Pressure effect on the structural relaxation and glass transition in metallic glasses

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Abstract

Two different enthalpy recovery methods were applied to investigate the effects of pressure on structural relaxation and glass transition temperature ($T_g$) in two metallic glasses (Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$). The pressure-induced enhancement of $T_g$ ($dT_g/dP$) was derived to be 6 K/GPa in Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ glass, while an increment of 50 K/5 GPa was observed in Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ glass. Activation (formation and migration) volumes of the flow defect were used to interpret the pressure dependence of the structural relaxation and $T_g$ in terms of the free volume model. According to the measured results, the activation volume of relaxation was derived to be 16.7 Å$^3$ for Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$, which is much smaller than that of the polymers.

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1. Introduction

The phenomenology of glass transition has been known for decades in many amorphous materials and refers to a transition between the glassy state and the undercooled liquid state. But a full understanding of this transition is yet to be reached [1–3]. From experimental observations, mostly in polymers and inorganic materials, we know that glass can be formed from liquid in two different routes by slowing down the dynamics of the molecular motion: i.e. by lowering the temperature rapidly enough below the glass transition temperature $T_g$, or alternatively by elevating pressure above the glass transition pressure $P_g$ at a constant temperature [4–7]. Apparantly, pressure, in addition to temperature, is one of the crucial parameters for the glass transition process, and the pressure effect on the structural relaxation and glass transition of amorphous solids is vital for understanding the nature of glass transition and the glass forming liquids.

In the literature [4–7], most of the experimental investigations of the pressure effect on relaxation and glass transition were reported in non-metallic
(e.g. polymeric or inorganic) glasses. These studies reveal that the pressure dependence of the relaxation time $\tau$ can be expressed as an activation process by

$$
\tau = \tau_a \exp \left( \frac{P \Delta V}{RT} \right),
$$

where $\Delta V$ denotes the activation volume of relaxation (relaxation volume) [8–10]. Usually, pressure can reduce the relaxation rate and increase the relaxation time due to the positive value of $\Delta V$ (about $10^2$ cm$^3$/mol for some polymers), which results in the enhancement of $T_g$. One of the widely used definitions of the glass transition temperature, $T_g$, is the temperature at which the structural relaxation time approaches a characteristic value (usually 100 s). Accordingly, the pressure dependence of $T_g$ can be determined by the experimental measurements of the relaxation time under different pressures. By using this method, the pressure effect on $T_g$, usually characterized by $(dT_g/dP)$, is measured to be typically $10^1$–$10^2$ K/GPa for some polymeric liquids [5,11–13].

Metallic glasses have been expected to be beneficial for the understanding of the intrinsic nature of the glass transition due to the non-directional metallic bonding and its unique dense atomic structure, which is quite similar to the “dense random packing of spheres” model. However in metallic systems, very few studies have been reported on the pressure dependence of structural relaxation and glass transition [14,15]. One of the difficulties for studying the pressure effect on glass transition experimentally might be the poor thermal stability of the undercooled liquid against crystallization in metallic systems. The gap between the glass transition temperature $T_g$ and the onset temperature of crystallization ($T_x$), $\Delta T_x = T_x - T_g$, is normally very small for most metallic glasses, which causes practical difficulties for experimental measurements of the glass transition and the relative effects. Recent development of the new bulk metallic glasses [16,17], which exhibit a wide supercooled liquid region, opens a unique possibility of studying the nature of the supercooled liquid and the glass transition also in metallic systems.

In this study, we present the investigation of the pressure effect on relaxation and glass transition in Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glasses by using two different enthalpy recovery methods, respectively. Pressure was found to enhance the glass transition temperature in both samples. Activation volumes (including formation volume and migration volume) of the flow defect were suggested to interpret the pressure effect on glass transition and structural relaxation in terms of the free volume model. The activation volume of relaxation ($\Delta V$ in Eq. (1)) was also estimated according to the experimental results.

2. Experimental

2.1. Specimen preparation and heat treatments under different pressures

The glassy ribbons with nominal composition of Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ were prepared by means of single roller melt spinning. The amorphism of the as-quenched and the heat-treated specimens was confirmed by X-ray diffraction (XRD) and differential scanning calorimeter (DSC).

Pressure dependence of the structural relaxation and the glass transition was investigated by using two different methods in two metallic glasses:

(1) Pressure effect was investigated on the isochronal and isothermal relaxation of a Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ glassy specimen. (a) Isochronal structural relaxation was performed under ambient pressure (0.1 MPa) and at an applied pressure of 1.0 GPa, respectively, by heating the as-quenched glassy specimen up to 593 K (which is higher than the end temperature of glass transition, $T_{g\text{-end}}$, about 580 K at a heating rate of 1 K/min) at a rate of 10 K/min, and holding at this temperature for several minutes to bring them into equilibrium, then cooling to 423 K (which is far below $T_g$) at a constant rate of 1 K/min. (b) Isothermal relaxation was carried out by annealing at 548 K for 43200 s under 0.1 MPa and 1.0 GPa, respectively. Before isothermal annealing of the glassy specimens under different pressures, the as-quenched glassy specimens were pre-annealed under ambient pressure at 548 K for 39600 s to bring them into metastable equilibrium (supercooled liquid). Heat treatments
were carried out on a piston–cylinder pressure vessel with internal diameter of 8 mm, in a furnace with a vacuum of $5 \times 10^{-3}$ Pa. The specimen was surrounded by NaCl powder as a pressure medium, so that a nearly hydrostatic condition prevailed. A thermocouple was placed right under the specimen to monitor the temperature directly.

(2) In a Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glass, pressure effect on $T_g$ was investigated by monitoring the variation of enthalpy of the relaxed glassy specimen with temperature upon heating. A pre-annealing relaxation treatment to the as-quenched Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ ribbon was performed at 613 K for 36000 s in order to bring its enthalpy (the relaxed specimen) into a very low state. No crystalline phase was observed after the relaxation treatment according to the subsequent XRD analysis. The relaxed specimens were then annealed at different annealing temperatures ($T_a$) by heating to $T_a$ at a constant rate of 35 K/min and immediately quenched to ambient temperature (at a cooling rate of above 100 K/min). Annealing was performed under different pressures (0.1 MPa, 2 and 5 GPa), respectively. The high-pressure experiments were performed on cubic anvil type high-pressure equipment in which a pressure of 5 GPa can be approached. The relaxed glassy ribbons were cut into small pieces and embedded into a BN tube. The tube was then inserted into a graphite sleeve, which serves as an electrical heater in the subsequent high-pressure experiments. As a medium, cubic pyrophyllite was utilized to transmit pressure during the treatments. A thermocouple was placed very close to the specimens to measure the sample temperature directly. The details of this apparatus and the experiment were described in Ref. [18].

2.2. Characterization of the enthalpy state of the glassy specimens

Thermal analysis of the as-treated metallic glass specimens was carried out in DSC (Pyris 1, Perkin–Elmer) in a flowing argon atmosphere. The temperature (with an accuracy of ±0.02 K) and energy measurements of the DSC were calibrated by using pure In and Zn standard samples. Al pans were used for both the sample and the reference.

The specific heat of the glass and the supercooled liquid with respect to their crystalline counterpart was determined by DSC measurements in this study. The glassy samples were heated directly up to 723 K (which is much higher than the crystallization temperature $T_c$) at a constant rate. And a second run was directly carried out without change in the measurement condition, in order to obtain a baseline. Heat flow measured by DSC scan comprised of the contribution of the specific heat of the specimen and the container (Al pan):

$$\frac{dQ}{dt} = \left(\frac{dQ}{dt}\right)_s + \left(\frac{dQ}{dt}\right)_{pan}$$

$$= (C_p + C_{pan}) \frac{dT}{dt} M,$$  \hspace{2cm} (2)

where $dQ/dt$ is the heat flow (power), $C_p$ the specific heat, $m$ the mass, and $M$ the mole mass. Subscripts $s$ and $pan$ represent the sample and the Al pan, respectively. Therefore, the specific heat difference $\Delta C_p$ of the glass/liquid (first run) with respect to crystalline (second run) is derived by

$$\Delta C_p = C_{pg,1} - C_{pc}$$

$$= \left[ \left(\frac{dQ}{dt}\right)_{g,1} - \left(\frac{dQ}{dt}\right)_{c} \right] \frac{dT}{dM},$$  \hspace{2cm} (3)

where subscripts $g$, $l$, and $c$ represent the glass, liquid and crystal, respectively. $(dQ/dt)_{g,1}$ and $(dQ/dt)_{c}$ are the heat flow measured in the first run and second run of DSC scans, respectively. Compared with the conventional “iso-step-iso” method, this method is less accurate in determining the absolute value of the specific heat, but is more accurate in measuring the enthalpy difference between the two glassy samples. Because the specific heat difference curves were all directly derived from the DSC measurements, as a matter of convenience, all specific heat curves are still called as “DSC traces” in this paper.
3. Results

3.1. \textit{Pd}_{40}\textit{Ni}_{10}\textit{Cu}_{30}\textit{P}_{20} metallic glass

3.1.1. Isochronal relaxation under different pressures

Fig. 1(a) shows the DSC traces (at a heating rate of 40 K/min) of the glassy specimen obtained by cooling through the glass transition at a constant rate of 1 K/min under 0.1 MPa and 1 GPa, respectively. For comparison, the DSC trace of the as-quenched specimen was also plotted in this figure. It is clearly shown in this figure that for the glassy specimens treated by slowly cooling throughout glass transition region, an evident endothermic peak appears during glass transition. However, for the as-quenched specimen, the overshoot is not apparent, but a broad relaxation exothermic peak appears before glass transition, indicating that the shape of glass transition in DSC trace is very sensitive to the thermal history of the sample. It is noticed in this figure that the DSC traces of specimens treated under different pressures coincide each other almost in the whole measurement temperature region, except that the peak height of “overshoot” is a little lower for specimen treated under 1.0 GPa than that treated under 0.1 MPa.

Previous studies [19] in many amorphous alloys revealed that for a very relaxed glass, an irreversible “overshoot” peak appears during glass transition in the DSC trace upon heating, which originates from the recovery of the enthalpy reduced during relaxation process. The height (or area) of the overshoot peak has also been proven to be sensitive to the enthalpy state of the relaxed specimens prior to the DSC scan, which has been quantitatively interpreted in terms of the free volume model by van den Beukel et al. [20]. A higher overshoot peak usually refers to a lower enthalpy state and smaller amounts of the free volume. The difference in the enthalpy of two samples can be obtained by measuring the area between their overshoot peaks. Accordingly, experimental results shown in Fig. 1(a) indicate that the specimen cooled through glass transition region under higher pressure (1.0 GPa) exhibits higher enthalpy and free volume than that cooled under lower pressure (0.1 MPa). It might be due to the fact that under higher pressure, the liquid was frozen into glass at a higher temperature, and the enthalpy state and the free volume of the liquid at higher temperature were retained.

A similar experiment has been reported in another bulk metallic glass, ZrTiCuNiBe (Vit 4) [15]. However, they did not observe any change in the shape of DSC scans of the glassy specimens cooled under different pressures throughout the glass transition. It is noticed that no evident over-
shoot peak is detectable in the DSC curves in their study for the specimens continuously cooled from supercooled liquid region under different pressures, indicating that the glassy samples they obtained exhibit a relatively high enthalpy state, which may have resulted from the high cooling rate applied. Previous experimental observations revealed that for the rapidly quenched metallic glasses, there exists a broad exothermic relaxation peak before glass transition in the DSC curve, and the overshoot peak during glass transition is not evident. The width and the area of the exothermic peak are an indication of the enthalpy state of the glass at the beginning of the DSC measurement. The higher is the cooling rate applied, the higher is the enthalpy state of the glass obtained, and the broader is the exothermic peak. But for specimens with low enthalpy state (either specimens relaxed at temperatures below \( T_g \), or the specimens slowly cooled from supercooled liquid region), the exothermic relaxation peak may be very weak, or may even disappear if the enthalpy state is low enough and further relaxation is too slow before the glass transition, and a sharp endothermic overshoot peak occurs during glass transition in the DSC curves. And the lower the enthalpy state of the glass samples before DSC scans, the higher is the overshoot peak. Apparently, the shape of the DSC curve is more sensitive to the enthalpy differences for the samples with low enthalpy state compared with those with high enthalpy state, because the changes in the sharp overshoot peak are easier to be distinguished compared with those of the exothermic relaxation peak which occurs in a much wider temperature region. Therefore, the experimental observations reported in Ref. [15] are not puzzling because the difference of the enthalpy state for specimens treated under different pressure might be too little to be distinguished by DSC measurements. A similar experimental result was also observed in a Zr-based metallic glass, which will be presented later (in Fig. 5) in this paper. The advantage of the low cooling rate applied in this study is that the enthalpy state of the glass obtained is low and slight change can be detected by the changes in the height (or area) of their overshoot peaks.

3.1.2. Isothermal relaxation under different pressures

Fig. 1(b) shows the DSC traces of the specimens isothermally annealed at 548 K under different pressures. Thermal analysis shows that the height of “overshoot” peak is different for these two specimens, indicating that the specimens have been annealed into different equilibrium states under different pressures. The “overshoot” peak is higher for the specimen annealed under 1.0 GPa, indicating that under higher pressure, the metallic glass tends to relax into a state with lower enthalpy state, which is in good agreement with the literature [14,15]. In other words, under higher pressure, the completely relaxed glass, which refers to the supercooled liquid at the annealing temperature, exhibits a lower enthalpy and smaller amount of free volume.

3.1.3. Pressure effect on \( T_g \) in the Pd\(_{40}\)Ni\(_{10}\)Cu\(_{30}\)P\(_{20}\) metallic glass

One knows that the liquid would be frozen into different enthalpy states at different temperatures when different cooling rates were applied. Alternatively, the enthalpy state of the as-quenched glass is an indication of glass transition temperature at corresponding cooling rate. Therefore, it is possible to obtain the pressure effect on \( T_g \) indirectly, due to the different enthalpy states of the glass obtained and the supercooled liquid under different pressures.

By measuring the DSC traces during glass transition upon cooling, variation of the enthalpy with temperature around \( T_g \) was roughly obtained for this alloy, as shown in Fig. 2(a). In order to minimize the error from experimental measurement, we measured a DSC trace during cooling from 623 K to the ambient temperature at a rate of 10 K/min. By integrating this DSC trace with respect to corresponding value of glass, a \( \Delta H-T \) curve was attained. Accordingly, for the cooling rate of 10 K/min, glass transition temperature can be simply defined as the temperature of an intersection point at which the extrapolated line of liquid and glass enthalpy line cross (as shown in Fig. 2(a)). Fig. 2(b) shows the comparison of the DSC trace between specimens, which were cooled throughout the glass transition region at a rate of 10 and 1
Fig. 2. (a) Variation of enthalpy with the temperature during glass transition at different cooling rates (10 and 1 K/min), with respect to that of the glassy state. (b) DSC traces (performed at 40 K/min) of the specimens treated by cooling throughout $T_g$ at cooling rate of 10 and 1 K/min, respectively. A difference in the height (area) of the "overshoot" peak was clearly observed. By integrating the area between them, a value of about 130 J/mol was estimated, which refers to the enthalpy difference between the glassy specimens cooled at 10 and 1 K/min. According to this result, we shift the enthalpy of glass parallel to the dotted line and get a new intersection with the liquid line. The temperature of this point indicates the glass transition temperature under 1 K/min. A reduction of about $8 \pm 2$ K was derived for $T_g$ while the cooling rate was reduced from 10 to 1 K/min, which is in good agreement with the direct measurements in other Pd-based metallic glasses [21,22].

Likewise, by using this method, pressure dependence of glass transition temperature can also be obtained indirectly according to the experimental results shown in Fig. 1. In Fig. 3, the solid lines represent the enthalpy of the supercooled liquid and the glass obtained by cooling throughout the glass transition region under ambient pressure (as in Fig. 2(a)). As mentioned above, the intersection of the supercooled liquid and the glass indicates the glass transition temperature (551 K) at 1 K/min under ambient pressure. Measurement of the area between the two DSC scans shown in Fig. 1(a) indicates that the enthalpy of the glass, which was obtained by cooling throughout the glass transition region under 1.0 GPa, is 34 J/mol higher than that of the specimen obtained by cooling under ambient pressure. Accordingly, the enthalpy line of the glass (in Fig. 3) was shifted up to the dashed one, which represents that obtained by cooling under 1.0 GPa. In the same way, measurement in Fig. 1(b) shows that the enthalpy of the supercooled liquid under 1.0 GPa at the annealing temperature (548 K), is 59 J/mol lower than that of the supercooled liquid under ambient pressure. Therefore, the solid line of supercooled liquid was shifted down to get the enthalpy of the supercooled liquid under

Fig. 3. Indirect determination of glass transition temperature under 0.1 MPa and 1.0 GPa at cooling rate of 1 K/min by means of enthalpy recovery method. Solid lines represent the enthalpy of the supercooled liquid and the glass under ambient pressure. Dotted lines represent the enthalpy under 1.0 GPa, which was obtained by parallel shifting of solid lines according to the experimental results shown in Fig. 1.
1.0 GPa (dashed line). The intersection of two dashed lines, the point (557 K) at which the supercooled liquid was frozen into glass under 1.0 GPa, is the glass transition temperature under 1.0 GPa. Therefore, an increase of glass transition temperature from 551 to 557 K was indirectly derived for the cooling rate of 1 K/min, while the applied pressure was increased from 0.1 MPa to 1.0 GPa. The pressure dependence of glass transition temperature \( (dT_g/dP) \) was determined to be \( 6 \pm 2 \) K/GPa for this alloy for the cooling rate of 1 K/min.

3.2. Zr_{65}Al_{7.5}Cu_{27.5} metallic glass

3.2.1. Indirect determination of glass transition temperature

One of the characteristics of the glass transition is the continuous change of the enthalpy between the glass and the supercooled liquid at \( T_g \) upon heating or cooling. This change is more evident while the glass exhibits a lower enthalpy state (which can be approached by annealing at temperatures below \( T_g \)) at the beginning of the heating, compared with the as-quenched one. By measuring the enthalpy state of the annealed sample upon heating, one would obtain a variation of the enthalpy state (change) as a function of the annealing temperature, from which the glass transition temperature can be correlated to be the annealing temperature at which the enthalpy begins to recover. With this approach based on the enthalpy recovery experiments, one can monitor the glass transition temperature indirectly. Compared with the method mentioned above (in Pd-based metallic glass), the advantage of this method is that the glass transition temperature can be measured under different pressures and at high heating rates.

Fig. 4(a) shows the DSC traces (at a heating rate of 40 K/min) of the relaxed (pre-annealed) specimen and the annealed specimens, which were obtained by heating the relaxed specimen to different temperatures at a rate of 35 K/min and then quenched to ambient temperature immediately. A typical DSC trace of the relaxed glassy specimen shows an evident overshoot peak during glass transition which results from the recovery of the enthalpy induced by the relaxation treatment. DSC measurements of the annealed specimens show that the height of the overshoot peak is sensitive to the annealing temperature \( T_a \), indicating an annealing temperature dependence of the enthalpy state of the glassy specimen. When \( T_a \) is below the onset temperature of glass transition \( T_{g-onset} \) (~649 K at a heating rate of 35 K/min), no obvious change is observable in the peak height with different annealing temperatures, indicating that the enthalpy changes during annealing at these temperatures can be ignored. But for the specimens annealed above \( T_{g-onset} \), the peak height begins to
decrease, indicating that the enthalpy of the specimen increases with an increasing annealing temperature, and gradually tends to a saturated state. This saturated state corresponds to the state of the glass attained by continuously cooling from the supercooled liquid at a constant rate, which depends on the cooling rate applied and is independent of the temperature from which the supercooled liquid was cooled, provided no devitrification was involved in annealing.

By measuring the difference of the overshoot peak area between the relaxed and the annealed specimens, we obtained the enthalpy change of the annealed specimens with respect to that of the relaxed one \((\Delta H - \Delta H_0)\), where \(\Delta H\) and \(\Delta H_0\) denote the enthalpy of the annealed and the relaxed specimens, respectively. Fig. 4(b) shows a plot of \((\Delta H - \Delta H_0)\) as a function of the annealing temperature. For comparison, the DSC trace at the same heating rate (of 35 K/min) of the relaxed specimen is also depicted in Fig. 4(b). One may notice that the onset temperature of the glass transition detected in the DSC trace corresponds to that of the increment of \((\Delta H - \Delta H_0)\), and the end temperature of glass transition (\(T_g\)-end, ~683 K at a heating rate of 35 K/min) to the temperature of saturation in \((\Delta H - \Delta H_0)\). Obviously, the variation of \((\Delta H - \Delta H_0)\) measured from the enthalpy recovery experiments of the annealed glassy specimens shows a good correspondence to the glass transition peak in the simple DSC trace. In other words, the glass transition process may alternatively be characterized by the variation of \((\Delta H - \Delta H_0)\) determined from the enthalpy recovery experiments for individual annealed glass samples. More importantly, one of the distinct advantages of this approach to characterize the glass transition process is that it is possible to monitor the glass transition of the glass samples that had undergone external treatments (such as high-pressure annealing treatments), so that the external effects on glass transition of glasses can be experimentally measured.

3.2.2. Pressure effect on \(T_g\) in Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{27.5}\) metallic glass

In order to investigate the pressure effect on the glass transition temperature, the enthalpy recovery experiments as stated above were repeated under different pressures. The relaxed glassy specimens were annealed under different pressures (2 and 5 GPa, respectively) by heating up to various temperatures \(T_a\) at a rate of 35 K/min and immediately quenching to ambient temperature before release of pressure. The DSC traces of the pressure-annealed specimens are shown in Fig. 5. Analogous to the samples annealed under ambient pressure, the overshoot peak for glass transition in the DSC traces is weakened with an increase of the annealing temperature, for the glass samples annealed under high pressures. And it is clearly shown in this figure that the height of the overshoot peak of the treated specimen is not only dependent on the annealing temperature but also on the treating pressure. The annealing temperature at which the height of the overshoot peak begins to drop is...
higher when the applied pressure is increased. By measuring the area of the overshoot peak, we obtained the enthalpy change \((\Delta H - \Delta H_0)\) as a function of the annealing temperature under different pressures, as shown in Fig. 6. Obviously, the enthalpy change curve \((\Delta H - \Delta H_0) \sim T_a\) shifts to higher temperatures when the sample was annealed at higher pressures. According to the correlation between the \((\Delta H - \Delta H_0) \sim T_a\) curve and the glass transition measured in DSC, it can be derived that in the metallic glass Zr_{65}Al_{7.5}Cu_{27.5}, the glass transition temperature increases apparently under high pressures. The increment of \(T_g\) for this alloy is 7 and 50 K under a pressure of 2 and 5 GPa, respectively, for the heating rate of 35 K/min.

It is also noticed in Fig. 5 that for the specimens treated under different pressures, by heating up to 733 K (far above \(T_g\)) and immediately cooling to ambient temperature, there was no evident overshoot peak appearing on their DSC scans during glass transition upon heating. And no difference is detectable in DSC scans for the glass cooled under different pressures, which shows good consistency with the observations reported in Ref. [15]. As we have stated earlier, this is due to the relatively large amount of the free volume retained in the glass. And the difference of the enthalpy state of the metallic glass can only be distinguished clearly for the samples with relatively low enthalpy state or small amount of the free volume (which can be approached by cooling at a slow rate, as applied in this study in PdCuNiP metallic glass).

The increment of the glass transition temperature is summarized in Fig. 7 as a function of applied pressure for both alloys studied in this paper. The glass transition temperature increases with the increasing applied pressure, which is in good agreement with previous studies in non-metallic glasses. Such an enhancement of \(T_g\) induced by pressure is comparable with the observation in another Zr-based bulk metallic glass (~5 K/1.4 GPa) [15], but is much smaller than that observed in non-metallic glasses which is typically \(10^1\)–\(10^2\) K/GPa [5,11–13].

4. Discussion

Because of an abrupt (but continuous) change in specific heat and thermal expansion at \(T_g\), glass transition is occasionally treated as a second order phase transition. However, more and more experimental results revealed that the glass transition is basically a kinetic phenomenon that relates to the time scales of the structural relaxation and of the experiment [14,15]. Hence, in this paper, we will not discuss the glass transition from the thermodynamic point of view on phase transformations, instead of which, the kinetic aspects of the relax-
ation and glass transition are mostly considered. As an example, Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ will be discussed in this study, because Pd-based metallic glasses have been studied for decades and some parameters for the calculations have been known in this alloy.

### 4.1. Free volume model

For metallic glasses, a model based on free volume theory [23, 24] was developed by van den Beukel et al. [20], in which the structural relaxation and the glass transition can be quantitatively described as a result of the competition between production and annihilation of free volume. The change in the flow defect concentration $c_{f}$ (which can be calculated by the reduced free volume $x$ by $c_{f} = \exp(-1/x)$) during the DSC scan is governed by the equation:

$$\frac{dc_{f}}{dt} = -k_{c}c_{f}(c_{f} - c_{f,eq})$$  \hspace{1cm} (4)

where $k_{c}$ is the rate constant of the form $k_{c} = k_{0}\exp(-E_{f}/RT)$, and $c_{f,eq}$ the equilibrium defect concentration of the supercooled liquid. Then, the DSC trace can be calculated by assuming that the heat flow $\Delta C_{p}$ is proportional to $dx/dT$. The temperature dependence of the equilibrium defect concentration $c_{f,eq}$ is given by a Fulcher–Vogel type equation:

$$c_{f,eq} = \exp[-B/(T-T_{0})],$$  \hspace{1cm} (5)

where $B$ and $T_{0}$ are constants. Upon heating, the glass transition is described as a continuous approach of free volume towards its equilibrium state. If the initial defect concentration of the glass before heating is low, a sudden increase of the free volume would be observed towards equilibrium near $T_{g}$, giving rise to an overshoot peak upon glass transition in the DSC trace. Studies of the isothermal annealing revealed that under a high pressure, the glass tends to be relaxed into a lower enthalpy state [14, 15], which corresponds to a smaller amount of the free volume. It is indicated that under high pressure, the equilibrium defect concentration of the supercooled liquid is reduced, originating from the modified equilibrium between the production and annihilation rate of the defect. In Ref. [14], a formation volume $\Delta V_{f}^{0}$ for diffusion defect was introduced to describe the pressure dependence of equilibrium diffusion defect concentration $c_{D}$ as $c_{D}(T, P) = c_{D}(T, P = 0)\exp(-P\Delta V_{f}^{0}/kT))$. According to the relationship of $c_{f} = c_{D}^{2}$, it can be assumed that the pressure dependence of equilibrium flow defect concentration can be expressed by a similar equation:

$$c_{f,eq}(T, P) = c_{f,eq}(T, P = 0)\exp\left(-\frac{P\Delta V_{f}}{kT}\right)$$  \hspace{1cm} (6)

where $\Delta V_{f}$ is the formation volume of the flow defect. In terms of this equation, the formation volume $\Delta V_{f}$ of flow defect can be derived by $\Delta V_{f} = -kT\partial \ln c_{f,eq}/\partial P$. In Ref. [14], the formation volume of diffusion defect has been determined to be 5.9 Å$^{3}$ for Pd$_{40}$Ni$_{40}$P$_{20}$ amorphous alloy. By doubling this value, we obtained the formation volume of flow defect as 11.8 Å$^{3}$ due to the relationship of $c_{f} \propto c_{D}^{2}$ [25]. Taking the place of $c_{f,eq}$ in Eq. (4) by $c_{f,eq}(T, P)$, the change in $c_{f}$ under different pressure can be obtained by:

$$\frac{dc_{f}}{dt} = -k_{c}c_{f}\left[c_{f} - \exp\left(-\frac{B}{T-T_{0}}\right)\right] \exp\left(-\frac{P\Delta V_{f}}{kT}\right)$$  \hspace{1cm} (7)

Because some parameters of Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ are still unknown, for the sake of simplicity, in this study, we performed the calculations by using the parameters of Pd$_{40}$Ni$_{40}$P$_{20}$, for which many calculations have been reported earlier. In fact, the specific heat and the glass transition temperature of two alloys are very close. Taking the formation volume $\Delta V_{f}$ (11.8 Å$^{3}$) into account, DSC traces of the Pd$_{40}$Ni$_{40}$P$_{20}$ amorphous alloy under different pressures were calculated according to Eq. (7), as shown in Fig. 8(a) and (b). All parameters involved are gained from Ref. [26]. The calculations show that: (1) the glass transition temperature increases with increasing pressure by about 6 K/GPa (Fig. 8(a)), which is in good agreement with the experimental results presented in this study; (2) The amount of the free volume of supercooled liquid is lower for higher pressure, but it cannot be
Fig. 8. Calculated variation of the free volume with temperature (c, d), and the calculated DSC scans (a, b) upon heating or cooling performed at 1 K/min under 0.1 MPa and 1 GPa, respectively, in terms of Eq. (8). Calculations were performed by using two groups of parameters: (a), (c): \( \Delta V_f = 11.8 \, \text{Å}^3, \Delta V_m = 0 \); (b), (d): \( \Delta V_f = 11.8 \, \text{Å}^3, \Delta V_m = 4.7 \, \text{Å}^3 \).

obtained by parallel shifting from that of the specimen treated under ambient pressure due to the different slope (Fig. 8(c)). It results in the reduction of the specific heat under higher pressure (about 12% for the pressure of 1.0 GPa) for the supercooled liquid with respect to the crystalline counterpart (Fig. 8(a)), of which experimental observation has not been reported; (3) The amount of the free volume is higher for the specimen cooled under ambient pressure than that treated under higher pressure (Fig. 8(c)), which is in contrast to the experimental results shown in this study.

This discrepancy indicates that Eq. (7) cannot describe the pressure effect on relaxation rate very well. In this equation, only the change in the final state induced by pressure was considered. In order to describe the pressure effect on the relaxation rate, a migration volume of flow defect \( \Delta V_m \) as well as that of diffusion defects could be introduced in Eq. (7). Therefore, the relaxation rate under pressure is given by

\[
\frac{dc_f}{dt} = -k_0 \exp\left( -\frac{E_f + P \Delta V_m}{kT} \right) c_f \cdot \exp\left( -\frac{B}{T-T_0} \right) \exp\left( -\frac{P \Delta V_f}{kT} \right).
\]

However, the migration volume \( \Delta V_m \) is unknown. In this study, we tried calculating using a series of values (ranging from 0 to 10 \( \text{Å}^3 \)) for \( \Delta V_m \). It was found that for cooling rate of 1 K/min and pressure of 1 GPa, when the migration volume was set as 4.7 \( \text{Å}^3 \), the calculated free volume of the glassy specimen isochronally relaxed under 1.0 GPa equals to that of the specimen relaxed under ambient pressure, as shown in Fig. 8(d). While the migration volume exceeds 4.7 \( \text{Å}^3 \), the free volume of the glassy specimen cooled under 1 GPa is higher than that cooled under 0.1 MPa, as that observed in this study. Therefore, calculations suggest a migration volume exceeding 4.7 \( \text{Å}^3 \) of flow defect in Pd-based metallic glass.

All these calculations indicate that in metallic glasses, a non-zero migration volume of the flow defect might dominate the relaxation rate under different pressures. Because the structural relaxation is a consequence of the atomic rearrangement, the relaxation rate is governed by the atomic mobility as well as diffusion processes. Then, migration volume of flow defects should relate to the (diffusion) migration volumes of all atoms involved. Some experimental results on the migration volume of diffusion (5 \( \pm \) 4 \( \text{Å}^3 \) for Au
diffusion in Pd$_{40}$Ni$_{40}$P$_{20}$ amorphous alloy [14]) also hint at a non-zero migration volume of the flow defect for relaxation.

4.2. Activation volume of the relaxation

As mentioned above, activation (formation and migration) volumes of the flow defect were suggested to interpret the pressure effect on the structural relaxation. For isothermal annealing, the final state of the relaxation under pressure is determined by the formation volume. The relaxation rate, and the relaxation time (time required to approach the equilibrium) depend on both the formation volume and migration volume, while different pressures were applied. At the beginning of the relaxation, if the glass is far from equilibrium, the migration volume dominates the relaxation rate (and the relaxation time). Most of previous studies did not concern the difference of the glass sufficiently relaxed under different pressures. Only the variation of the relaxation time under different pressures is considered. An activation volume of relaxation (or activation volume) is simply used to describe the pressure effect on relaxation time by Eq. (1). This relaxation volume might be relative to (but not the sum of) the formation volume and migration volume of the flow defect suggested in this study.

According to Eq. (1), the activation volume of the relaxation can be determined by measuring relaxation times $\tau$ under different pressures at a given temperature. By using this method, the activation volume has been measured in many non-metallic glasses. However, as far as the authors know, the activation volume of relaxation has not been measured in metallic glasses yet, which is important in understanding the kinetics of the structural relaxation and the glass transition under different pressures. In this study, we obtained the pressure dependence of $T_g$ in a Pd-based metallic glass, which provides an opportunity to determine the activation volume of relaxation also in metallic systems.

Previous studies indicated that for most glass-forming liquids, the temperature dependence of relaxation time could be described by a Vogel–Fulcher–Tamman (VFT) type equation

$$\tau = \tau_0 \exp \left( \frac{B}{T-T_0} \right)$$

(9)

where $\tau_0$ is the relaxation times at very high temperatures, $B$ is the fragility parameter, and $T_0$ the Vogel temperature. The fragility parameter $B$ and $T_0$ were usually determined by fitting to the viscosity of the liquids with temperature by equation $\eta = \eta_0 \exp(B/T-T_0)$. While the relaxation was carried out under different pressures, according to Eq. (1), the relaxation time can be expressed by

$$\tau = \tau_0 \exp \left( \frac{B}{T-T_0} \right) \exp \left( \frac{P \Delta V}{RT} \right).$$

(10)

Under different pressures $P_1$ and $P_2$, glass transition occurs at $T_{g-1}$ and $T_{g-2}$, respectively. Because the two samples were heated (or cooled) at the same constant rate, the time scales of both experiments are equivalent, which give rise to the relationship $\tau_1(T_{g-1}) = \tau_2(T_{g-2})$. Consequently, activation volume of relaxation $\Delta V$ can be derived as:

$$\Delta V = B \cdot R \left[ \frac{1}{T_{g-1}-T_0} - \frac{1}{T_{g-2}-T_0} \right] \left[ \frac{P_2}{T_{g-2}} \frac{P_1}{T_{g-1}} \right].$$

(11)

For the metallic glass Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$, the fragility parameter $B$ and $T_0$ have been determined to be 4135 K/s and 447 K in Ref. [27]. Using these parameters, and the data obtained in this study, according to Eq. (11), the activation volume of relaxation ($\Delta V$) of this alloy was derived to be 10 cm$^3$/mol (16.7 Å$^3$), which is almost one order of magnitude smaller than that observed in some polymers.

The activation volume $\Delta V$ of the relaxation is different, but related to the two activation volumes (formation volume $\Delta V_f$ and migration volume $\Delta V_m$) of flow defects, which were suggested in this paper to interpret the pressure effect on the relaxation rate in terms of the free volume model. If the initial state (including enthalpy state, amount of the free volume and the defect concentration) of the glass is far from equilibrium, the formation volume of the flow defect would make a minor contribution to the pressure dependence of the relaxation rate in terms of Eq. (8). Therefore, the relaxation times
required to approach the equilibrium under different pressures are dominated by the migration volume. And the activation volume of relaxation measured in terms of Eq. (1) should be close to the value of the migration volume of the flow defect. To some extent, the activation volume we obtained (16.7 Å³) is also in good agreement with the calculations in this study, which suggests a migration volume exceeding 4.7 Å³ for this alloy.

5. Conclusions

(1) Compared with the glassy sample treated under ambient pressure, an increase in enthalpy (and amount of the free volume) was observed for the specimen cooled at 1 K/min through glass transition under a pressure of 1.0 GPa, while a decrease of enthalpy was observed for the sample isothermally annealed at 548 K under 1.0 GPa. The pressure dependence of $T_g$ is then indirectly derived to be about 6 ± 2 K/GPa for this alloy at a cooling (or heating) rate of 1 K/min.

(2) By means of the enthalpy recovery experiments for the relaxed specimens, an obvious change of the enthalpy across glass transition was observed, which corresponds to the glass transition peak in the DSC scan. This correlation provides a new approach to determine glass transition temperature indirectly. By using this method, an obvious increase in glass transition temperature under high pressure (50 K/5 GPa) was identified in the Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glass at a heating rate of 35 K/min.

(3) In terms of the free volume model, activation (formation and migration) volumes of the flow defect were suggested to describe the relaxation and glass transition under different pressures for metallic glasses. Calculations indicate a positive migration volume (>4.7 Å³) of flow defect for Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ metallic glass. The activation volume of the relaxation is derived to be 10 cm$^3$/mol (16.7 Å³), which is almost one order of magnitude smaller than that of some polymers. The smaller activation volume might be responsible for the smaller ($dT_g/dP$) of the metallic glass relative to that of non-metallic glasses.

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