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Pressure effects on irreversible and reversible contributions to the glass transition of $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass

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Pressure effect on the glass transition of a $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass is investigated by using a temperature-modulated differential scanning calorimetry technique. The pressure dependence of the irreversible and reversible components extracted from the total transition signal is revealed. It is found that the isothermal relaxation below the glass transition temperature under various pressures causes the changes of the irreversible and reversible thermodynamic properties. The time scales for the irreversible and reversible processes as well as their pressure dependence are obtained. The structural relaxation and the enthalpy recovery are discussed.

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The glass transition has been a subject of continued interest for decades. However, the basic understanding of the glass transition is still an unresolved problem.[1,2] On one hand, many glass formers display unusual thermodynamic properties near the glass transition such as entropy, enthalpy, and volume; on the other hand, the transition process reflects the freezing-in of liquidlike modes and is thus related to the slowing dynamics.[3–6] Differential scanning calorimetry (DSC) measurements allow the direct observation of a glass transition with the sudden increase of the specific heat capacity during heating.[7,8] However, an irreversible and a reversible process are often entangled in the glass transition, which increases the difficulties in extracting capacity and impedes the investigation of the glass transition. Recently, a new technique, temperature-modulated differential scanning calorimetry (TMDSC), is developed based on the conventional DSC with two additional predominant features; one is that irreversible and reversible heat flow can be separated from total heat flow, and the other is that capacity can be accurately derived from the reversible heat flow signal.[9–11] The technique provides a powerful tool to investigate the glass transition.

Recently, Pd-, Zr-based bulk metallic glasses (BMGs) have been developed and show excellent glass forming ability and wide supercooled liquid region.[12–15] Comparing with other amorphous materials such as oxide glasses and polymers, the BMGs provide structurally simpler systems to study the nature of the glass transition. In this work, we investigate the pressure effects on the irreversible and reversible contributions to the glass transition of a $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG with TMDSC measurements. It is expected that the manner in which the pressure changes the thermodynamics and kinetics in the two subprocesses can be revealed.

A 6-mm-diam-PdNiCuP glassy rod was prepared by the water quenched method.[16] The composition was quantified to be $Pd_{39}Ni_{10}Cu_{30}P_{21}$. X-ray diffraction (XRD), DSC, and transmitted electron microscopy (TEM) confirmed the amorphous nature and homogeneity. Slices of 1-mm thickness were cut from the rod. Then, the samples were isothermally relaxed for 1 h at 543 K under various pressures. The relaxation temperature was decided below the calorimetric glass transition temperature T_g of 564 K determined on a TA DSC-2910 at a heating rate of 10 K/min. No crystallization was observed in the relaxed samples. High-pressure relaxation experiments were performed on a belt-type apparatus.[17] Subsequently, TMDSC measurements were performed on the TA instrument at an underlying heating rate of 2 K/min. The time period for one sinusoidal temperature oscillation was 60 s. The amplitude of the temperature modulation was held constant at 1 K. It is important to note that these measurements were performed on different slices from the homogeneous glassy rod under identical conditions just varying the pressure. Each TMDSC curve can be well repeated.

The TMDSC result of the unrelaxed $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG is shown in Fig. 1 with a total heat flow curve and its irreversible and reversible components. The glass transition is observed near 560 K, around which a small endothermic valley in the irreversible heat flow curve and a drop of heat flow in the reversible curve are exhibited, respectively. From the irreversible endothermic valley, the irreversible enthalpy ΔH_{IHF} is determined to be ~1.4 J/g. It is clear that an irreversible and a reversible transition process are simultaneously involved in the glass transition of the unrelaxed BMG, whereas the subsequent remarkable crystallization behavior, as we know it, is just irreversible.

Figure 2 exhibits the pressure dependence on the irreversible contribution to the glass transition in the relaxed samples. The irreversible heat flow curves are shown in the

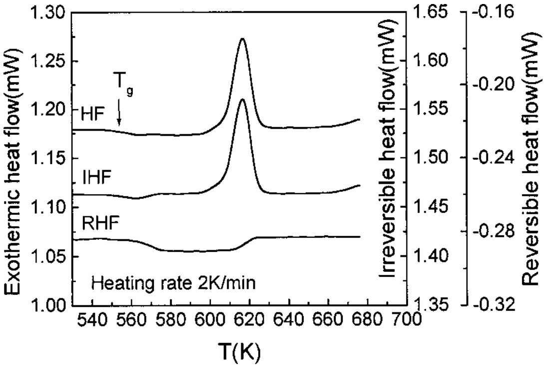

FIG. 1. The TMDSC curves of the unrelaxed $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass. HF, IHF, and RHF stand for the total, irreversible, and reversible heat flow, respectively.

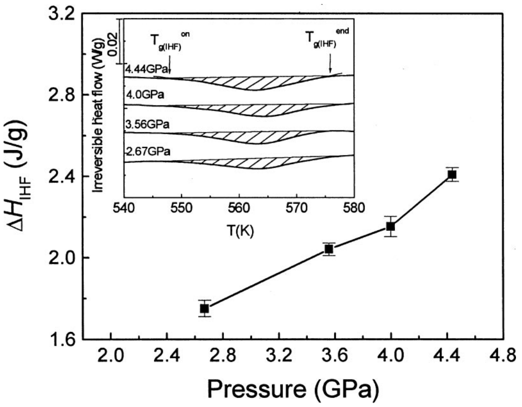

FIG. 2. Dependence of the relaxation pressure on the irreversible recovery enthalpy involved in the glass transition of the relaxed $Pd_{39}Ni_{10}Cu_{30}P_{21}$ bulk metallic glass. The irreversible heat flow curves are shown in the inset.

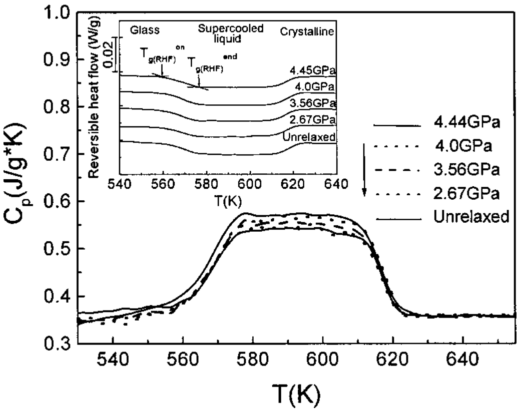

FIG. 3. Specific heat capacity curves of the differently processed samples as a function of relaxation pressure. The reversible heat flow curves are shown in the inset.

inset of Fig. 2, which are measured at ambient pressure at the constant heating rate of 2 K/min. The shade regions in the inset manifest the irreversible endothermic behaviors in the differently processed samples. It is pointed out that the endothermic behaviors reflect the enthalpy recovery processes, where the released heat during the preceding relaxation is recovered upon the glass transition when reheating the samples.[8,18] Thus, the degree of relaxation can be evaluated according to the values of ΔH_{IHF}. For the relaxed samples, the irreversible recovery enthalpy is equivalent to the released heat during the isothermal relaxation at high pressure. One can see in Fig. 2 that ΔH_{IHF} increases with the relaxation pressure, which indicates that increasing pressure induces deeper relaxation. It is inferred that more frozen-in enthalpy in the glassy samples is released after the relaxation at higher pressure, and then lower enthalpic states are attained. The present experiments exhibit a similar result to the reported pressure dependence of enthalpy recovery in metallic glasses measured by means of conventional DSC techniques.[18,19] Within the experimental pressure range, an approximately linear correlation between ΔH_{IHF} and pressure can be well described with a slope of ~0.37 J/gGPa.

The specific heat capacity C_p curves, which are derived from the reversible heat flow curves, of the differently processed $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG samples are shown in Fig. 3, indicative of their pressure dependence. The reversible heat flow curves are given in the inset of Fig. 3. Upon the glass transition, C_p sharply increases, and from the glassy state to the supercooled liquid, an increase of ~50% is estimated in the unrelaxed sample, which is in agreement with the result of Hu *et al.*[11] More strikingly, it is found that the relaxed samples show a slight but monotonous increase in the capacity of the supercooled liquid when the relaxation pressure is above ~3 GPa. Roughly, after the sample is relaxed at 4.44 GPa, the capacity of the supercooled liquid increases by ~5% relative to that of the unrelaxed sample. This indicates that the relaxation processes performed at high enough pressure bring about the detectable thermodynamic change in the reversible transitions. So far, the cause responsible for the pressure-induced increase of the capacity of the supercooled liquid is not clear. Weitz *et al.* find that in a colloidal system, as the glass transition is approached, the microstructure of the supercooled liquid gradually varies; at the glass transition, a sudden structural change occurs.[20] Thus, the increase of the capacity of the supercooled liquid in Fig. 3 implies that, upon the glass transition, the sudden structural changes may be different among the samples relaxed at the different pressures, and then the supercooled liquid with different enthalpic states are attained. Based on the results in Fig. 3, we argue that the relaxation at high-pressure (above ~3 GPa) may cause the deviation of the glass transition from the glassy states to an ergodic supercooled liquid state in the BMG.

The onset and end glass transition temperatures in the irreversible and reversible processes are marked in the two insets of Figs. 2 and 3 to demonstrate the pressure effect on the kinetics of the glass transition of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG. $T_{g(\mathrm{IHF})}{}^{\mathrm{on}}, T_{g(\mathrm{RHF})}{}^{\mathrm{on}}$ are referred to as the onset temperatures in the irreversible enthalpy recovery and the reversible transition, respectively, and $T_{g(\mathrm{IHF})}{}^{\mathrm{end}}, T_{g(\mathrm{RHF})}{}^{\mathrm{end}}$ as the end temperatures. Figure 4 shows the pressure dependence of

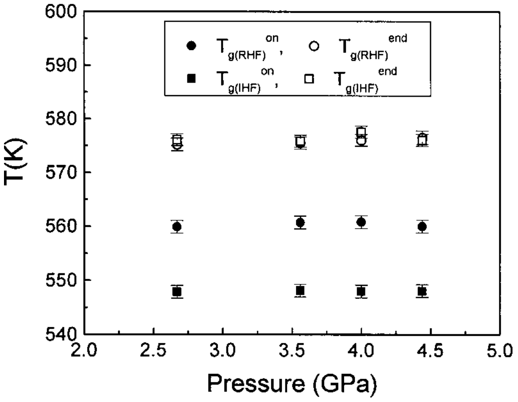

FIG. 4. Pressure dependence of the onset and end temperatures in the irreversible and reversible processes involved in the glass transition. $T_{g(\mathrm{IHF})}{}^{\mathrm{on}}, T_{g(\mathrm{RHF})}{}^{\mathrm{on}}$ stand for the onset temperatures in the irreversible enthalpy recovery and the reversible transition, respectively, and $T_{g(\mathrm{IHF})}{}^{\mathrm{end}}, T_{g(\mathrm{RHF})}{}^{\mathrm{end}}$ for the end temperatures.

these characteristic temperatures. For the relaxed samples, no marked pressure effect is seen on the characteristic temperatures within the measurement error, and ${T_{g(\mathrm{IHF})}}^{\mathrm{on}}$, ${T_{g(\mathrm{RHF})}}^{\mathrm{on}}$, ${T_{g(\mathrm{IHF})}}^{\mathrm{end}}$, and ${T_{g(\mathrm{RHF})}}^{\mathrm{end}}$ roughly keep constants of 548, 560, 576, and 576 K, respectively. Accordingly, the constant temperature intervals for the irreversible enthalpy recovery and the reversible transition are derived to be 28 and 16 K at the heating rate of 2 K/min. It is known that when heating, the glass transition is a relaxation process toward a metastable supercooled liquid from a glassy state, which depends on the crossing of the experimental time scale and the time scale for relaxation.[5,21] Thus, the time interval for the glass transition is dominated by the two processes. In view of the identical heating rate during the measurements, it seems that the pressure-induced structural densification does not impede the relaxation rate toward the supercooled liquid in the differently processed samples. In addition, two significant features are found in Fig. 4. First, the irreversible enthalpy recovery always takes place about 12 K earlier than the reversible transition. This indicates that the enthalpy recovery begins to occur prior to the appearance of supercooled liquid, i.e., within the glass region. Consequently, the enthalpy recovery process can be divided into two parts, the beginning relaxation toward the metastable glassy state and the subsequent one toward the metastable supercooled liquid. Below ${T_{g(\mathrm{RHF})}}^{\mathrm{on}}$ of about 560 K, the enthalpy recovery is dominated by the approach to the metastable glass. The second feature is that the irreversible and the reversible process end simultaneously at about 576 K in the relaxed samples, which indicates the complete arrival at the metastable supercooled liquid.

From Figs. 2 and 3 it is concluded that the relaxation at high pressure changes the irreversible and reversible processes involved in the glass transition of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG. Comparing the two figures, it is clear that the pressure dependence of the capacity of the supercooled liquid is out of step with that of the irreversible recovery enthalpy. Only when the degree of the relaxation is high enough can it cause the change of the reversible transition behavior. Apparently, the pressure effects on the irreversible and reversible transitions are different, which may be attributed to the different transition mechanisms. In any case, the pressure-induced increases of the irreversible recovery enthalpy and the capacity of the supercooled liquid confirm that the relaxation at high pressure thermodynamically changes the glass transition of the BMG. On the other hand, from Fig. 4 one can see that within the experimental pressure range, the relaxation processes does not bring about marked changes in the time scales for the irreversible enthalpy recovery and the reversible transition. Considering the relatively pronounced increase in ΔH_{IHF} and C_p with pressure, it is possible that the kinetics of the glass transition in the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG has a weak dependence on the pressure-induced thermodynamic changes.

In conclusion, the pressure dependence of the irreversible enthalpy recovery and the reversible transition are exhibited upon the glass transition of the $Pd_{39}Ni_{10}Cu_{30}P_{21}$ BMG. Within the experimental pressure range, the irreversible recovery enthalpy approximately linearly increases with the relaxation pressure. Above ~3 GPa, the relaxation at high pressure causes the increase of the capacity of the supercooled liquid. However, it is found that the relaxation processes do not produce marked changes on the kinetics of the irreversible enthalpy recovery and the reversible transition.

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