Correlation between dynamic flow and thermodynamic glass transition in metallic glasses

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We report the values of steps of heat capacity (ΔC_p) during the glass transition in a variety of metallic glasses (MGs). It is found that ΔC_p is around 13.69 J mol^{-1} K^{-1} and almost invariable for the MGs. Based on the Eyring's theory [N. Hirai and H. Eyring, J. Polym. Sci. **37**, 51 (1959)], the phenomenon corresponds to a critical reduced free volume value. This exhibits that the glass transition takes place when the reduced free volume approaches to ~2.35% in the MG systems. The value, consistent with that of the yielding of MGs, confirms that temperature and stress are equivalent for fluidizing MGs. Our results give an implication to understanding the glass transition in MGs as a Lindemann-type melting behavior [F. A. Lindemann, Z. Phys. **11**, 609 (1910)]. © *2010 American Institute of Physics*. [doi:10.1063/1.3455337]

The nature of the glass transition and the cause of the dramatic slowdown in the vicinity of the glass transition are major challenges in condensed matter physics and have received considerable interests.[1–7] Some kinetic phenomena take place at the glass transition temperature T_g. One common feature of the glass transition is a step in heat capacity (ΔC_p).[8] Previous investigations of ΔC_p have been focused on polymers, oxides glass, and molecular liquids.[9,10] Even though metallic liquids and glasses are good model systems for the study the complex behavior of viscous liquids close to the glass transition since they have relative simple microstructure,[11] little work has been done on the ΔC_p in metallic glasses (MGs).

In Hirai and Eyring's viewpoint,[12] ΔC_p is related with the change in the free volume during the glass transition. According to the free volume model,[5,13] the viscosity η is related to the free volume by a simple equation

$$\eta = \eta_0 \exp\left(\frac{\gamma v^*}{v_f}\right), \tag{1}$$

where γ is a constant of the order 1, and v^* is the average hard-sphere volume of the atom. v_f, the average free volume per atomic volume, is defined by $v_f = \bar{v} - v^*$. $\bar{v}$ is the average volume per atom. Recent studies reveal that MGs start to yield as the critical reduced free volume (RFV) (defined as $x = \gamma v^*/v_f$) value reaches ~2.4% even the loading stress for the onset of yielding is much less than the macroscopically measured yield strength.[14] Liu *et al.*[15] suggested that the yielding of MGs is intrinsically associated with the glass transition. Therefore, it is of significance to identify the relationship between free volume change and the glass transition in MGs. The results would be helpful to understand the glass transition as well as its relation to yielding.

In this paper, we measure the step in the specific heat ΔC_p during the glass transition for 18 MGs as listed in Table I. We find that the values of ΔC_p are almost invariable for various MGs, which corresponds to a critical RFV value. Our results imply that glass transition occurs when the RFV gets to a critical value in a MG-forming system. Combining with the evolution of the free volume for yielding of MGs, we confirm that temperature and stress are equivalent to fluidizing MGs and a lot of phenomena in MGs can be attributed to the nature of flow.

The MG samples were prepared by a copper mold suction casting method.[15] Their amorphous nature was ascertained by x-ray diffraction. The MGs chosen here have a wide range of T_g from 365 to 722 K. The heat capacity measurement was performed in Perkin-Elmer DSC7. It was calibrated for temperature and enthalpy at various heating rates with high-purity indium and zinc under protection of a purified argon atmosphere. The process to measure the ΔC_p was as following: first, the sample was held for 3 min at an initial temperature of 323 K with an initial heat flow of 20 mW, then heated at a "standard" rate of 20 K/min to a temperature of ~(T_g+20) K and immediately cooled down to 323 K at 80 K/min in order to eliminate the interference of physical aging; Afterward, the sample was held for 3 min

TABLE I. The composition, glass transition temperature T_g, molar mass M and steps in heat capacity ΔC_p of various 18 kinds of MGs.

MG composition	T_g (K)	M (g/mol)	ΔC_p (J mol^{-1} K^{-1})
1. $Zr_{44}Cu_{44}Al_6Ag_6$	722	76.2	14.4
2. $Zr_{65}Cu_{15}Ni_{10}Al_{10}$	652	77.4	12.4
3. $Mg_{65}Cu_{25}Gd_{10}$	417	47.4	15.36
4. $Zr_{55}Cu_{25}Ni_{10}Al_{10}$	685	74.6	14.55
5. $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	650	78.3	12.5
6. $La_{55}Al_{25}Ni_5Cu_{10}Co_5$	455	95.4	11.79
7. $La_{62}Al_{14}Cu_{20}Ag_4$	404	106	12.4
8. $Cu_{46}Zr_{46}Al_8$	701	73.3	14.73
9. $Zn_{40}Mg_{11}Ca_{31}Yb_{18}$	400	72.4	13.68
10. $Zr_{55}Al_{10}Ni_5Cu_{30}$	682	74.8	11
11. $Pd_{40}Ni_{40}P_{20}$	570	72	16.54
12. $Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$	365	140.9	14.24
13. $La_{57.6}Al_{17.5}Cu_{12.45}Ni_{12.45}$	435	100	14.1
14. $Ca_{65}Mg_{15}Zn_{20}$	375	42.8	13.61
15. $Zr_{50.7}Cu_{28}Ni_9Al_{12.3}$	719	72.6	11.94
16. $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	640	59.7	12.87
17. $Pd_{40}Cu_{30}Ni_{10}P_{20}$	571	73.7	15.3
18. $Ce_{62}Al_{10}Cu_{20}Co_3Ni_5$	378	107	15.09

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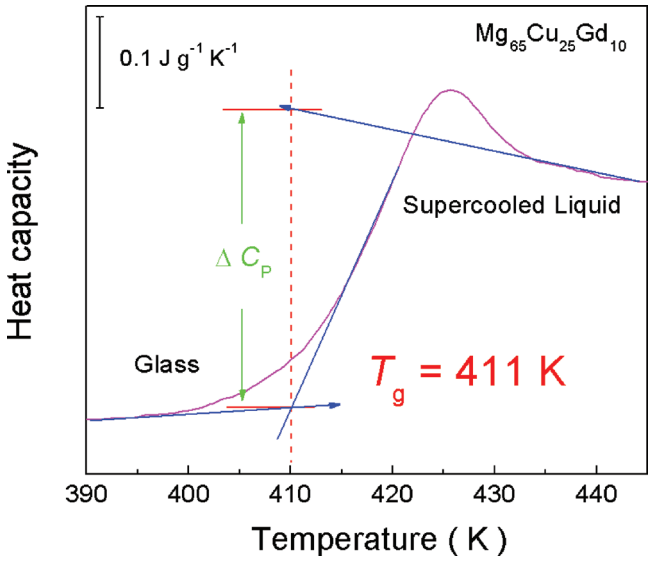

FIG. 1. (Color) Schematic diagram for the determination of T_g as well as ΔC_p on the final specific heat curve of $Mg_{65}Cu_{25}Gd_{10}$ at the heating rate of 20 K/min (black solid line). The blue lines with arrow represent the extrapolated heat capacity of glass state and supercooled liquid state at the vicinity of T_g.

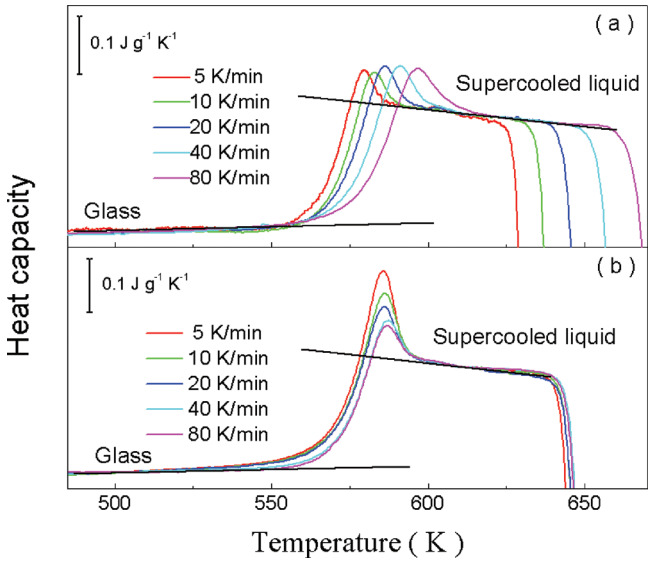

FIG. 2. (Color) Heat capacity curves of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ at different heating rates (a) and different cooling rates (b).

again and reheated to supercooled liquid temperature region at the standard rate. The value of T_g was determined as the temperature of intersection between the extrapolated lines of the glass C_p and the rapidly rising C_p during the glass transition (see Fig. 1). ΔC_p was the difference between the extrapolated C_p value of the supercooled liquid state and the extrapolated C_p value of the glass state at T_g (see Fig. 1).

Figure 1 exhibit the final differential scanning calorimetry (DSC) curve of $Mg_{65}Cu_{25}Gd_{10}$ MG. A typical characteristic of the glass transition of MGs can be found.[16–19] An obvious increase in heat capacity takes place as temperature increases during the glass transition. At the end, temperature of the glass transition an overshot is observed. The overshot arises from the rejuvenation of enthalpy, and interrupts the measurement of the ΔC_p. In order to measure ΔC_p, two extrapolation lines for the heat capacity of supercooled liquid and glass are drawn in Fig. 1. The value of ΔC_p reduced from the extrapolation lines is 0.324 J g^{-1} K^{-1} at T_g. The value of T_g is 411 K, and agreement with other reports.[20] The C_p curves of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ with different heating and cooling rates are present in Fig. 2. In Fig. 2(a) T_g rises slightly with increasing heating rate. The region of supercooled liquid changes also as the heating rate alters. But the heat capacities of the metallic supercooled liquid and glass are merged nearly into two linear lines. Figure 2(b) shows that the height of the overshot decreases with increasing cooling rate, while ΔC_p is weakly affected by the cooling rate. Thus, the effects of heating and cooling rates on ΔC_p can be ignored. Previous investigation has been revealed that heating and cooling rates had weak effects on the values of T_g and ΔC_p.[16] Therefore, Fig. 2 exhibits that the way to reduce the ΔC_p is reasonable since the value of ΔC_p can be invariable within the experimental error. The data of ΔC_p and T_g for 18 kinds of MGs are list in Table I and drawn in Fig. 3. ΔC_p is almost invariable ($\Delta C_p = 13.69 \pm 2.05$ J mol^{-1} K^{-1}) for different MGs with T_g ranging from 365 to 722 K.

The invariable ΔC_p in MGs can be explained by the free volume theory related to the glass transition. The heat capacity of glass can be assumed to consist of two components, $C_{p-\text{total}} = C_{pv} + C_{ph}$. The first part being due to the lattice vibrations and the latter part being due to the creation of free volume. The first part does not contribute to the change in heat capacity at the glass transition. Only the latter part accounts for ΔC_p. As proposed by Hirai and Eyring[12] C_{ph} is expressed as

$$C_{ph} = \frac{R v_o}{v_h}\left(\frac{\varepsilon_h}{RT}\right)^2 e^{-\varepsilon_h/RT}, \tag{2}$$

where v_0 is the average atomic volume equal to v^* in Eq. (1), v_h is the volume of a hole, and ε_h is the excess energy needed to form such a hole, R is the gas constant, and T is the temperature. The volume of a glass or liquid is considered to be the sum of the volumes of atoms and of the holes. According to the Eyring model,[12] $v_0/v_h \approx 5-6$ and $\varepsilon_h/RT_g \approx -\ln x_{cri}$. The RFV x is defined as the fraction of the total holes volume in the glass or liquid state. At T_g x has a critical value x_{cri}. Taken $\Delta C_p = C_{ph} = 13.69$ J mol^{-1} K^{-1}, $v_0/v_h = 5$ and $R = 8.31$ J mol^{-1} K^{-1} at T_g, we get $\varepsilon_h/RT_g = 3.75$. So the

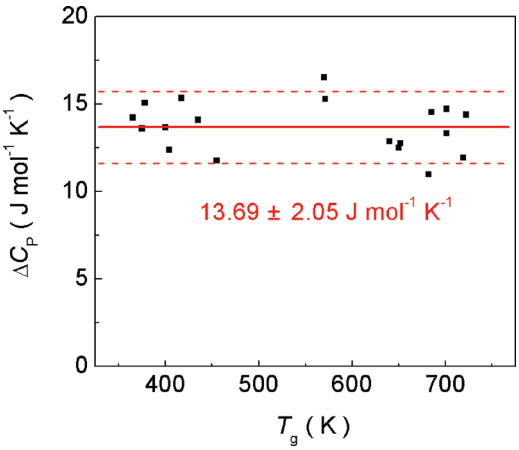

FIG. 3. (Color) Correlation of the step in heat capacity ΔC_p with the glass transition temperature T_g for 18 kinds of MGs.

critical free volume $x_{cri}=e^{-\varepsilon_h/RT_g}$ is 0.0235. That means, the glass transition for MGs corresponds to the state where the fraction of the free volume reaches a universal value of 0.0235. It is interesting to find that the value is also close to the critical RFV value for the onset of yielding in various MGs.[14]

This phenomenon is useful to understand the glass transition from the prospective of the thermodynamics theorem of equipartition of energy. It is well known that each degree of freedom contributes $R/2$ to the heat capacity of the system.[21] Thus, the ΔC_p is directly related to the change in the number of freedom degrees of the system. According to the value of ΔC_p (13.69 J mol^{-1} K^{-1}) that is close to $3R/2$, we find 3 degrees of freedom appear in the MGs system when temperature increases from glassy state to supercooled liquid. Thereby, the freezing atoms in the glassy solid can flow easily in all directions of the supercooled liquid as the glass transition takes place. It confirms that the glass transition in MGs has a similar behavior as the melting of a solid.

Melting is considered as dynamic instability behavior of a solid. As proposed by Lindemann,[22] melting takes place as the amplitude of the thermal vibrations of atoms exceeds a critical fraction (around 10%) of the atomic spacing for crystals. A critical fraction of the atomic spacing (around 6%–8%) for glass during glass transition in MGs has been found.[23] Combining with our results, we consider the glass transition as a softening process. During heating, when temperature is above the glass transition region, the metallic glassy solid becomes a supercooled liquid. The formation of free volume in liquids or glasses is related to the limiting mean-root-square displacement of a kinetic unit (an atom or a group of atoms) from an equilibrium position. Thereby, the critical RFV during the glass transition in the MG-system characterizes a critical atom displacement, above which the structure of the MG would be disintegrated. According to the harmonic Debye model, the mean-square thermal displacement is proportional to $T/M\theta_D{}^2$ (where M is the molar mass and θ_D is the Debye temperature).[24] Owing to the critical atom displacement at T_g, the $T_g/M\theta_D{}^2$ has a critical value (around 8%) for MGs as reported in Ref. 23.

Our results could give a simple picture to the glass transition of the MGs. The glass transition is a distinguishing feature from an elastic solid to a flowing fluid. For MGs, the free volume was thought to be evenly distributed in the materials. The packing density around the free volume is lower than the surroundings. Therefore, these regions combined weakly and became the preferred sites at which the MGs begin to become instable caused by increasing temperature (glass transition) or applied stress (yielding). Wang *et al.*[14] demonstrated that yielding occurs when the RFV evolutes to arrive at a critical value of 0.024. Here we deduced that glass transition also happens as the RFV reaches to 0.0235. Thus, both yielding and glass transition can be attributed to the increase in the volume fraction of atoms per unit volume (or decreasing the density) which would induce the softening. Temperature and stress are equivalent to make the glass flow. It is consistent with Liu and Nagel's[25] suggestion, in which raising temperature, applying a stress, or decreasing the density can unjam the jammed system. The jammed systems include glass, grains, bubbles, droplets, etc., disordered systems. Therefore, several approaches including heating, application of stress, and decrease in the volume fraction of atoms per unit volume are equivalent to fluidize a glass.[26] Many phenomena such as the formation, deformation, stability, and relaxation of glass can be attributed to flow, and flow is crucial to understand the characteristics and nature of glass.

In conclusions, there is a critical RFV of 0.0235 for the glass transition taking place in various MGs, which is consistent with that for yielding of MGs. Based on the observations, it is proposed that temperature, stress, and decreasing density are equivalent approaches for fluidizing MGs.

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