index of the number of cooperatively activated flow units,[27] i.e., the spatial correlation between flow units.

Based on the illustrations above, Fig. 3(a) shows the transient time Δt of supercooled metallic liquids in flow. It is shown that Δt decreases with $\dot{\varepsilon}$ at all temperatures indicating the rapid assembling process of flow units and reproduces the staged-feature of the Van Hove's self-correlation function $F(\vec{k},t) = \langle \exp\{i\vec{k}\cdot[\vec{r}_i(t)-\vec{r}_i(0)]\}\rangle$ fairly well,[3,31,32] where t is the time; $\vec{k}$ is the wave vector; $\vec{r}_i(t)$ is the position vector of the i-th particle at t instant, taking Δt as the correlation intensity, $\dot{\varepsilon}$ as the equivalent time, and the temperature T as the control parameter[3,31,32] of the dynamic correlation between flow units. Specifically, at lower temperature of 703 K and 713 K, the transient time shows steeper decreasing tendency with $\dot{\varepsilon}$ and at sufficiently high rate, similar to below T_g, shear fracture of sharply localized form in Fig. 1(c) bursts, suggesting the dominant dynamic correlation.[26] While at relatively higher temperature of 723 K and 733 K, the transient time decreases much slower and a two-staged[31] variation can be observed, implying that the dynamic correlation (stage I) becomes less distinct enabling the strain rate softening (stage II) to exist and the shear band in Fig. 1(d) to occur. Fig. 3(b) shows the overshoot strain $\Delta\varepsilon$ in flow. It can be seen that $\Delta\varepsilon$ increased with $\dot{\varepsilon}$ at all temperatures. As indicated by the dashed line, a change in the increasing mode can be observed as the curves exhibit a concave feature (exponential-like) at 703 K and 713 K and a convex feature (logarithmic-like) at 723 K and 733 K. This result again indicates the dominant dynamic correlation near T_g, corresponding well to Fig. 3(a). With the results in Fig. 3, the non-monotonic evolution of dynamic correlation[33] approaching T_g can be effectively characterized. Moreover, the dynamic correlation is more distinct approaching glass transition for its steeper increased spatial scale and decreased temporal scale. This decoupling[3] of the spatial and temporal aspects of correlation, i.e., increased spatial scale and decreased temporal scale, from the initial meta-equilibrium supercooled state with increasing flow rate demonstrates the critical role of dynamic correlation in the precipitation of shear band.

The picture of shear banding in supercooled metallic liquids is illustrated in Fig. 4. The yellow circles represent elastic matrix and the brown circles represent potential sites of flow units. Internal back stress indicated by the short dashed arrow will develop between flow units over the elastic matrix in flow. Via the back stress (i.e., Eshelby stress) between flow units, correlation between flow units works. Upon yielding, the correlation effect assembles the spatial cooperative activation of flow units which is reflected by the right flank of stress overshoot and the percolation of flow units which is underpinned by the diffusion of free volume (i.e., Maxwell relaxation) and revealed as the transient process in flow.[16] With increasing flow rate, the diffusion distance of free volume (dashed circle in Fig. 4) is highly constrained for the decreasing transient time and the spatial correlation increases rapidly to diverge. Correlation between nearest neighbor granular particles in the form of normal interfacial force has been reported as a structure signature of jamming.[34] As flow units or excitations in space-time can be described in trajectory phase space, in the same way as granular particle in Euclidean space,[3] and the back stress works

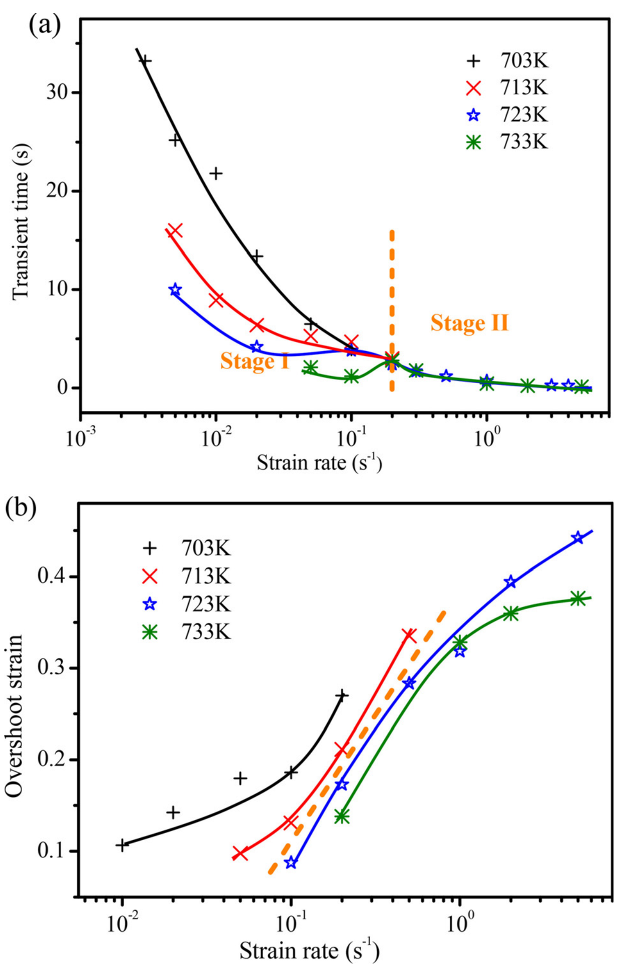

FIG. 3. Dynamic correlation extracted from the SS response, the solid lines are drawn as eye guides. (a) Temporal correlation between flow units reflected by transient time Δt on the stress-time curve with increasing strain rates at 703 K, 713 K, 723 K, and 733 K reproducing the staged-feature of the Van Hove's self-correlation function, the dashed line indicates the two-staged variation tendency of Δt at 723 K and 733 K; (b) spatial correlation between flow units reflected by overshoot strain $\Delta\varepsilon$ on the stress-strain curve with increasing strain rates at 703 K, 713 K, 723 K, and 733 K. The dashed line indicates the change of the form of the curves, i.e., concave at 703 K and 713 K and convex at 723 K and 733 K.

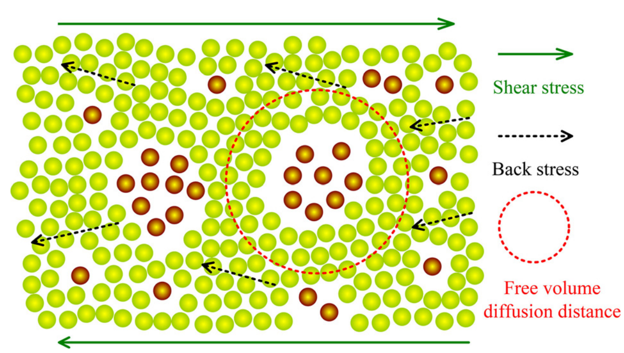

FIG. 4. Schematic illustration of flow units and dynamic correlation, the yellow atoms represent elastic matrix and the brown atoms represent potential sites of flow units. Upon loading, back stress (Eshelby stress) develops between flow units over the elastic matrix. The level of back stress determines the spatial correlation and the free volume diffusion distance to percolating determines the temporal correlation between flow units. With increasing flow rate, the diffusion of free volume underlying the temporal correlation will be highly constrained and the spatial correlation will diverge.

in the same way as the interfacial force, the increasing correlation with $\dot{\varepsilon}$ would finally drive the supercooled liquid to non-ergodic and jamming and induce shear banding.[21,35] So would be the case for the adiabatic shear band of hundreds of micrometers in thickness corresponding well to the shear banding of millimeter in thickness in glass, taking crystals as "phonon glasses." As shear banding of supercooled metallic liquid is observed at temperatures where correlation is slight, as shown in Fig. 3, and only localized shear fracture in Fig. 1(c) and sharp nano-sized shear bands exist at temperatures where correlation is prominent, noting the drastically increased dynamic correlation with flow rate at temperature close to T_g (e.g., at 703 K and 713 K, as shown in Fig. 3), it is concluded that dynamic correlation dominates near and below T_g and glass transition is more than jamming or *frozen*.[22] For the dominant correlation, which develops with the precipitation of dynamic heterogeneities[15,36–38] approaching glass transition, it is anticipated that advanced specific structure characterization on the density fluctuation or heterogeneity, exactly its scale and the space-time distribution,[3] via scattering tests where dynamic correlation develops would endow us more comprehensive messages concerning the origin of shear banding in metallic glasses and the nature of glass transition.

In conclusion, it is proved that the origin of shear banding in metallic glasses is the dominant dynamic correlation between the flow units. The spatial aspect and the temporal aspect of the dynamic correlation effect between the flow units of supercooled metallic liquid have been characterized in an empirical approach. The staged-feature of the Van Hove's self-correlation function can be reproduced. For the dominant correlation effect near T_g characterized by the proposed approach, it is concluded that glass transition is more than *frozen*.

This work was financially supported by the National Basic Research Program of China under Grant No. 2012CB937500, the CAS/SAFEA International Partnership Program for Creative Research Teams, and the National Nature Science Foundation of China under Grant Nos. 51271082 and 52171081. The authors are also grateful to the Analytical and Testing Center, Huazhong University of Science & Technology for technical assistances.

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