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Structural perspectives on the elastic and mechanical properties of metallic glasses

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The flow units of glasses are generally perceived to be a local rearrangement of atoms that are microstructural origin for plastic deformation and relaxations in metallic glasses. We find a relationship of the effective concentration of flow units and some properties such as elastic moduli, micro-hardness and plasticity of metallic glasses. The relationship helps in understanding the softening phenomenon, structural heterogeneous, evolution process of flow units, and widespread mechanical behavior of metallic glasses and can reveal the essential structural mechanism of the Poisson's ratio criterion for plasticity in metallic glasses. The relationship also indicates that the flow unit is a key structural parameter for understanding and controlling the properties and the performance of metallic glasses. [http://dx.doi.org/10.1063/1.4829028]

I. INTRODUCTION

Crystal materials have the structural defects, such as dislocation, grain boundary, and twin, and these defects have crucial effects on their properties such as the strength and the plasticity.[1,2] The mechanical properties and deformation mechanism especially the great gap between theory and actual strength of crystal metals had been a long-standing problem until the establishment of the structural defects theory in 1930s.[1] After the direct observation of the dislocations by a transmission electron microscope (TEM), the dislocation theory as a practical model has been developed.[3] Nowadays, the structural defect is a critical factor for materials design and properties controlling of crystalline metallic materials.

Metallic glasses (MGs), as non-crystalline materials, have unique combination of mechanical and physical properties, and potential structural and functional applications.[4,5] However, the microstructural characteristics and the key structural parameters which control properties of MGs are far from well understood. Some models such as free volume model[6] and shear transformation zone (STZ) model[7] have been proposed successfully to explain the behaviors of MGs. However, it is elusive to define the free volume or STZ, which is not a structural defect but a local transient event which cannot be experimentally visualized like a dislocation.[8]

Recently, intensive work shown that the structure of MGs is not uniform in nanoscale as thought before.[9–17] Using X-ray diffraction (XRD) and anisotropic pair-density function analysis, Dmowski *et al.*[12] show that only about three-quarter in volume fraction of MGs deforms elastically, whereas the rest of the volume is anelastic which deforms without resistance and this anelastic portion was considered as residual liquidity in the glass. Dynamic micropillar tests also indicate the inelastic deformation zones exist in MGs[13] and the nanoscale mechanical heterogeneity in MG is characterized by dynamic force microscopy.[14] It is also found that the local elastic properties of a PdCuSi MG exhibit a wide distribution on a scale below 10 nm using an atomic force acoustic microscopy.[15] Dynamical mechanical analyzer (DMA) results show that MG is viscoelastic and can be divided into solid regions, which are the source of storage modulus, and the liquid like regions without stress resistance, which offer the loss modulus.[18] This kind of intrinsic nanoscale liquid like regions can be considered as the structural "defect" of MGs and the actual structure of MGs can be regarded as these liquid like regions (which act as the viscous flow units for deformation and glass transition) embodied in the elastic solid matrix.[11,19–24] Compared with the elastic matrix, these defects of flow units are a group of atoms exhibiting a lower packing density, a higher energy dissipation rate and lower modulus, and high energy states in the energy landscape,[14,15,22] and the flow units show a collective rearrangement process when temperature approaches the glass transition temperature T_g or in the stress induced deformations.[25–27]

In crystalline metals, the density of dislocations can be changed and controlled through heat treatment, plastic deformation or microalloying. By controlling the density of dislocations, the mechanical and physical properties of metallic materials can be modulated.[28] To control and modulate the properties of MGs, it is essential to know the effects of the concentration of structural defects of flow units on their performance. However, it is difficult to directly observe and characterize the flow units in MGs using scattering experimental methods. Due to the elastic moduli of MGs have clear correlations with the microstructural features, T_g, relaxation behaviors, mechanical properties and deformation of MGs,[29] they could be used as key parameters for characterizing the concentration change of the flow units as well as their effects on the properties of MGs.

In this paper, we studied the change of the elastic moduli, plasticity and micro-hardness upon isothermal annealing far below the T_g of a typical high thermal stable

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$Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ (Vit 105) MG to understand the relationship between the flow units and these properties. Through the properties change, we attempt to characterize the flow units in the MG and to establish the quantitative correlation between the properties and the concentration of the flow units in MGs. We show that the flow unit model have implications for understanding the structural heterogeneous, evolution process of flow units, elastic and mechanical properties, and the structural origin of the Poisson's ration criterion for plasticity in metallic glasses.

II. EXPERIMENTS

We selected the $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ MG because it has high thermal stability and glass-forming ability and the long-time isothermal annealing would not induce the crystallization. The $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ (at. %) master alloy ingots were prepared by arc-melting the mixture of the elements under a Ti-gettered argon atmosphere. Glassy alloy rods with 2–5 mm in diameter were prepared by copper mold suck-casting method. The fully glassy structures of the as-cast samples were verified by the differential scanning calorimetry (DSC, Perkin-Elmer DSC7) and XRD (Cu K_α,). The annealed samples were obtained by annealing the cast samples encapsulated in a quartz crucible with vacuum of 10^{-4} Pa, at 600 K (0.89 T_g) for different times. The amorphous rods with diameter of 5 mm for elastic modulus measurement were cut to a length of about 8 mm, and their ends were carefully polished flat and normal to the longitudinal axis. The acoustic longitudinal velocity and shear velocity of the MG were measured at room temperature using a pulse echo overlap method.[29] The travel time of ultrasonic waves propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitive of 0.5 ns. The carrying frequency of the ultrasonic is 10 MHz. The density ρ was measured by Archimedes' principle in distilled water with an accuracy of 0.5%. Specimens about 4 mm long and 2 mm in diameter were cut from MG rods, and then carefully ground into compression specimens with an aspect ratio of 2:1. Uniaxial compression tests were performed with an Instron 3384 electromechanical test system at a constant strain rate of 1×10^{-4} s^{-1} at room temperature. Vickers micro-hardness (VH) was determined using an EVERONE MH series unit.

III. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of the as-cast and 512 h annealed Vit105 MGs. The appearance of a broad halo and the absence of any diffraction peaks associated with crystalline phases indicate that the glassy structure before and after annealing within the examining limit of XRD. The inset in Fig. 1 is the DSC trace of the MG, the onset of the glass transition temperature T_g of the MG is 670 K and crystallization begins at T_x of 725 K. The selected annealing temperature of 600 K is about 125 K lower than T_x. Both XRD and DSC results confirm that the long time isothermal annealing doesn't cause crystallization of the MG samples.

The MG was isothermal annealed at 600 K for various times, and the annealed sample was monitored using ultrasonic method and mechanical properties measurements. Figure 2 presents the change of Young's modulus E and shear modulus G (determined by ultrasonic velocities) with annealing time t. It can be seen that both the E and G increase sharply at the beginning of the annealing, and approaches a saturation value after 100 h annealing. After 512 h annealing, the moduli approach a saturation value. The results demonstrate that there is significant structural change during the annealing, especially at the initial annealing stage. The MGs are prepared by fast quenching from liquid state,

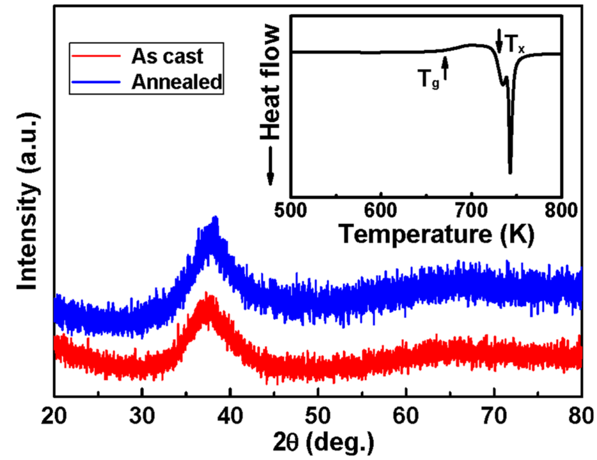

FIG. 1. X-ray diffraction patterns of the as cast and 512 h annealed $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ samples. The inset is the DSC curve of the as cast MG.

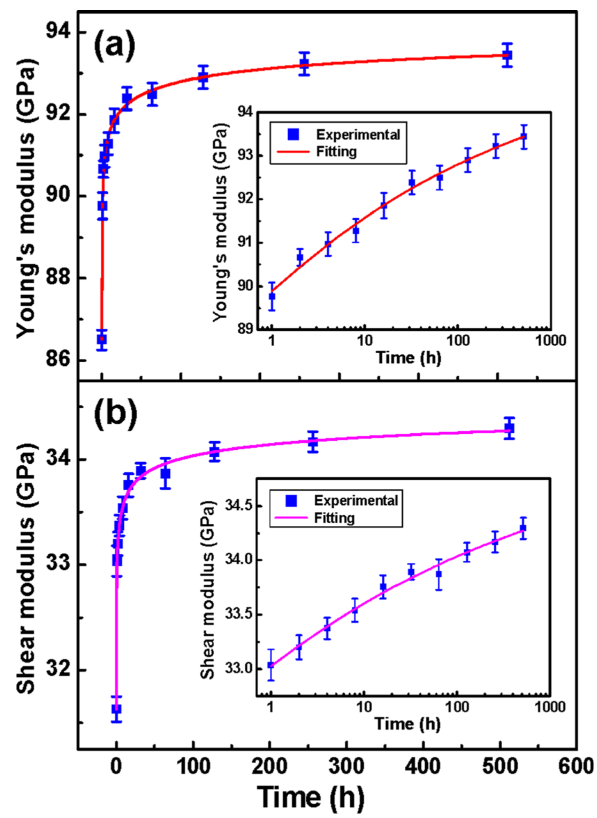

FIG. 2. (a) The change of Young's modulus (b) shear modulus of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ metallic glass with annealing time and the logarithmic time (inset) at 600 K.

not all parts of the alloy can be solidified uniformly, and many structural defects of the flow units were frozen-in.[11–13] Investigations confirm that the structure of MGs can be considered as consists of the strong bonded solid regions and weak bonded liquid-like regions.[13–16,30] Actually, the softening phenomenon compared to their crystalline counterparts, which is attributed to the existence of the defects, has been widely observed in MGs.[31,32] Therefore, the increase of the elastic moduli upon annealing or the widely observed softening phenomenon can be attributed to the annihilation of some frozen-in structural defects of flow units in MGs.

The change of elastic modulus M of the MG versus the variation of the concentration of flow units with time (t) can be fitted with an equation of

$$M(t) = \frac{M_\infty}{1+c}, \tag{1}$$

where $c = (\frac{\tau_a}{\tau_b+t})^\beta$ is a factor of the total effect of the aggregated flow units; τ_a and τ_b is a constant for a given annealing temperature; The sensitivity factor of β (is 0.1573 and 0.1340 for E and G of Vit105, respectively) characterizes how fast of the flow units annihilation with annealing time. According to Eq. (1), when $t=0$, $c=(\tau_a/\tau_b)^\beta$. It is a constant corresponding to the initial concentration of flow units of as-cast MG; When $t\to\infty$, $c\to 0$, and the MG approaches more stable glass state almost without defects or flow units and very low energy valley in energy landscape. And the elastic moduli M_∞ is the elastic moduli of the MG when annealing time approaches unlimited, and it is roughly equal to the elastic moduli of the corresponding perfect crystal of a MG (or the ideal glassy state of the MG).[33] The parameter c can reflect the change of the concentration of flow units in MG. The as-cast MGs with high concentration of flow units have lower modulus due to the flow units that offer no resistance to the external force and no contribution to the modulus.[12] Along with the annealing below T_g, more and more flow units annihilate and induce the elastic moduli increase. At a given annealing temperature, the concentration of flow units will approaches an equilibrium value, and the modulus will reach to a saturation value of M_∞. The obtained Eq. (1) is in accord well with the nanoidentation results.[22]

Granato proposed an interstitialcy model to explain thermodynamic properties of condensed matter, which considers dumbbell interstitials or similar defects to be the main structural defects of crystalline, liquid, and glassy states.[33] The interstitialcy theory is used to monitor the G change upon structural relaxation of MGs and gives an exponential decrease of G in the form of: $G=G_x\exp(-\beta' C)$, where G_x is the shear modulus of the perfect crystal, β' is a shear softening parameter and C is the total concentration of dumbbell interstitials defects. In the actual structure of MGs at room temperature, $\beta' C$ is in the order of 10^{-2} to 10^{-1}. The first-order approximation of this equation is $G\approx G_x(1-\beta' C)$. The first-order approximation of Eq. (1) is $M(t)=M_\infty/(1+c) \approx M_\infty(1-c)$. It can be seen that the two equations accord well with each other. So it is reasonable to conclude that the change of the modulus during annealing process is result from the decrease of the concentration of the structural defects of flow units, and the flow unit is a key parameter for controlling the elastic moduli.

The change of the concentration of flow units also can be characterized by microhardness (Hv) measurements. Figure 3 presents the Hv value change of the MG annealed at 600 K upon annealing time. One can see that the value of Hv monotonically increases with increasing annealing time. The increase also mainly occurs at the earlier annealing stage and approaches a saturation value for long time annealing. The variation tendency can be described by:

$$H(t) = \frac{H_\infty}{1+c}, \tag{2}$$

where H_∞ is microhardness when the annealing time approaches unlimited at 600 K. The equation is similar to Eq. (1), and the result indicates that decrease of concentration of flow units correlates with the increase of micro-hardness and a more compact structure, and further confirms that the flow unit is a key parameter for description the mechanical behavior of metallic glasses

It has been demonstrated that the flow units in MGs have a low effective viscosity in the order of 10^8 Pa s, which is near the value of the supercooled liquid,[13,21] and the flow units accommodate the plastic deformation under the stress. Meanwhile, it is found that the Poisson's ratio v is related to the ductility of MGs.[34] The MGs with higher Poisson's ratio have larger plasticity, and the Poisson's ratio-ductility criterion is widely applied to explore ductile MGs. However, the mechanism behind the Poisson's ratio-ductility criterion is still unclear.[34] And Poisson's ratio based approach does not capture the essential features of the structural mechanism of plasticity in metallic glasses. A comprehensive description for the plastic flow behaviors of MGs requires the understanding of the interplay between their structure and properties. We studied the relationship between the concentration of flow units and ductility by monitoring the change of the compression plasticity of the MG upon the isothermal annealing, and the results are shown in Fig. 4. With the increase of the annealing time, both the plasticity and Poisson's ratio decreases significantly and follow the same change trend [see Figs. 4(a) and 4(b)]. Figure 4(c) shows the

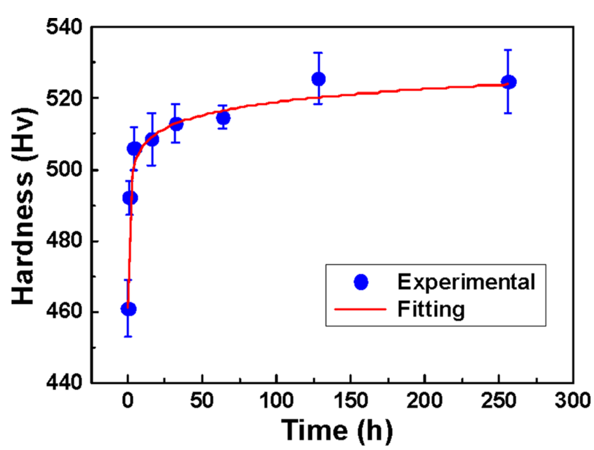

FIG. 3. The change of Vickers micro-hardness of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ MG with annealing time at 600 K.

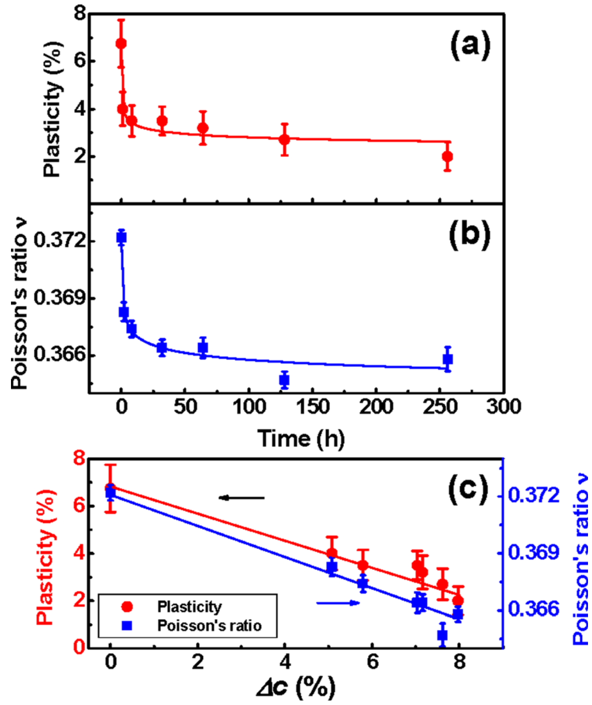

FIG. 4. The change of compressive plasticity (a) and Poisson's ratio (b) of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ metallic glass with annealing time at 600 K. (c) The relationship among compressive plasticity, Poisson's ratio, and the relative change of the concentration of flow units Δc [$=c-c(0)$] to the as-cast MG.

correlation of Poisson's ratio and plasticity of the MG with the relative change of concentration of flow units Δc [$\Delta c = c\text{-}c(0)$, $c(0)$ is the flow unit concentration of the as-cast MGs], and both of them show the similar change tendency with the change of c, and the MG with high concentration of flow units has a large Poisson's ratio or global plasticity. This indicates that the Poisson's ratio criterion for the plasticity intrinsically reflect the effect of the concentration of flow units on the plastic deformation of a MG. The results also suggest that any metallic glass can be ductile or brittle if it has enough high or small concentration of flow units. The result is helpful for designing tough MG. For example, a $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$ MG with high concentration of flow units exhibits a large global plasticity, even the pronounced macroscopic tensile plasticity near room temperature, because high density of flow units in the MG can accommodate the plastic deformation.[18,27] The correlation between the plasticity and flow units indicate that the flow unit is a key structural parameter for understanding and controlling the plasticity of metallic glasses.

Based on above results, we propose a general relationship between some properties $P(t)$ of MGs and the concentration of flow units c in the form of

$$P(t) = \frac{P_\infty}{1+c}, \tag{3}$$

where P_∞ is certain property when the annealing time approaches unlimited. Actually, the changes of density, the structural relaxation enthalpy and the fictive temperature as a function of c also fit Eq. (3).[35,36] This also means the concentration of flow units of a MG can be determined by monitoring the change of certain properties of the MG upon isothermal annealing, and the flow units concept helps in understanding the widespread mechanical behavior of metallic glasses.

IV. CONCLUSIONS

We find the relationship of the concentration of flow units c and some properties P such as elastic moduli, hardness of MGs can be expressed in the form of:$P(t) = \frac{P_\infty}{1+c}$. We show that the conception of flow units is a key structural parameter for determining and controlling the properties and the performance of MGs. The relationship is helpful for a deep understanding of the structural features, Poisson's ratio and ductility criterion, softening phenomena, the relationship between the structure and the plastic deformation mechanism and the relaxations in MGs.

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