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Compression behaviour of Pd₃₉Ni₁₀Cu₃₀P₂₁ bulk metallic glass up to 23.5 GPa

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Abstract

The compression behaviour of a Pd₃₉Ni₁₀Cu₃₀P₂₁ bulk metallic glass is investigated at room temperature up to 23.5 GPa using *in situ* high pressure energy dispersive x-ray diffraction with a synchrotron radiation source. Pressure induced structural relaxation of the bulk metallic glass is exhibited within the pressure range. It is found that below about 5 GPa, the existence of excess free volume contributes to rapid structural relaxation, which gives rise to rapid volumetric change. Under higher pressure, further relaxation results in structural stiffness.

1. Introduction

Recently, multicomponent Pd- and Zr-based glass bulk metallic glasses (BMGs) of large size have been developed by a conventional casting process with a low cooling rate [1–4]. Among the BMGs, PdNiCuP alloy systems have the highest reduced glass transition temperature, and can be prepared into glass with a maximum thickness of over 70 mm at a cooling rate less than 1 K s⁻¹ [2, 3]. The new materials have brought new opportunities for fundamental investigations and technological applications. Generally, relative to the crystalline state, as-quenched metallic glasses have excess free volume, which will be annihilated upon structural relaxation and crystallization [5–7]. Structural relaxation is always linked to atomic rearrangements, which involve two sub-processes, topological short range ordering and chemical short range ordering. Compared to conventional metallic glasses that require a rather high cooling rate above 10⁴ K s⁻¹ for glass formation [5], less excess free volume is frozen in the BMGs with more stable structures [8, 9]. However, not much has been reported on the understanding of the behaviour of the excess free volume in metallic glasses under high pressure [10]. Moreover, it is not clear what the effect of a little excess free volume would be

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on the volumetric change under high pressure. The compression properties of materials are dependent on their interatomic potential and are related to atomic configurations [11, 12]. Thus the measurement of compression properties provides a powerful tool for obtaining information about configurational changes under pressure. In this work, we investigate the compression behaviour of a Pd₃₉Ni₁₀Cu₃₀P₂₁ BMG at room temperature. From the results, the contribution of the excess free volume to the volumetric change is revealed, and the structural information about the atomic configurations in the BMG is exhibited.

2. Experiment

A 6 mm diameter rod of the PdNiCuP BMG was prepared by the water quenching method [9]. The composition was quantified to be Pd₃₉Ni₁₀Cu₃₀P₂₁ by chemical analyses. The amorphous nature as well as the homogeneity of the BMG was ascertained by x-ray diffraction, transmission electron microscopy and differential scanning calorimetry. Some powder was prepared from the amorphous rod for pressure experiments. The pressure was generated by using a diamond anvil cell (DAC) driven by an accurately adjustable gear–worm-level system. The culet of the diamond anvil was 470 μm in diameter. The amorphous powder sample together with the pressure–calibrator Au powder was loaded into a 200 μm diameter hole of a L605 stainless steel gasket, which was pre-indented to a thickness of about 61 μm. A mixture of methanol, ethanol and water was used as the pressure–transmitting medium. The *in situ* high-pressure energy dispersive x-ray diffraction measurements were carried out at the Beijing Synchrotron Radiation Laboratory. The x-ray spot size was 130×130 μm². A Si (Li) detector was used to collect the diffraction signal under various pressures. The experimental pressure was determined from the position of the (111) diffraction peak of Au, as its equation of state is well established. The basic relation in the energy dispersion technique is

$$E_{hkl} \cdot d_{hkl} = \frac{hc}{2 \sin \theta} = \frac{0.61993}{\sin \theta} \quad (\text{keV nm}) \quad (1)$$

where E_{hkl} is the energy at which the diffraction line (hkl) is located, d is the interplane spacing, h Planck's constant, and c the speed of light in vacuum. The diffraction angle θ was determined to be 5.842° in our experiment. The relation between E_{hkl} and the channel in the energy dispersion spectrum was calibrated from the fluorescence peaks of Sn, Pt, Cs and Br prior to the diffraction experiments.

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns of the Pd₃₉Ni₁₀Cu₃₀P₂₁ BMG under various pressures at room temperature. A broad diffusive peak is observed with a superimposition of the (111) and (200) diffraction peaks of Au, and no crystallization is detected from the curves up to 23.5 GPa. With increasing pressure, one can see an obvious shift of the diffusive peak towards higher energy, indicating the compression of the BMG. We use a procedure of diffraction peak separation to determine the positions of the broad diffusive peaks under various pressures. According to equation (1), the d_{peak} values, which correspond to the diffusive peaks of the BMG, are quantified, and their pressure dependence is shown in figure 2. For amorphous materials, due to the lack of a three-dimensional periodic lattice, the d -spacing is not exact enough to describe amorphous structures. However, the parameter d_{peak} is important in the sense that the change in d value can reflect the compression behaviour of amorphous alloys [13], so d_{peak} is still used here to investigate the compression characteristics of the BMG. Figure 2 also gives the pressure dependence of the corresponding wave number q_{peak} . It is seen in

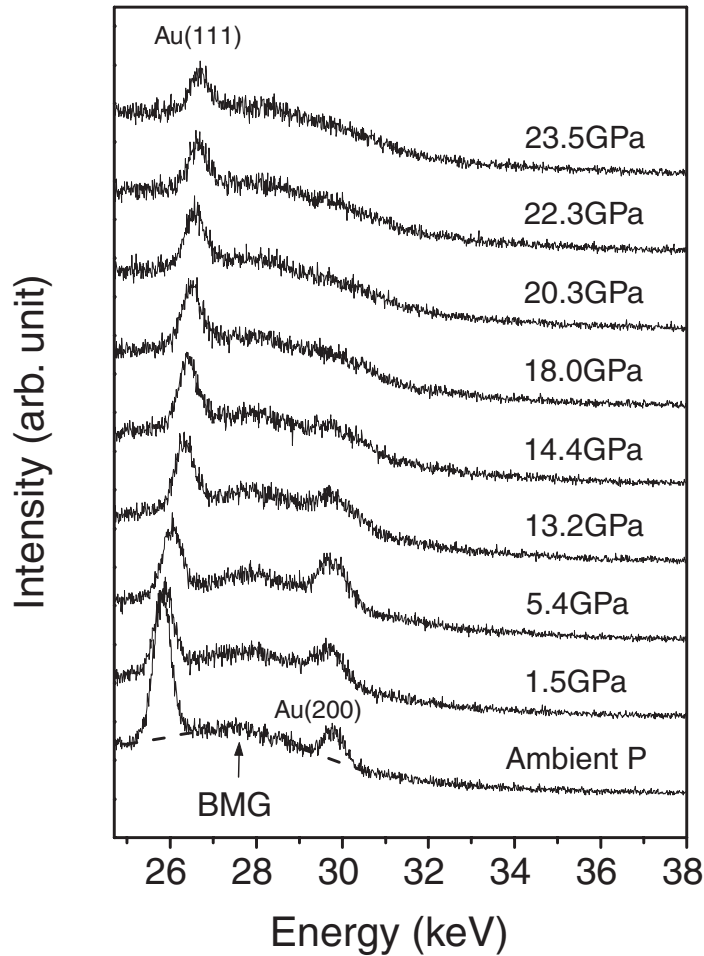


Figure 1. Energy-dispersive x-ray diffraction patterns of Pd₃₉Ni₁₀Cu₃₀P₂₁ BMG at room temperature under various pressures.

figure 2 that in the beginning stage, the d_{peak} value rapidly reduces with increasing pressure, and subsequently a small pressure dependence appears, which indicates the decrease of the average interatomic distance of the BMG. By contrast, the wave number q_{peak} exhibits an opposite pressure dependence and increases with pressure.

The structural investigation of Pd₄₀Ni₁₀Cu₃₀P₂₀ and Pd₄₀Ni₄₀P₂₀ metallic glasses shows that the metallic glasses have dense random packed atomic configurations [8, 14]. Considering the metallic components Pd, Ni and Cu in the BMGs are of face-centred cubic structure, it is likely that the atomic configuration in the Pd-based metallic glasses is close to that of the crystalline face-centred cubic structure. This argument has been verified by our recent experimental results [15]. Thus it can be assumed that the relative volumetric change V/V_0 is comparable to $(d_{peak}/d_{0(peak)})^3$ and, accordingly, the relative volumetric change can be derived and plotted as a function of pressure, as shown in figure 3.

To demonstrate the pressure effects on the structural change of the BMG up to 23.5 GPa, the experimental results are compared with the measured pressure dependence of volumetric change of the BMG within the elastic region up to 0.5 GPa [15]. It is often assumed that

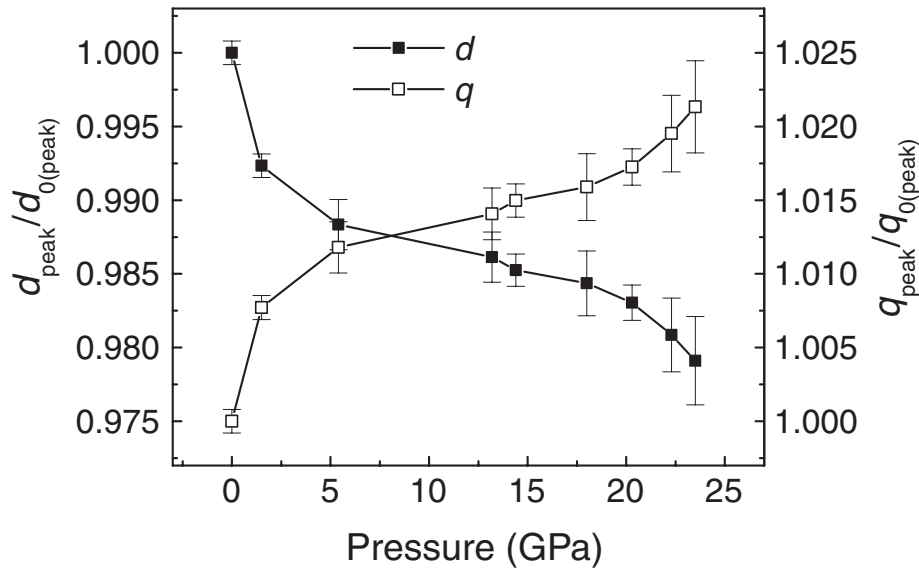


Figure 2. Relative change of d -spacing and wave number q corresponding to amorphous diffraction peak of $\text{Pd}_{39}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{21}$ BMG as a function of pressure; d is determined by the energy dispersion relation.

without pressure-induced phase transformations, the equation of state of a substance can be described in terms of a second-order Birch–Murnaghan (B–M) relation [16, 17]:

$$P = \frac{3}{2}K_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \left\{ 1 - \frac{3}{4} (4 - K'_0) \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\} \quad (2)$$

where K_0 and K'_0 are the bulk modulus and its pressure derivative at zero pressure, respectively. We have obtained the values of K_0 and K'_0 of the $\text{Pd}_{39}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{21}$ BMG to be 159.2 GPa and 6.28, respectively [15]. According to equation (2), the pressure dependence of the volumetric change of the BMG can also be described by the solid curve of figure 3. It is clear that the experimental data deviates from this assumed equation of state curve. It should be noted that the premise for the application of equation (2) is that no phase transformations occur under pressure, and that the change in volume is elastic and reversible. Recent investigations on the compression behaviour of icosahedral Al–Cu–TM alloys have shown that equation (2) gives a very good fit to the P – V relation obtained from high pressure x-ray diffraction up to 20 GPa [18]. Therefore, the difference between the experimental data and the assumed equation of state curve reveals that under high pressure, structural change is involved in the thermodynamically unstable bulk metallic glass which, further, leads to the deviation of compression behaviour of the glass from the B–M equation.

It is well known that under high pressure the average interatomic distance tends to shorten. For amorphous materials, the inhomogeneity of the local distribution of excess free volume together with the existence of density fluctuation gives rise to the inhomogeneity of local stress under pressure. Unlike crystalline materials, in which under increasing pressure the interatomic distance uniformly reduces with unchanged interatomic relative position, in amorphous alloys compression induces redistribution of the average excess frozen volume. Thus, continuous inhomogeneous rearrangement of atoms or groups of atoms will occur in the high stress regions towards metastable equilibrium states through various thermodynamically accessible

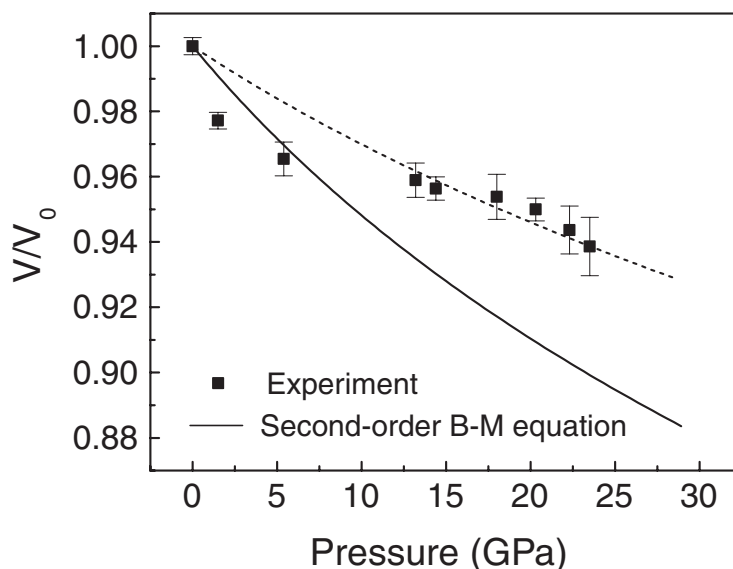


Figure 3. Pressure dependence of relative volumetric change of Pd₃₉Ni₁₀Cu₃₀P₂₁ BMG. The solid curve represents the equation of state assumed from the second-order Birch–Murnaghan relation. The dashed curve is fitted according to the B–M relation.

configurations. This results in continuous structural relaxation. Within a certain low pressure range, this structural relaxation is reversible. It can be expected that if the change of average atomic position is small, a short relaxation time is required to establish a new equilibrium. In figure 3, one can see that below about 5 GPa, a rapid decrease of the volume of the Pd₃₉Ni₁₀Cu₃₀P₂₁ BMG appears, indicating the ease of compression during the beginning stages. A bigger volumetric change than that expected from the B–M equation indicates that under higher pressure, the pattern of structural change is different from that occurring in the lower pressure range from zero to 0.5 GPa, where the structural change proves to be roughly reversible. We can therefore conclude that below about 5 GPa, a larger relaxation is induced which gives rise to large volumetric change.

Phase transformation investigations of amorphous alloys show that atomic long-range diffusion is impeded under pressure [19]. Therefore, the structural relaxation under high pressure at room temperature should be dominated by the topological atomic short-range ordering or structural densification, rather than the chemical ordering. The density measurements of the as-quenched Pd₃₉Ni₁₀Cu₃₀P₂₁ BMG and its crystallized state show that there is only an increase of $\sim 0.6\%$ in density upon crystallization [9], indicating that a little excess free volume is frozen in the BMG. From the present experimental results, it follows that the frozen excess free volume contributes a lot to the structural relaxation of the BMG though it is just a little more than in crystalline materials. Further, it is deduced that the existence of excess free volume in BMGs greatly affects their compression behaviour during the pressure-induced structural relaxation under high pressure.

With progressive increase of pressure, less pressure dependence of the volumetric reduction is exhibited. This suggests that above about 5 GPa it is more difficult than expected to compress the BMG. The smaller pressure dependence should stem from either a bigger bulk modulus K_0 or a bigger pressure derivative of the bulk modulus K'_0 . It is also likely that both cases are true, indicating structural stiffness. In general, compared with K_0 , the change of

K'_0 has a negligible effect on the pressure dependent volumetric change. Thus, the present smaller pressure dependence is ascribed to the increase of K_0 . By recourse to equation (2), a bigger bulk modulus of ~ 290 GPa is obtained when fitting to the experimental data. This value is not unphysically large, since some metals such as Mo, Pt and W have similar or bigger bulk moduli [20]. The large bulk modulus implies that the interatomic interaction potential is greatly changed under high pressure. This result may be ascribed to the establishment of relatively more stable atomic configurations in the BMG under higher pressure. Clearly, these atomic configurations are denser. That is to say, after big structural relaxation in the beginning stages, the original amorphous material is transformed into denser amorphous states. The new atomic configurations make it more difficult for the volume to change with increasing pressure.

4. Conclusion

Our investigation of the compression behaviour of a $\text{Pd}_{39}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{21}$ bulk metallic glass at room temperature up to 23.5 GPa reveals pressure-induced structural relaxation. The existence of excess free volume in the BMG greatly affects the compression behaviour during the pressure-induced structural relaxation. Progressively elevated pressure gives rise to structural stiffness of the BMG, which results in a smaller pressure dependence of the volumetric change.

Acknowledgments

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