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Characterization of flow units in metallic glass through structural relaxations

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We characterize the evolution of flow units associated with the flow "defects" in metallic glass by monitoring the fictive temperature change of a typical metallic glass upon isothermal annealing below its glass transition temperature. The correlations between the fictive temperature T_f, enthalpy change, and the concentration of flow units have been obtained. Such correlations help in understanding the evolution process of flow units, structural feature, and structural relaxation behaviors in metallic glasses, and can rationalize effects of the cooling rate, aging, and annealing on properties and structure of metallic glasses. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819484]

I. INTRODUCTION

Metallic glasses (MGs) undercooled from the liquid are in a metastable state[1–3] and tend to undergo structural rearrangement when excited by external agitations either in the form of stress or temperature. During the structural relaxation process, the properties sensitive to the structure can be utilized to characterize the structure, which include the viscosity,[4,5] enthalpy,[6–8] density,[9,10] internal friction,[11–13] etc. Enthalpy has often been used as the property to characterize the structural change and evolution via differential scanning calorimetry (DSC).[6–8] Beukel and Sietsma[14] have used the enthalpy to quantify the free volume in MGs, and proposed a linear relationship between the enthalpy change and the free volume change, which was experimentally verified by Slipenyuk and Eckert.[15] The free volume theory[16,17] which described the glass structure as a mixture of liquid-like and solid-like cell is the most often used structural model of MGs. Granato proposed the interstitialcy theory[18] which claims that the interstitialcies inherited from the liquid are the defects in the glass, and these defects decrease the shear modulus of glass compared to the crystalline counterparts, and the enthalpy relaxation in MG is attributed to the generation of interstitialcy-like defects.[19] Egami *et al.*[20] put forward a local-density-fluctuation model which claims that the structural relaxation occurs through annihilation of the liquid-like regions which include both the *n*-type defects (low-density regions, standing for the distributed free volume) and the *p*-type defects (high-density regions, resembling the distributed antifree volume). All the above mentioned models indicate the structure of the MGs is heterogeneous.[17,21]

Indeed, recently many experiments have mediately[22,23] or directly[24,25] shown that the structure of MG is heterogeneous, which includes the liquid-, semi-solid-, and solid-like regions. Through x-ray scattering and anisotropic analysis, Dmowski *et al.*[23] reported that the portion of the residual liquidity region in the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ MG is about a quarter, which is far more than the defect level of 1% according to the free volume theory.[16] Different regions in the MG show diverse properties: The liquid-like regions exhibit lower elastic modulus, lower viscosity, and lower packing density, and these regions are the initial regions that undergo structural rearrangement which leads to the deformation event or the fast β-relaxations.[22] Based on properties of the liquid-like regions, a concept of "flow unit" has been proposed,[26–29] and the flow units are regarded as both the deformation units of the anelastic and plastic deformation behaviors and the structural origin of the β-relaxation in MGs.[27] Thus the "flow unit" is closely related to the deformation mechanism and glass transition in the MGs.

The fictive temperature (T_f) of a glass[30] is the temperature at which the property of interest, e.g., specific volume or enthalpy, when extrapolated along the glass line intersects the equilibrium liquid line.[31] The T_f is a useful parameter to describe the thermal history and microstructure evolution of a glass,[32] and represents the departure from equilibrium of the glass.[33] T_f is also an important parameter for the glass technology because mechanical and optical properties of a glass strongly depend on its thermal history, structure, and T_f.[34,35] As a result, T_f is tied to many important processes such as structural relaxation and mechanical properties, and the change of T_f can be used to characterize the variation of structure.[36] Very recently, Kumar *et al.*[37] proposed a critical fictive temperature to predict the room-temperature mechanical behavior and its sensitivity to cooling rate and annealing-induced embrittlement for MGs.

In the present study, we investigate the evolution of the flow units of a $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (Vit105) alloy below T_g by measurements of the variation of T_f and enthalpy. Correlations between the T_f, the enthalpy change, and the concentration of flow units are established. Furthermore, the activation energy of flow units and their evolution during isothermal annealing was determined and characterized.

II. EXPERIMENTS

The Vit105 MG was prepared by arc melting and copper mould suction casting. The amorphous nature of the glass was confirmed by X-ray diffraction (XRD) and DSC. The DSC experiment was performed with a power compensated Perkin-Elemer DSC 8000 with a heating rate q_c of 0.33 K/s under a constant flow of high purity argon gas. The DSC was

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calibrated according to the melting points of indium and zinc. Isothermal annealing was carried out for the MG at different annealing temperatures below T_g. The annealing samples were divided into two groups: One group of samples whose annealing time is less than 2 h were annealed in the DSC. First, the samples were heated to the annealing temperature T_a at a heating rate of 0.33 K/s, and then holding isothermally for a certain amount of time, after completion of the anneal, the samples were cooled to the room temperature at 0.66 K/s. The other group of samples whose annealing time is more than 2 h was annealed in an annealing furnace, and the samples were immediately water-quenched after the annealing. The annealed samples were then subsequently studied by DSC.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the DSC curve of Vit105 MG scanned at a heating rate q_h of 0.33 K/s in which the glass transition and crystallization signals can be clearly seen. The onset temperatures of the glass transition T_g and the crystallization event T_x are 671 and 727 K, respectively. The inset shows the XRD patterns for the as-cast Vit105 MG and the MG annealed at $T_a = 600$ K for 702 000 s. No obvious crystallization peaks can be seen from the XRD patterns even after annealing for up to 702 000 s, indicating its high thermal stability of the amorphous structure.

Figure 2 presents the DSC curves of the as-cast and MG samples annealed at 600 K (71 K below T_g) for different times (as listed in Fig. 2). It is seen that T_g keeps almost the same in the experimental error within short annealing time, but increases with prolonging annealing time (T_g is obtained by the intersection of the two lines, one is extrapolated from the glass, while the other is obtained from point of inflection of the sigmoid-shape curve). Similar phenomenon has been observed by Aji and Johari.[38] Besides, the samples annealed with longer time absorbed more heat to reach the equilibrium supercooled liquid region. That is because the enthalpy relaxed during isothermal annealing can be recovered in a subsequent DSC run, resulting in an overshoot in the DSC signal. The enthalpy decreases to a lower state with annealing.

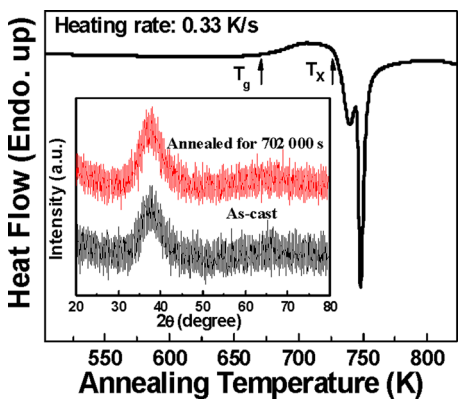

FIG. 1. DSC trace of the as-cast Vit105 MG. The inset shows the XRD patterns of the as-cast and an annealed sample (annealed at 600 K for 702 000 s).

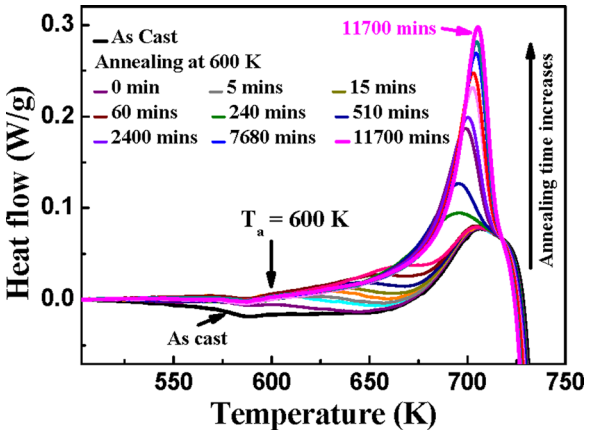

FIG. 2. DSC curves of Vit105 MG for the as-cast and annealed samples at $T_a = 600$ K for various times.

The definition and use of the fictive temperature T_f have been given by Moynihan *et al.*[39] and Hodge.[40] Fictive temperatures have been defined in terms of properties, such as enthalpy, volume, refractive index, and so on.[39] In our case, we determined the definition of T_f based on the enthalpy.[39,40] The variation of T_f during isothermal annealing is illustrated in Fig. 3(a), it can be seen that the T_f decreases and approaches to the Kauzmann temperature T_K,[41] which is determined to be about 638 K for Vit105 MG.[42] The variation of T_f with the annealing time at 600 K was plotted in

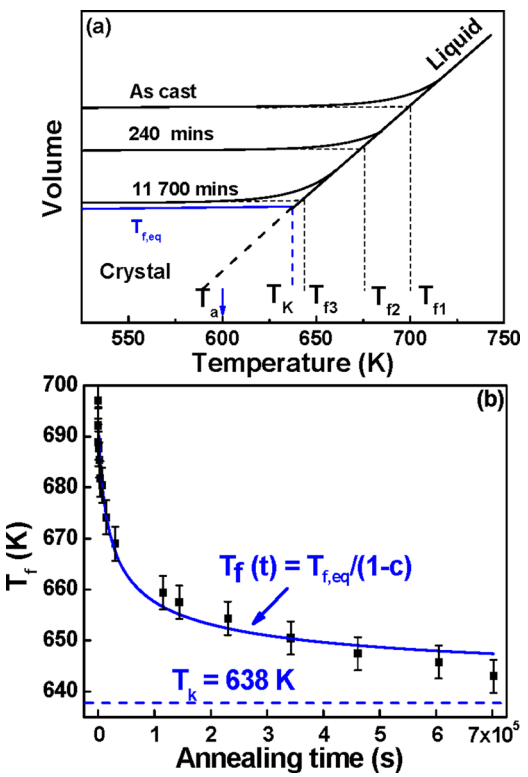

FIG. 3. (a) The schematic illustration of variation of T_f during isothermal annealing. T_{f1}, T_{f2}, and T_{f3} are the fictive temperatures of the as-cast sample and samples annealed for 240, 11 700 min, respectively. T_K represents the Kauzmann temperature. (b) The variation of T_f as a function of annealing time. The solid line represents the fit of Eq. (1) to the experimental data. The dashed line represents the Kauzmann temperature which is equal to the equilibrium value of $T_{f,eq}$.

Fig. 3(b). The MG can be regarded as elastic matrix combined with liquid like flow units.[22–29] During the structural relaxation process, the flow units undergo structural rearrangement by altering their configurations, and the MGs become more ordered and denser and approach to a lower energy and a more stable state. As a result, the fraction of the flow units will decrease, and some of flow units will annihilate and transform into the elastic solid regions. The annealing induced atomic motion has limited impact on the local solidity of the elastic matrix or solid region. The overall result of the structural relaxation is that the fraction of the flow units decreases either through the reduction of the number or the volume contraction of the flow units, leading to the increase of the density, viscosity, the modulus,[4,10,43–46] and decrease of the enthalpy and the T_f.

Based on the experimental data, the relationship between the fictive temperature T_f and the concentration of flow units, c, has been derived as follows:

$$T_f(t) = \frac{T_{f,eq}}{1-c}, \tag{1}$$

where $T_{f,eq}$ is the equilibrium fictive temperature. For the annealing temperature, T_a is less than the ideal glass transition temperature T_K, so the theoretical value of $T_{f,eq}$ value should be equal to T_K. $c = [a/(b+t)]^{\beta}$ is a parameter related to the concentration of flow units in MG (where a, b, and β are 12.07, 9062.59, and 0.39, respectively): when $t = 0$, c is a constant, which corresponds to the initial concentration of the flow units in the as-cast MG; when $t \to \infty$, $c \to 0$. The fictive temperature decreases with decrease of the concentration of flow units.

In the DSC curves of the MGs, the heat flow is almost zero indicating that structural relaxation does not take place before 503 K. At 717.5 K, all samples are in the supercooled liquid region where the enthalpy is assumed to be the same regardless of the thermal history. The enthalpy change ΔH of the MG was calculated by integrating the heat flow from 500 to 717.5 K as illustrated in Fig. 4(a). Figure 4(b) presents the calculated values of ΔH (t) as a function of annealing times, and the relationship between ΔH and concentration of flow units c can be obtained by fitting the data of ΔH vs. t as follows:

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

where ΔH_{eq} is the equilibrium enthalpy change at $t \to \infty$, and $c = [a/(b+t)]^{\beta}$ is a parameter that is correlated to the concentration of flow units in MG. The enthalpy change increases with the decrease of c, and then approaches to the saturation state or the equilibrium state with prolonging annealing time. The enthalpy and T_f have similar correlation with the concentration of flow units in the MG. The correlation is helpful for revealing the microscopic origin of the fictive temperature and confirms that the MGs can be regarded to consist of solid matrix and liquid like flow units and indicates that the concentration of flow units determines the configurational state of a MG. For the T_f represents the glassy state and relates to many properties of MGs, the correlation

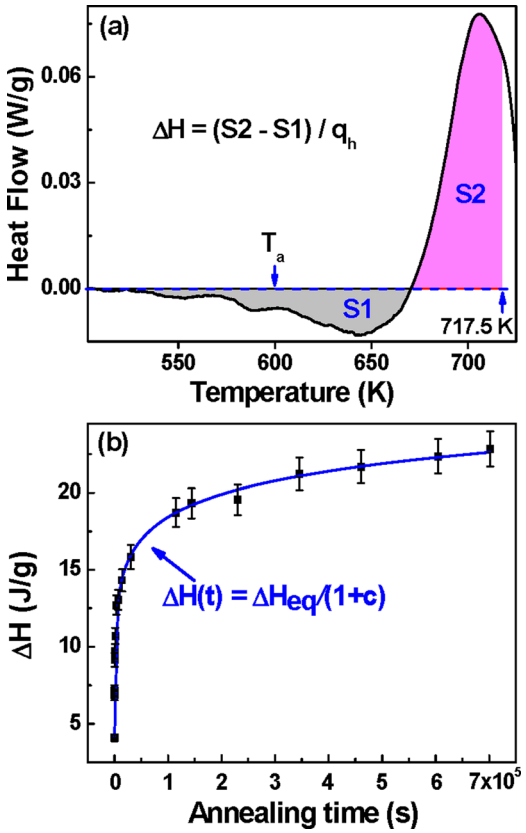

FIG. 4. (a) The illustration of the calculation of enthalpy change ΔH on DSC curve. S_1 and S_2 represent the absolute area of the shadow areas. (b) The experimentally determined enthalpy change $\Delta H(t)$ after isothermal annealing of Vit105 MG at 600 K. The solid line is the fit of Eq. (2) to the experimental data.

could provide a comprehensive framework to account for the diverse mechanical and physical behaviors of MGs based on the knowledge of flow units.

As the fraction of the flow units decreases and the enthalpy of the glass approaches to the equilibrium state, the activation energy of flow units also changes during the isothermal structural relaxation. An isothermal-isoconversional method[47] can be adopted to estimate the activation energy of the flow units during the isothermal annealing processes. Three annealing temperatures of 600, 630, and 660 K have been chosen to determine the enthalpy recovery. Figure 5(a) presents the recovered enthalpy values of $\Delta H_r(t)$ [here $\Delta H_r(t) = \Delta H(t) - \Delta H(0)$, $\Delta H(0)$ is the enthalpy change of the MG annealed for 0 min] as a function of annealing times and the results are fitted by a single Kohlrausch-Williams-Watts (KWW) stretched exponential function.[48] The activation energy at different conversion degrees α ($\alpha = \Delta H_r(t)/\Delta H_{r,eq}$) can be determined from the slope of the curve of $\ln t \sim 1/T$.[47,49] The logarithm of annealing time t is plotted as a function of the reciprocal of T_a [see Fig. 5(b)]. The activation energy of flow units during annealing processes is plotted in Fig. 5(c). It can be seen that the activation energy increases almost linearly with α (α is in an inverse relationship with the concentration of flow units c). This means that the activation energy of flow units increases with decrease of c. This confirms that some flow units with lower activation energy are annihilated and some of them are relaxed into a more stable state (with higher

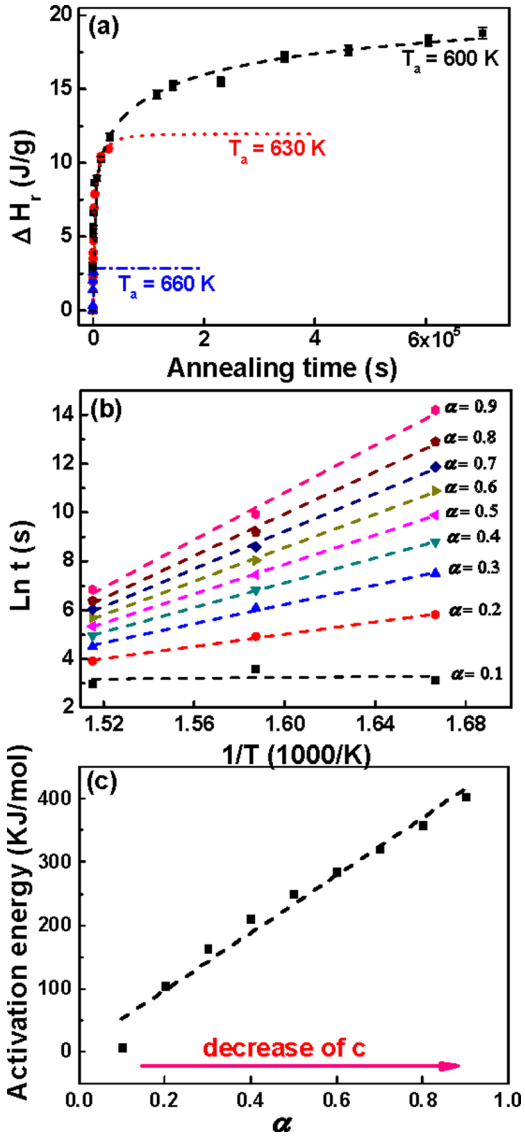

FIG. 5. (a) The change of the recovered enthalpy ΔH_r of the Vit105 MG isothermally annealed at various times for different temperatures. The dashed lines show the fits of the KWW equation to the experimental data. (b) The logarithm of annealing time as a function of the reciprocal of the annealing temperature at different conversion degrees. The dashed lines represent the linear fitting results. (c) The activation energy of flow units as a function of α which relates to the concentration of flow units.

activation energy), and the average activation energy of flow units increases during isothermal annealing.

Based on the above results, we illustrate the evolution of flow unit during annealing in Fig. 6. As shown in Figs. 6(a) and 6(b), the red and pink atoms represent the defects of flow unit in MGs with higher potential energies and looser packing densities compared with the relatively homogenous matrix denoted by the black atoms. The atoms in the flow units are the preferred sites for the relaxation caused by annealing, and the atom rearrangements initiate preferably in these active zones and cause the atoms to relax into a lower energy state, which is schematically illustrated by the disappearance of the higher energy pink and red atoms and the spread of black atom area. During annealing, some flow units with lower activation energy are annihilated and some of them are relaxed into a more stable state with smaller

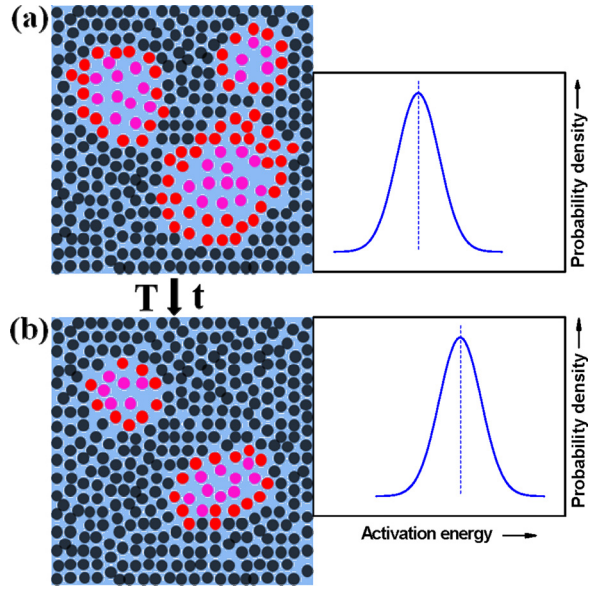

FIG. 6. Schematic illustrations of the evolution of flow units in MG (a) before and (b) after annealing (pink spheres = loosely packed atoms, red spheres = less loosely packed atoms, and black spheres = densely packed atoms). After annealing, the volume fraction of flow units decreases and some smaller flow units annihilate, and the average activation energy moves to higher value with annealing illustrated in (c) before and (d) after annealing.

volume. So, the average activation energy of flow units increases with annealing as illustrated in Figs. 6(c) and 6(d). It is found that during the isothermal annealing, the shear modulus G increases.[50,51] According to elastic model, the activation energy of flow units is mainly determined by G,[46,52,53] this indicates that our result is also in accordance with the elastic model.

IV. CONCLUSIONS

We find that the fictive temperature T_f and the enthalpy change during annealing correlate with the variation of the concentration of flow units. The decrease of the concentration of flow units in MGs will induce the decrease of T_f. For the T_f represents the glassy state and relates to many properties of MG, the correlation could provide a comprehensive framework to account for the diverse mechanical and physical behaviors of MGs based on the knowledge of flow units.

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