



A quasi-phase perspective on flow units of glass transition and plastic flow in metallic glasses

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ABSTRACT

We describe the activation and evolution processes of flow units for glass transition and plastic flow in metallic glasses using a quasi-phase model. We model the flow units as liquid-like quasi phases embedded in solid-like glassy substrate, and the formation and growth of the liquid-like phases in glasses are treated as a phase transition process. Our model can capture the main features of glass transition and mechanical behavior of metallic glasses and agree with experimental observations. The work may present a new perspective for structural origins of deformation and glass transition of metallic glasses.

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1. Introduction

The topological defects in the metallic glasses (MGs) well below the glass transition temperature T_g , which are proposed to be the “carriers” or the flow units of the plastic flow and relaxations in the glass [1–6], have attracted substantial interests. However, unlike crystalline solids, the topological defects in disordered glasses are difficult to be defined. Simulations have shown that some soft regions similar to the defects in crystalline solids exist in glass, which are closely related to the deformation and glass transition [3–5]. Several models including shear transformation zone (STZ) [6–8] and free volume model [9,10] have also been proposed to describe the flow units and understand their influence on the mechanical behaviors and glass transition [6–12]. However, specific structural features and picture accounting for the flow units are still elusive.

Previous studies [2–8,13–16] on the comparability of glass transition and plastic flow show that the flow during the glass transition or in the plastic deformation in MGs can be regarded as the succession jumping of the configuration among the minima of the potential energy landscape through overcoming the energy barrier. These studies suggest that both the glass transition and plastic flow may originate from the activation of the flow units [1–6]. However, effective experimental and theoretical characterizations of the flow units, especially from a thermodynamic point view, are still lacking.

In this letter, we propose a model to describe the activation and evolution processes of the flow units in MGs. The model can capture the main features of glass transition and mechanical behavior of MGs and agree with experimental observations. The study offers a compelling physical picture on the underlying structural origins of the two most important fundamental issues of deformation on and glass transition of MGs.

2. Model

Based on the experimental facts that soft regions in MGs can be activated into flow units by applied stress and/or thermal fluctuation of MGs [17–21], we simply assume that the shape of the flow unit is sphere with radius r (see Fig. 1(a)). We consider the elastic glassy regions and flow units respectively as two different quasi-phases: the solid-like matrix substrate phase and the liquid-like flow unit phase. The former shows elastic characteristics and can store elastic energy, while the flow units exhibit liquid-like characteristics which cannot store but dissipate the applied elastic energy. The flow units are assumed to accommodate the deformation and initiate the glass transition in MGs. We note that the glass transition actually is not true phase transition process, so the two phases are termed as quasi-phases.

For the activation of the flow units, the formation of the spherical interface between the flow unit and substrate phases will introduce an additional interfacial energy of $4\pi r^2\sigma$ [22], where σ is the interfacial energy density. The activation and evolution of flow unit can induce the infinite growth of flow unit phase from the substrate phase. Since the growth of flow units will increase the free energy of the system, external driving energy W is needed to transform the substrate phase into

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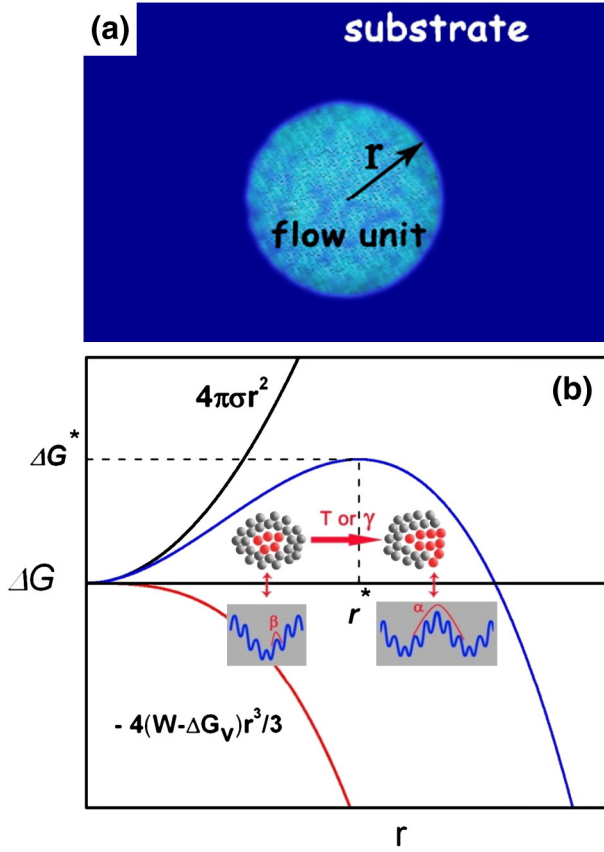


Fig. 1. (a) Schematic diagram of a flow unit in metallic glass. The dark region and light spherical region represent the substrate phase and flow unit phase, respectively. (b) The relationship between free energy and the radius r of the flow unit (blue curve). A critical radius r^* exists on the free energy curve. The flow units with $r > r^*$ will be activated (growing infinitely) corresponding to the irreversible α -relaxation. The activated flow units with $r < r^*$ corresponds to the reversible β -relaxations.

the flow unit phase and increase the interfacial energy. The total free energy change for the formation flow unit with radius r is:

$$\Delta G = -\frac{4}{3}\pi r^3 W + \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \sigma, \quad (1)$$

where ΔG_V is the free energy difference between the flow unit and substrate phases. Since free energy of flow unit is larger than that of the substrate, i.e. $\Delta G_V > 0$, the growth of the flow units leads to an increase of the free energy of a system. Thus, from thermodynamic point of view, no flow units can stably exist in MGs without external activation.

3. Experiments

The $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_6\text{Dy}_2$ metallic glass was prepared by arc melting under a Ti-gettered purified argon atmosphere and cast in a water-cooled copper mold [2]. The tensile stress relaxation was carried out in dynamic mechanical analyzer (DMA) model TA Q800. To avoid the effect of the physical aging, the glassy samples were previously heated up above its glass transition temperature T_g , isothermal for 3 min, and cooled down from the supercooled liquid state in the argon atmosphere prior to the measurements. The stress relaxation measurements were performed on the specimens at 0.3% tensile strain for 100 min. Before the experiment, a 3 min delay was applied to allow the samples to equilibrate at the test temperature.

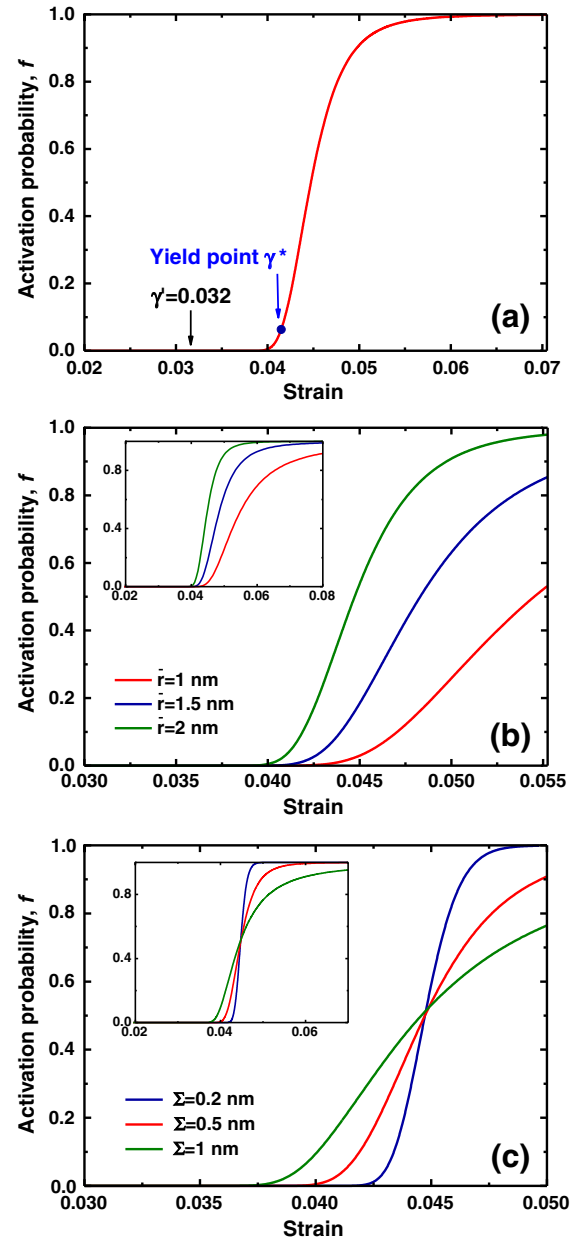


Fig. 2. (a) A typical curve of activation probability f of flow units as a function of strain with $\bar{r} = 2$ nm and $\Sigma = 0.5$ nm. (b) The dependence of the S-curve on $\bar{r}$ with $\Sigma = 0.5$ nm. (c) The dependence of the S-curve on Σ with $\bar{r} = 2$ nm.

4. Results

The ΔG for the activation of a flow unit with size r is shown in Fig. 1(b). If W is not large enough, the activated flow unit is unstable. To maintain the extension and the sustainable growth of the flow unit, W must be larger than ΔG_V . As shown in Fig. 2, there is a critical radius for the growth of flow units when $W > \Delta G_V$:

$$r^* = \frac{2\sigma}{W - \Delta G_V}. \quad (2)$$

Fig. 1(b) also shows that when $r > r^*$, ΔG decreases monotonously. This means that the flow unit will grow infinitely, which corresponds to the α -relaxations in MGs [2,23]. For $r < r^*$, the flow unit cannot grow from the substrate phase and thus is reversible corresponding to the

reversible β -relaxations [2,23]. The prediction is consistent with the experimental observations [2,23].

We then assume that the flow units are activated from the intrinsic “defects” and immersed in homogeneous substrate quasi-phase, and their sizes obeys quasi-Gaussian distribution [24]:

$$p(r) = \begin{cases} p_0 \exp\left[-\frac{(r-\bar{r})^2}{2\Sigma^2}\right] & (r \geq 0) \\ 0 & (r < 0) \end{cases}, \quad (3)$$

where $\bar{r}$ is the apparent average radius and Σ is the standard deviation. The $p(r)$ is probability of flow units with size of r , which can be normalized by $A = \int_0^\infty p(r)dr$. The activation probability (f) of stable flow units in MGs can be expressed as: $f = \frac{1}{A} \int_0^\infty p(r)dr$.

The glass transition and plastic flow of MGs can be considered as the different activation processes of the flow units [2,23]: the former is due to the thermal activation of the large scale of the flow units, and the latter is the activation and percolation of flow units in shear bands under the applied stress at low temperature. That is, the driving energy

W can be either the mechanical elastic energy of $\frac{1}{2}E\gamma^2$ as stored in the substrate phase or the thermal energy of αT , or both: $W = \frac{1}{2}E\gamma^2 + \alpha T$, where E is the Young's modulus of MGs, γ is the elastic strain, T is the temperature and α is a constant coefficient.

For the activation process of flow units at 0 K, $W = 1/2E\gamma^2$. For calculation of f vs. γ using Eqs. (2)–(3), the value of E is chosen as 100 GPa for typical MGs [29]. The α , which should be much less than the surface tension coefficient of supercooled liquid, is in the order of 0.1 N/m [26], and ΔG_V is in the order of 0.1 GPa [27]. The obtained yielding strain γ^* of the elastic substrate phase is close to the ideal upper limit of strain ($\sim 4.5\%$) of a MG [25]. The average size of flow units $\bar{r}$ estimated by Eq. (2) is about 2 nm, which accords with the STZ size measured by various experimental methods [28,29].

Fig. 2(a) is a typical curve of f versus γ for $\bar{r} = 2$ nm and $\Sigma = 0.5$ nm. The distribution curve shows an S-like shape (S-curve) with an intersection point with the x-axis which is denoted as the initial strain γ' ($\gamma' = (2\Delta G_V/E)^{1/2}$). We can see that when strain $\gamma \leq \gamma'$, the W can only be stored in the substrate phase and thus cannot compensate for the growth of the flow units. When $\gamma > \gamma'$, the f increases much slowly at the beginning, followed by a sharp increase. As shown in Fig. 2(a), a yield-like point γ^* can be defined as $d^3f/d\gamma^3|_{\gamma=\gamma^*} = 0$ (the inflection point of the curve). Once the strain reach this point, the f will increase rapidly, indicating a yielding like behavior occurs because of large fraction of activated flow units reaches a percolation limit. This is consistent with previous experimental results that the yield is a percolation process of flow units and a typical critical phenomenon [30].

The macroscopic plastic flow of MG is related to the size and the distribution of flow units. We then investigate the influence of $\bar{r}$ and Σ on the macroscopic plastic deformation. Fig. 2(b) shows the influence of variant $\bar{r}$ on the shape of the activation probability curve in MGs where Σ is fixed to be 0.5 nm. The γ^* drops remarkably when $\bar{r}$ increases from 1 to 2 nm, indicating that the bigger the average size of the flow units the smaller the yield strength. Fig. 2(c) also shows the change of the S-curve with Σ (here $\bar{r} = 2$ nm, and Σ is set for 0.2, 0.5 and 1 nm, respectively), which indicates the change of the distribution of the flow units in MGs. When Σ increases from 0.2 to 1 nm, the γ^* value drops accordingly suggesting that the MG with more uniform distribution of flow units is difficult to be yielded. Previous experimental results have shown that the yielding of MGs is created when the fraction of activated flow units reaches a percolation limit [1,28]. The phenomena that the flow units with a larger r and inhomogeneous distribution tend to easy percolation and lower

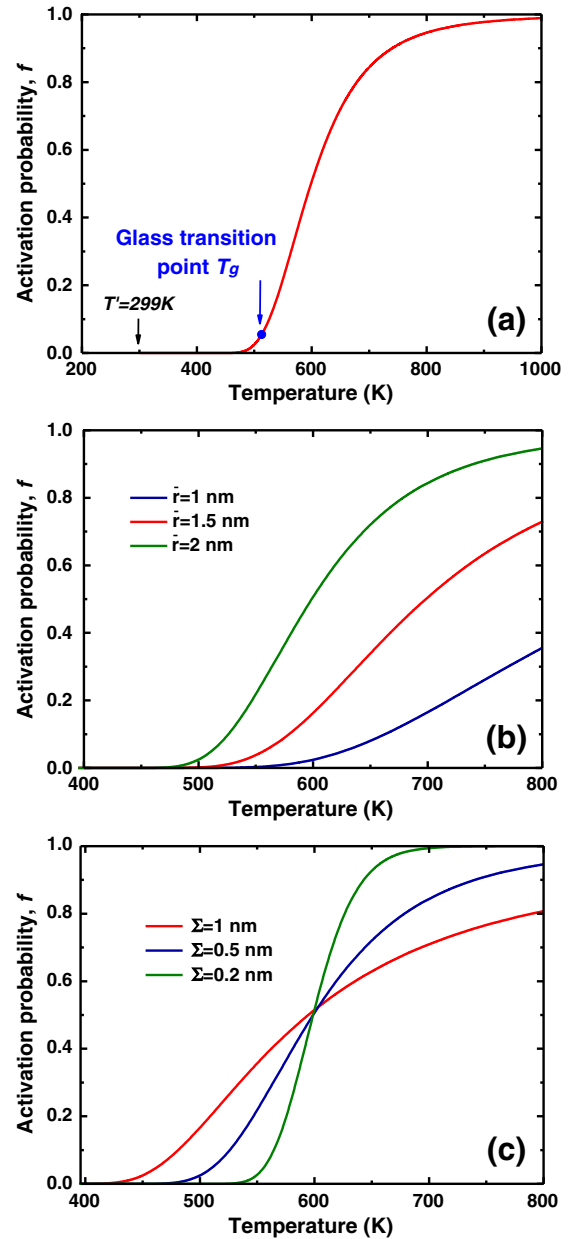


Fig. 3. (a) A typical curve of the activation probability of flow units as function of temperature with $\bar{r} = 2$ nm and $\Sigma = 0.5$ nm. (b) The dependence of the curve on $\bar{r}$ with $\Sigma = 0.5$ nm. (c) The dependence of the curve on Σ with $\bar{r} = 2$ nm.

yield strength have been widely confirmed in MGs by experiments [28].

Now we consider the case that flow units are activated solely by the thermal energy of $W = \alpha T$. The $\bar{r}$ and Σ are chosen to be 2 nm and 0.5 nm, respectively, and the T_g is about 600 K. Fig. 3(a) shows f as function of temperature (T) in MG. One can see the shape of the curve is similar to that activated solely by mechanical energy. Similar to the initial strain γ' in Fig. 2(a), an initial temperature T' ($T' = \frac{\Delta G_V}{\alpha}$) also exists in the curve. A critical temperature corresponding to T_g (the inflection point of $d^3f/dT^3|_{T=T_g} = 0$) can be seen, and the critical T is equivalent to γ^* . Once $T > T_g$, the f displays a sharp increase, and the applied thermal energy induces the high-density of activated flow units or a drastically viscosity change, and finally lead to the glass transition.

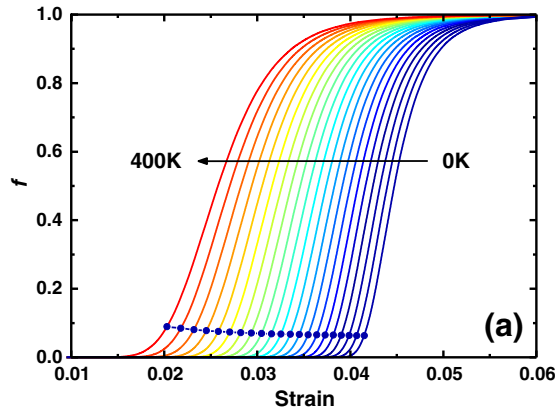


Fig. 4. The curve of the f of flow units for deformation of MGs at different temperatures. The yield point marked in the curves decrease with T increase.

Fig. 3(b) exhibits the thermal energy activation probability of flow units upon $\bar{r}$. For fixed $\Sigma = 0.5$ nm, $\bar{r}$ varies from 1, 1.5 and 2 nm. With the increase of $\bar{r}$, the T_g drops remarkably, illustrating that MGs with a distribution of larger flow units can be activated easier and transformed to the supercooled liquid state at lower T . In Fig. 3(c), $\bar{r}$ is fixed to be 2 nm, and Σ is chosen to be 0.2, 0.5 and 1 nm. One can see that T_g reduce remarkably as Σ increases. This means that inhomogeneous distribution of flow units in MGs reduces T_g i.e. the glass transition occur easily. The predictions of Fig. 3(b)–(c) are also in agreement with the experimental observations that the glass transition is a percolation and critical phenomenon [2–6,9], indicating that our flow unit model can also capture the main features of glass transition in MGs.

In practice, both the mechanical energy and thermal energy contribute to the activation of the flow units in MGs. The f curves of flow units with $\bar{r} = 2$ nm and $\Sigma = 0.5$ nm under different temperatures (below T_g) are shown in Fig. 4. In these cases, the initial strain is $\gamma' = [2(\Delta G_V - \alpha T)/E]^{1/2}$. As shown in Fig. 4, with the increase of T , the curve gradually shifts to the left which means that T increase leads to the decrease of the yielding strain. To confirm the model, we performed the stress relaxation experiments which can show the change of the fraction of the flow units with relaxation time.

Fig. 5 shows normalized isothermal stress decays $f(t)$ ($f(t) = 1 - \frac{\sigma(t)}{\sigma_0}$, where σ_0 is the initial stress) with time for $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_6\text{Dy}_2$ MG performed at 640 K (70 K lower than its T_g) with an applied constant strain of 0.34%. One can see that the stress reduces gradually

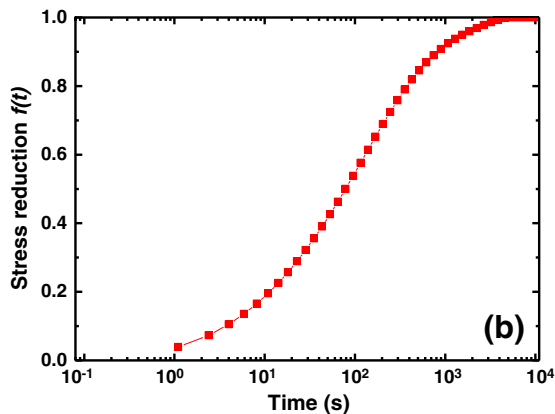


Fig. 5. The S-curve of normalized stress reduction fraction vs. time (or the dissipation of storage elastic energy) of the $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_6\text{Dy}_2$ metallic glasses.

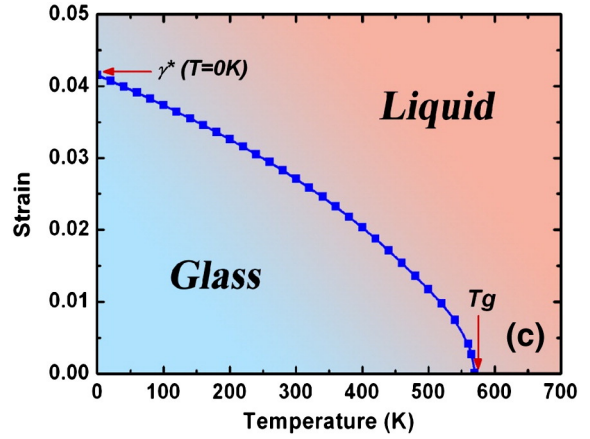


Fig. 6. The obtained diagram of glass transition in MG. The boundary of the glass and liquid state is the curve of yield strain under different temperatures or glass to liquid transition under different strains (or stresses). The indicated two cross points of the curve and axis correspond to the glass transition point of unstrained material and the yielding point under temperature of 0 K.

with relaxation time to zero, and the elastic strain is gradually converted to the inelastic portion, and the stress reduction fraction corresponds to the increase of the flow units in MG confirmed by simulation [1]. The increase of flow units with time (or the dissipation of storage elastic energy) is in the S-shape which is agreement with the prediction of our model.

5. Discussions

A relationship between T and applied strain on the transition between glass and supercooled liquid states can be obtained from our model as shown in Fig. 6, which is a quasi-phase diagram of glass transition of MGs. The curve in Fig. 6 displays a convex shape with the curvature increasing with decreasing T . According to the diagram, the transition between glass and supercooled liquid can be realized either by T , or by external stress (strain). In other words, a glass may have a lower glass transition temperature under high applied strain, or the glass will have lower yield strain at higher applied temperature. In the case of no applied strain ($\gamma = 0$), the glass transition temperature reaches the normal value of T_g as indicated in Fig. 6. The obtained diagram for the glass transition from our model is consistent with the glass transition diagram by computer simulation [31,32] and the jamming phase diagram [33]. The obtained glass transition phase diagram also agrees with the recent experimental observations and simulation results [2–6,32,34]. The results confirm the equivalent roles of temperature and stress in glass transition, and the correlation between the glass transition and plastic deformation in MGs [5,6,34–36].

6. Conclusions

We propose the model, which treats the flow units as a quasi phase immersed in the homogeneous elastic substrate, shows that the glass transition and plastic deformation in MGs can be considered as nucleus and the percolation of the flow units. The flow units can be activated thermally or/and mechanically, which respectively correspond to the glass transition and plastic deformation in MGs. The predictions of the model are in good agreement with the experimental observations, which indicate that the work may link the microscopic atomic structure with the macroscopic deformation and glass transition and present a perspective for understanding the flow units and other fundamental issues in MGs.

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