Glass transition in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ metallic glass under high pressure

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An approach is developed using differential scanning calorimetry with the characteristics of relaxation to exhibit a glass transition under high pressure in metallic glass, specifically, the glass transition in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk glass-forming alloy with a very stable supercooled liquid state. Through the approach, we obtain an averaged increase of the glass transition temperature with a pressure of 5.6 K/GPa. Based on free volume theory, the formation volume (ΔV_f) of 6.5 ± 0.5 Å^3 and migration volume (ΔV_m) of 6.5 ± 0.5 Å^3 for defect diffusion, which is related to pressure-dependent free volume change, are derived. The results contribute to the understanding of the nature of the calorimetric glass transition and diffusion in metallic glasses.

The nature of the glass transition (GT) in viscous liquids and glasses is a field of current interest.[1–5] Efforts in the past to understand the puzzle of the glass transition that had mostly been connected with chainlike or network-forming substances have experienced rejuvenation by the discovery of bulk metallic glasses (BMGs).[6] The BMGs are comparable to a hard-sphere system, rather easily describable in contrast to inorganic, nonmetallic glass formers or organic polymers.[7] The microscopic theories of the dynamics of the GT, such as free-volume theories[8] and Gibbs theories[9] are proposed to present understanding of relaxation and the GT. Nevertheless, the basic understanding of the GT is still a matter of debate. Pressure, similar to temperature, is an important variable that affects the GT and structural relaxation. The pressure-dependent structural relaxation and GT is of importance for understanding the nature of the calorimetric GT[10] and for giving insight into the diffusion mechanism in glasses.[11] However, because of the difficulty in obtaining direct access to the GT at high pressure and the long time needed to reach the equilibrium below the calorimetric glass transition temperature T_g, few high-pressure experiments above 1.5 GPa on the GT and structural relaxation have been preformed.

The GT crossing from a nonergodic to an ergodic state can exhibit the relaxation taken place under the annealing of an elevated temperature and high pressure, which is accompanied by the change of height of the calorimetric GT peak in a differential scanning calorimetry (DSC) trace.[10,12] The calorimetric GT, according to the free volume theory, is a process of approaching the free volume from a lower value to higher equilibrium value.[12] Based on the enthalpy recovery method Samwer *et al.*[11] and Ruitenberg *et al.*[10] developed a similar method to study the relaxation and GT under high pressure. However, the method in Ref. 10 was based on extrapolation, which could lead to large error and cannot directly exhibit the effect of high pressure on the GT. In this work, we used the quenching method to freeze the relaxation states in the glass transition region under high pressure to ambient conditions. Because the relaxation below the supercooled liquid region can be restricted at the experimental time scale, the high pressure and high temperature states within the GT region could be frozen into ambient conditions. Thus, the GT under high pressure in a metallic glass can be studied at ambient conditions.

Compared with enthalpy recovery method,[11] this approach can exhibit objectively the GT under high pressure. A $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG [$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ is named vit4; its critical cooling rate for glass formation is ~ 10 K/s (Ref. 13)] was chosen as a model system because it has a very high stability of the supercooled liquid state that offers a large experimentally accessible time and temperature window to investigate the relaxation and nature of the GT without the intervetion of deterioration such as phase separation or crystallization.[13] The alloy also has very sluggish kinetics in the supercooled liquid state, the structural feature of which can be easily frozen during quenching.[13] Via this approach, we can measure the changes in relaxation behavior and the GT under high pressure, and the formation volume (ΔV_f) and the migration volume (ΔV_m) for defect diffusion[11] of the glass can also be determined.

The $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG was produced by cooling the alloy from the melt into a glassy state in a copper mold. The BMG sheets (1 mm in width, 0.8 mm depth, and 5 mm length) were annealed first at 568 K (62 K below T_g) for 34.5 h in a furnace with vacuum of 2.0×10^{-3} Pa. The purpose of the preannealing was to achieve a relaxed glassy state with a pronounced endothermic "overshooting," which was used as scale and exhibited the change of the free volume with temperature and pressure in our method. No crystallization was observed by x-ray diffraction, DSC, and transmission electron microscopy in any sample after annealing. After preannealing each sample was heated to a temperature between 568 K and 703 K at a heating rate of 40 K/min followed by quenching to room temperature. The quenching temperature-dependent change of the relaxed state under ambient and high pressure conditions was determined by DSC. The quenching at ambient pressure is performed in a Perkin-Elmer DSC-7 calorimeter with the cooling rate of 120 K/min. Samples quenched at high pressure were carried out with a cooling rate of 1200 K/min (20 K/s) in a 1000-ton cubic anvil-type high-pressure equilibrium. The samples were put into a BN tube and then inserted into a graphite heater. A thermocouple touched with the specimen was used to monitor the temperature of specimen. Pressure was cali-
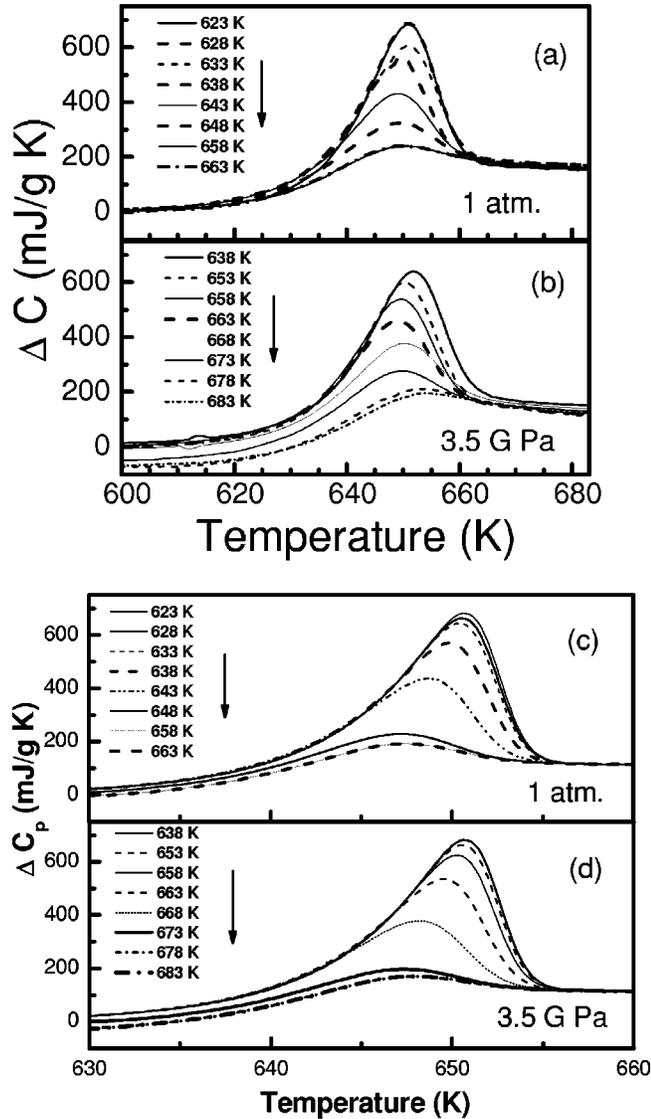
FIG. 1. The DSC curves of the relaxed samples after the different temperature quenching (a) under ambient pressure and (b) at 3.5 GPa with the heating rate of 40 K/min. The simulated DSC curves after the different temperature quenching (c) under ambient pressure and (d) at 3.5 GPa with the heating rate of 40 K/min.

FIG. 2. The quenching temperature dependence of the relative change $[\Delta C_{peak}(T) = C_{peak} - C_{peak}(T)]$ of the peak of the glass transition at different pressures, where C_{peak} is the height of the glass transition for the sample annealed at 568 K for 34.5 h.

brated using the phase transition point of pure Bi (II-III at 2.7 G Pa), Tl (II-III at 3.6 GPa), and Ba (I-II at 5.6 GPa) metals. After each treatment DSC was performed to determine the glassy state in a Perkin-Elmer DSC-7 calorimeter under flowing purified argon gas at a constant heating rate of 40 K/min.

Figure 1(a) shows DSC curves, given here as the change in the apparent specific heat $\Delta C(T) = C(T) - C(373\ \text{K})$, for the samples after each quench at various temperatures at ambient pressure. $C(373\ \text{K})$ and $C(T)$ are the apparent specific heat at 373 K and temperature (T), respectively. The quench below 633 K cannot change the relaxed state because of no change of the GT peak within the DSC sensitivity. Up to 633 K (above the onset T_g, 630 K) the peak begins to decrease. From 633 to 658 K the GT peak decreases gradually as the quenching temperature increases, implying that the glassy
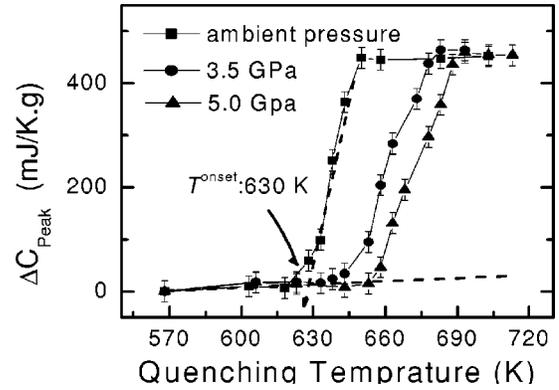
state of the preannealing samples is changed after each quench. When the temperature is over 650 K (above the end temperature of GT, 650 K) the peak of the GT remains unchangeable again, indicating that the glassy state is almost independent of the quenching temperatures (from 650 K to 703 K). Figure 1(b) shows the DSC curves of the BMG after a high-pressure quench at various temperatures at 3.5 GPa. The onset temperature of the decrease of the GT peak is about 653 K. Compared with that of Fig. 1(a), the temperature, at which the peak of the GT begins to decrease, shifts to higher temperature at 3.5 GPa. This indicates that pressure inhibits the change of the relaxed state. Figure 2 shows the spots of the relative change $[\Delta C_{peak}(T) = C_{peak} - C_{peak}(T)]$ of the GT peak of the samples after different pressure quenches, where $C_{peak}(= 698\ \text{mJ/g K})$ and $C_{peak}(T)$ are the apparent specific heats at the GT peak for the sample after the preannealing and quenching from temperature T under various pressures. The accuracy of $C_{peak}(T)$ is estimated to be 5%. The onset temperature of the change of the relaxed state corresponding to T_g can be found to increase with increasing pressure. The onset temperatures under ambient pressure, 3.5 GPa, and 5.0 GPa are 630, 650, and 658 K, respectively.

In order to clarify the quenching temperature and pressure dependence of the glassy state the defect concentration c_D related to the reduced free volume x in the system by $c_D = \exp(-1/x)$ is introduced.[14] The change in c_D due to structural relaxation during a DSC scan is governed by the differential equation[15]

$$\frac{dc_D}{dt} = -k_r c_D [c_D - c_D^{eq}], \qquad (1)$$

where t denotes time. k_r, a temperature-dependent rate factor for structural relaxation, has the form[15]

$$k_r = k_0 \exp\left(-\frac{E_f}{kT}\right) \exp\left(-\frac{p \Delta V_m}{kT}\right),$$

where E_f is the relaxation activation energy, k the Boltzmann constant, k_0 a constant, p the pressure, and ΔV_m the migra-

tion activation volume of the defect change necessary for the k_r to take place with pressure. c_D^{eq} is the defect concentration in thermodynamic equilibrium and has the form[15]

$$c_D^{eq} = \exp\left(-\frac{B}{T-T_0}\right)\exp\left(-\frac{p\Delta V_f}{kT}\right),$$

where ΔV_f is the formation activation volume of the defect change necessary for the c_D^{eq} to take place with pressure, T_0 is the Vogel-Fulcher temperature,[16] and B is a constant. For the continuous heating process, Eq. (1) can be changed into the form:

$$\frac{d(-1/x)}{dT} = -\frac{k_r}{\theta}[\exp(-1/x) - c_D^{eq}],\qquad(2)$$

where θ is heating rate. The calculated DSC signal is obtained by assuming that the observed heat flow, $\Delta C_p(T)$, to be related to x by $\Delta C_p(T) = Adx/dT$, A is a constant. The values of the parameters of E_f, k_0, and A used are 2.64 eV, 3.75×10^{34} s^{-1}, and 1.0 eV, respectively. The values of B and T_0 obtained from Ref. 16 are 9.64×10^3 K and 352 K, respectively. With the known parameters of E_f, k_0, A, B, θ, and T_0, the only fit parameter used to simulated DSC traces is the initial reduced free volume x_0.[10] The calculated DSC traces corresponding to Figs. 1(a) and 1(b) are shown in Figs. 1(c) and 1(d), respectively. The calculated DSC traces are consistent with the experimental data in the change tendency of the height of the GT peak. The shape of the calculated traces is relatively narrower compared to the DSC traces due to the ignorance of the chemical ordering effect, which cannot affect the height of the GT peak.[10,12,14,15] Therefore, the change of the calorimetric GT peak is correlated to the change of x_0 depending on the quenching temperature and pressure. The decrease of the calorimetric GT peak is accompanied with the increase of x_0.

Based on free volume theory[12,15] for the continuous heating process the calorimetric GT determined by DSC is accompanied with the free volume increasing from a low value to high equilibrium value in the system. The GT process can be exhibited by the temperature-dependent free volume x, which can be measured by quenching with rather a fast cooling rate. The resulting values of x_0 after the different pressure and temperature quenches are presented in Fig. 3(a). The quenching temperature dependence of the x_0 corresponds to the calorimetric GT.[15] The onset temperatures for increasing x_0 are 630, 650, and 658 K at ambient pressure, 3.5 GPa, and 5.0 GPa, respectively. So the onset temperature of the calorimetric GT is 630, 650, and 658 K at ambient pressure, 3.5 GPa, and 5.0 GPa, respectively. T_g increases with the increase of pressure loaded. Compared with Fig. 3(b) it is found that the temperature-dependent x_0 at 1 atm is very consistent with the DSC trace, affirming that the GT can be exhibited with the quenching-temperature-dependent x_0. Therefore, with this approach, we obtain an averaged increase of T_g with pressure of 5.6 K/GPa, which is larger than the 3.6 K/GPa determined by the enthalpy recovery method.[11] The difference is due to the different applied methods. The enthalpy recovery method depends on two
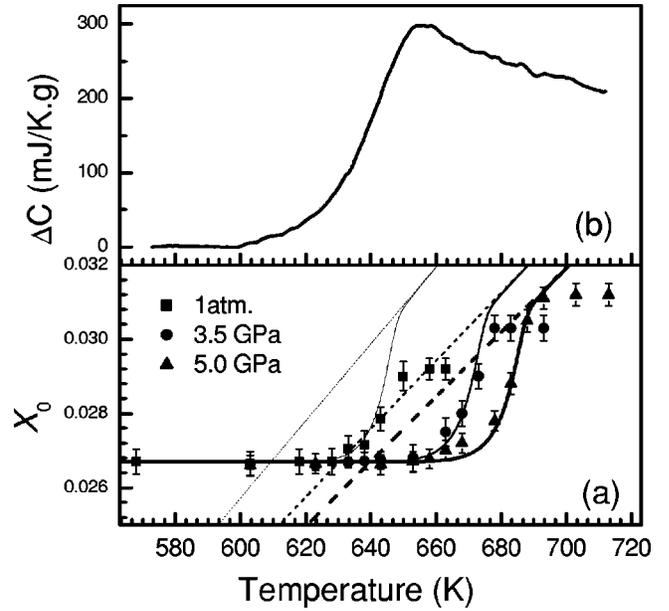

FIG. 3. (a) The quenching temperature dependence of the initial free volume, x_0, for the BMG at different pressures, determined from the fit of Fig. 2 with Eq. (1). The solid lines exhibit the calorimetric GT processes, which are the temperature-dependent x at different pressures, and the 3 dashed lines from thin to thick are the temperature dependence of the equilibrium x^{eq} at ambient pressure, 3.5 GPa and 5 GPa, respectively. (b) The DSC trace for the as-cast sample with a heating rate of 40 K/min.

assumptions.[11] One is that the thermal equilibrium glassy state below T_g can be reached by annealing below T_g within the experimental time scale. Another is that the value of enthalpy at high pressure can be determined by the parallel shifting of the enthalpy line at ambient pressure. Compared with the enthalpy recovery method, ours is objective and more accurate in determination of T_g under high pressure.

The fits of x_0 using Eq. (2) are shown in Fig. 3(a). The solid lines exhibit the calorimetric GT processes, which are the temperature-dependent x at different pressures, and the dashed lines, which are the temperature dependence of the equilibrium x^{eq} at different pressures. From the fit the two important quantities are obtained: $\Delta V_m = 6.5 \pm 0.5$ Å^3 and $\Delta V_f = 6.5 \pm 0.5$ Å^3 [less than 0.4Ω, where Ω ($= 19.3$ Å^3) is the mean atomic volume of vit4]. The disagreements with the data at high temperature, especially for the GT of ambient pressure and 3.5 GPa, are due to the fact that the quenching rate is not large enough to freeze the states at high temperature represented by x. The relaxation during the quench causes the difference between x and x_0. The effect of pressure on the calorimetric GT is due to two factors. One is the decreasing rate factor k_r with increasing pressure because the value of ΔV_m (6.5 ± 0.5 Å^3) is positive. The other is the decrease in equilibrium free volume with increasing pressure, the temperature-dependent x^{eq} shifting to lower value with increasing pressure. The activation volume, ΔV^* $= \Delta V_m + \Delta V_f$, consisting of a migration part and a formation part for thermal defect diffusion, is 13 ± 1 Å^3.[10] Comparing with ΔV_m and ΔV_f in common crystalline alloys, in which ΔV_m is small enough to be ignored and ΔV_f is about

$(0.5\sim 1.3)$ Ω,[17] ΔV_m is relatively larger while ΔV_f is smaller in vit4. This phenomenon can also be found in $Pd_{40}Ni_{40}P_{20}$ BMG, whose ΔV_f is about 5.9 ± 0.5 Å^3 and ΔV_m is about 5 ± 0.5 Å^3.[10] It may be due to the characteristic of glass, in which the free volume connected with the defect is distributed homogenously in the system and is much smaller than the value of Ω.[8]

Our study can present information on diffusion mechanism in the metallic glasses and supercooled liquids. From the viewpoint of diffusion via thermal defects.[18–20] the diffusivity D in the real glass state is given by $D(p)=k_r c_D$.[10,17] Through Eq. (1), in glassy states higher c_D are always approaching lower c_D^{eq} during isothermal annealing. Therefore, D decreases with increasing annealing time. The prediction is consistent with the results in Ref. 21. By using of Eqs. (1), ΔV^* can be given as

$$\Delta V^* = -kT\frac{\partial \ln D}{\partial P} = -kT\frac{\partial \ln k_r}{\partial p} - kT\frac{\partial \ln c_D}{\partial p}$$

$$= \Delta V_m + \Delta V_f^D. \tag{3}$$

The formation part of ΔV^* of a glass, $\Delta V_f^D = -kT(\partial \ln c_D/\partial p)$, is equal to 6.5 ± 0.5 Å^3 only when c_D approaches c_D^{eq}. The value of the formation volume in an equilibrium glass state for vit4 is 6.5 Å^3. Therefore, the obtained ΔV^* (about 0.7Ω, $\Omega = 19.3$ Å^3 for vit4) can be regarded as the pressure-dependent defect diffusion in the equilibrium glass state.[10] In vit4, a value of ΔV^* about 1.0Ω was reported for Ni diffusion in supercooled liquids.[22] The difference reveals that diffusion via thermal defects does not hold for the Ni diffusion in supercooled liquids. It is consistent with the recent result that diffusion in supercooled liquids is a collective process involving several atoms.[7,20]

The diffusion mechanism involving point defects and thermally activated jumps in glass is still under debate.[17] For example, Klugkist *et al.*[23] reported ΔV^* of ^{57}Co diffusion in $Co_{81}Zr_{19}$ as $(0.08\pm 0.1)\Omega$. The almost vanishing pressure dependence of ^{57}Co diffusion rules out vacancylike thermal defects such as diffusion vehicles in the glass. Relaxation in metallic glasses has been found to change the diffusion mechanism from single jump to collective motion.[23] The small value of ΔV_f ($<0.4\Omega$) for thermal defects in vit4 and $Pd_{40}Ni_{40}P_{20}$ BMG reveals the conclusion that for larger atoms vacancylike thermal defects as diffusion vehicles is not reasonable for BMGs. It is likely that the diffusion mechanism for larger atoms in the relaxed glassy state is collective diffusion.[24]

In conclusion, using the characteristics of the calorimetric GT a method is developed to study the glass transition under high pressure, and the calorimetric glass transition under high pressure is exhibited. An increase of T_g with a pressure of 5.6 K/GPa is derived. The effect of pressure on the GT indicates that the GT is a dynamic process. A quantitative interpretation of the effect yields the values of 6.5 ± 0.5 Å^3 for the formation volume and 6.5 ± 0.5 Å^3 for the migration volume of defect diffusion in vit4. The results support the conjecture that the diffusion mechanism of larger atoms in an equilibrium glassy state is collective diffusion.

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