Structural behaviour of Pd₄₀Cu₃₀Ni₁₀P₂₀ metallic glass under high pressure

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ABSTRACT

The structural behaviour of Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk metallic glass as a function of hydrostatic pressure up to 47.4 GPa was investigated by means of in situ high energy synchrotron X-ray diffraction patterns. Monotonic changes are observed in the diffraction data without any indication of a phase transition. In real space all maxima of the atomic pair correlation function including the nearest neighbour distance are decreasing and scale with pressure. The volume as function of hydrostatic pressure is extracted from the diffraction data. For the largest hydrostatic pressure of 47.4 GPa the volume is reduced by 18%. The bulk modulus $B_0 = 178$ GPa was calculated from the diffraction data. The dependence of volume on pressure of Pd₄₀Cu₃₀Ni₁₀P₂₀ metallic glass can be well described by the Birch–Murnaghan equation of state.

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1. Introduction

Under high pressure phase transition occurs in certain oxide and chalcogenide glasses having covalent bonding and low coordination numbers $N_1 \leq 6$ [1,2]. Even for covalent elemental glasses Si and Ge transitions were reported [3,4]. These polyamorphic transitions are accompanied by changes in density and coordination. Recently, indications of pressure induced phase transition were also found for different metallic glasses which are densely packed alloys with a high coordination number $N_1 > 12$. Several reports for Ce-based metallic glasses were published, as for Ce₅₅Al₄₅ [5], La₃₂Ce₃₂Al₁₆Ni₅Cu₁₅ [6] and Ce₇₅Al₂₅ [7]. The mechanism here is suggested to be related to delocalization of 4f electrons, which occurs in Ce under high pressure leading to bond shortening and volume collapse [5–7]. However, also for glassy Ca–Al [8], Pd- [9], Zr- [10], Gd- [11], and Pr-based [11] bulk metallic glasses, polyamorphic transitions were reported. The occurrence of the phase transition was concluded from observation of kinks in the pressure shifts of the first diffuse X-ray diffraction (XRD) peak or from the deviation of the pressure–volume relations of the well-established fundamental thermodynamic equation of state (EOS) [12]. However, there is no uniform picture between the different observations, and no

evidence of a sharp first order transition can be seen in the data. On the other side, molecular dynamics simulations of Ni₄₀Zr₆₀ glass under high pressure report continuous changes of topological and chemical short-range order in the model and different regimes of EOS at low and high pressure are discussed [13].

In this work we investigate the structural behaviour of glassy Pd₄₀Cu₃₀Ni₁₀P₂₀ as a function of high pressure by in situ high energy X-ray diffraction. The diffraction data in reciprocal space as well as the atomic pair correlation functions in real space will be analysed. It will be shown that up to the highest pressure of 47.4 GPa no phase transition occurs, and that the pressure dependence of Pd₄₀Cu₃₀Ni₁₀P₂₀ metallic glass can be well described by the equation of state.

2. Experimental

Samples of Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk glass were prepared in form of rods with 5 mm diameter and 50 mm length by copper mould casting of the pre-alloy from the pure elements and refined by fluxing in BO₃. Glassy Pd₄₀Cu₃₀Ni₁₀P₂₀ ribbons 40 μm in thickness and 3 mm in width were prepared by melt spinning using a part of the cast rods. Sample was compressed in a Diamond Anvil Cell (DAC) equipped with 0.3 mm culet diamond on the upstream side and a perforated 0.3 mm culet diamond (0.2 mm remained in the incident path) on the downstream side. Small pieces were cut from the ribbon with extensions of about 60 μm. The samples were

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inserted in a 0.1 mm gasket hole. The DAC was loaded with Ne as a pressure transmitting medium. The pressure was measured with the well-established Ruby pressure scale [14]. In situ high energy X-ray diffraction data were collected at the Extreme Conditions Beamline (ECB) P02.2 of new 3rd generation PETRA III synchrotron radiation source at DESY, Hamburg. Monochromatic X-ray beam of a wave length $\lambda = 0.02071$ nm (energy $E = 59.8$ keV) that was focused to $0.016 \text{ mm} \times 0.016 \text{ mm}$ using Aluminum Compound Refractive (CRL) lenses was used during the experiment. The scattered intensity was recorded by a Perkin Elmer XRD1621 Scl bonded amorphous silicon 2D detector covering a q -range ($q = 4\pi \sin \theta / \lambda$) from 1 to 140 nm^{-1} . The distance between sample and detector was 352 mm. For each pressure value the diffraction pattern of the DAC was measured next to the sample and used for background correction as well as for subtraction of the diamond reflections. For calibration of detector distance, a diffraction pattern of a polycrystalline CeO_2 (NIST SRM 674) standard was collected. For data analysis the Fit2D program was used [15]. The mass density of the ribbon was determined by the Archimedes principle by weighing samples in air and in dodecan ($\text{C}_{12}\text{H}_{26}$). The elastic moduli of $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ BMG were evaluated by ultrasonic measurements a 2 mm thick plate using an Olympus 5900 PR ultrasonic pulser-receiver.

3. Results

Fig. 1 shows the measured and background corrected scattering curves $I(q)$ of the $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ metallic glass at different pressure values. The diffuse diffraction patterns typical for the glassy state exhibit monotonic changes with pressure. The most obvious is the shift of the maxima positions to larger q -values. The position of the first diffuse maximum q_1 was determined by a Gaussian fit. For this only the data of the peak with $I > 0.8 \cdot I_{\text{max}}$ were used. The behaviour of q_1 versus pressure is shown in Fig. 2 for two samples, which were measured with two different high pressure cells in order to check the reproducibility. The accuracy of q_1 is estimated to be about $\Delta q_1 = \pm 0.02 \text{ nm}^{-1}$. A monotonic non-linear shift to higher q -values is evident. The pressure dependence of q_1 can be well described by a parabolic function which is also shown in Fig. 2.

Fig. 1. In situ X-ray diffraction patterns $I(q)$ of glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ at different pressure values.

Fig. 2. Position of the first diffraction maximum q_1 versus pressure p . Fit of the experimental data by a parabolic function is given by the line.

Fig. 3 shows the structure factor $S(q)_{p=2.5\text{GPa}}$ of $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glass at 2.5 GPa as well as the changes of $S(q)$ by different values of pressure. The structure factor $S(q)$ is calculated from the measured intensities $I(q)$ applying the usual corrections and normalization procedure to determine the coherent scattered intensity in absolute electron units :

$$S(q) = \frac{I_{\text{e.u.}}^{\text{coh}} - (\langle f^2 \rangle - \langle f \rangle^2)}{\langle f \rangle^2} \quad (1)$$

with $\langle f \rangle^2 = (\sum c_i f_i)^2$ and $\langle f^2 \rangle = \sum c_i f_i^2$, where f_i is the atom form amplitude of the element i and c_i is the concentration. The changes of the structure factor with pressure in Fig. 3b) are presented by the difference curves $\Delta S(q)_p = S(q)_p - S(q)_{p=2.5\text{GPa}}$ between the measurement at pressure p and that at $p = 2.5$ GPa. The observed changes of $S(q)_p$ exhibit a monotonic increase of the

Fig. 3. Structure factor and its changes versus pressure: a) structure factor $S(q)$ at $p = 2.5$ GPa, b) difference curves $\Delta S(q)_p = S(q)_p - S(q)_{p=2.5\text{GPa}}$ for $p = 11, 22, 31, 41, 47$ GPa, c) comparison of the difference curve $\Delta S(q)_p$ for $p = 47$ GPa with the first derivative of the structure factor $-q \cdot (\delta S / \delta q) \cdot 0.06$ corresponding to 18% volume change.

amplitude with p . The influence of pressure on $S(q)_p$ can be calculated in the case of a decrease of all inter-atomic distances by the same factor. Assuming that the relative arrangements of the atoms are not changed the length scales from r to $r(1+\epsilon)$ and the change $\Delta S(q)_p$ is given by :

$$\Delta S(q)_p = -q \cdot \frac{\partial S}{\partial q} \cdot \epsilon = -\frac{q}{3} \frac{\partial S}{\partial q} \cdot \frac{\Delta V}{V}, \quad (2)$$

with $\Delta V/V$ being the fractional volume reduction. Fig. 3c) compares the experimentally observed change of $\Delta S(q)_p$ with the calculation using Eq. (2) for 18% volume reduction. There is a general overall good agreement, however deviations between the two curves in Fig. 3c) point to the presence of additional non-affine transformations under applied pressure.

From the structure factor $S(q)$ the atomic pair correlation function $g(r) = \rho(r)/\rho_0$ was calculated by the Fourier transform of $S(q)$ between $0 \leq q \leq 120 \text{ nm}^{-1}$:

$$g(r) = 1 + \frac{1}{2r\pi^2\rho_0} \int (S(q) - 1) \cdot q \cdot \sin(q \cdot r) \cdot dq, \quad (3)$$

where $\rho(r)$ is the atomic pair density distribution function and ρ_0 is the mean atomic density. For the $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ metallic glass, a value of $\rho_0 = 76.0 \text{ nm}^{-3}$ is obtained from the mass density $\sigma_m = 8.30 \text{ g cm}^{-3}$ under normal conditions at $p = 0.1 \text{ MPa}$. At elevated pressure the corresponding values of ρ_0 were derived using the volume–pressure dependence as given later. For multi-component glassy alloys, the atomic pair density function $\rho(r)$ represents a weighted sum of the element-specific partial atomic function $\rho_{ij}(r)$. In general it is not possible to extract unambiguously partial inter-atomic distances and coordination numbers from only one total atomic pair density distribution function. Here, we analyse the changes in $g(r)$ with pressure and compare them with the expectations assuming linear decrease of inter-atomic distances. Fig. 4 compares the atomic pair correlation functions $g(r)_p$ for different pressure values. With increasing pressure the positions of the maxima are shifted to lower values. The shift of the first peak of $g(r)$ at r_1 , which corresponds to an averaged nearest neighbour distance, is given in Fig. 5. The pressure dependence of r_1 can be well approximated by a parabolic function: $r_1(p) = 0.274 - 5.146 \cdot 10^{-4}p + 3.50158 \cdot 10^{-6}p^2$ also shown in Fig. 5.

Fig. 4. Atomic pair correlation function $g(r)$ at different pressure. Only selected curves are shown here for clarity. The other curves are situated in between corresponding to the applied pressure.

Fig. 5. Nearest neighbour distance r_1 of $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glass as a function of pressure. Fit of the experimental values by a parabolic function is given by the line.

The overall changes of $g(r)$ with pressure are displayed in Fig. 6b) by the corresponding difference curves $\Delta g(r)_p = g(r)_p - g(r)_{p=2.5\text{GPa}}$. There is a monotonic increase of the amplitudes of $\Delta g(r)_p$ with pressure and, the relative change $\Delta g(r)_p/\Delta p$ does not depend on pressure p (at least within the error limits).

In the case of pure contraction ($\Delta r_i = r_i \epsilon$) the change $\Delta g(r)_p$ is proportional to the first derivative of the atomic pair correlation function $g(r)$:

$$\Delta g(r) = r \cdot \frac{\partial g}{\partial r} \cdot \epsilon = \frac{r}{3} \cdot \frac{\partial g}{\partial r} \cdot \frac{\Delta V}{V} \quad (4)$$

The corresponding curves of $\Delta g(r)$ measured and calculated for $\epsilon = 0.06$ are compared in Fig. 6c). The two curves are found to be quite similar however weak differences indicate the presence of additional structural changes under applied pressure. Fig. 7 shows

Fig. 6. Change of the atomic pair correlation upon pressure: a) atomic pair correlation function $g(r)$ at $p = 2.5 \text{ GPa}$, b) difference curve $\Delta g(r)_p = g(r)_p - g(r)_{p=2.5\text{GPa}}$ for $p = 11, 22, 31, 41, 47 \text{ GPa}$, c) comparison of the difference curve $\Delta g(r)_p$ for $p = 47 \text{ GPa}$ with the first derivative of the atomic pair correlation function $r^*(\partial g/\partial r)^*0.06$ corresponding to 18% volume change.

the atomic pair correlation functions at the lowest and highest pressure values. For the comparison the x -axis of $g(r')_{p=47.4\text{GPa}}$ is normalized to the first maximum position of $g(r)_{p=2.5\text{GPa}}$ in order to have coincidence for $r = r_1$ ($r' = (0.273/0.257)*r$). As can be seen all maxima positions are the same and also the shape and the width of the peaks of $g(r)$ are almost identical. Differences occur in the second neighbourhood pointing to changes of the atomic arrangements under applied pressure. The averaged nearest neighbour number N_1 can be calculated by integration over the first maximum of the atomic pair density function between r_1 and r_2 :

$$N_1 = \rho_0 \int_{r_1}^{r_2} 4\pi r^2 \cdot g(r). \quad (5)$$

An almost constant nearest neighbour number $N_1 = 12.1 \pm 0.2$ is obtained which does not show any systematic pressure dependence. As mentioned the absolute number N_1 is not conclusive because the underlying partials can not be resolved. However, the behaviour of the shape and the area of the first maximum of $g(r)$ give evidence that the topology of the nearest neighbourhood does not change with pressure.

4. Discussion

The monotonic behaviour of structure factor and atomic pair correlation function with pressure show no phase transition occurs for the Pd-glass (at least up to the highest measured value 47.4 GPa). The scaling behaviour of the shift of maxima positions of the atomic pair correlation function then justifies the assumption, that the volume V is proportional to inter-atomic distance r_1^3 and the volume change $\Delta V/V = 3\Delta r_1/r_1$ respectively. The pressure dependence $V(p)$ then can be described by:

$$V(p) = V_0 + \Delta V(p) = V_0 \left(1 + \frac{\Delta V(p)}{V_0}\right) = V_0 \left(1 + \frac{3\Delta r_1(p)}{r_1}\right). \quad (6)$$

The corresponding calculations are shown in Fig. 8. Beside the values directly calculated from the experimental r_1 data (represented by the points) also the result of the calculation using analytical expressions by the fit-functions (Figs. 2 and 5) are shown

Fig. 7. Comparison of the atomic pair correlation functions of Pd₄₀Cu₃₀Ni₁₀P₂₀ glass at low and high pressure. For the comparison, x -axis is normalized to the first maximum positions in order to have coincidence at $r = r_1$ ($r' = (0.273/0.257)*r$).

Fig. 8. Volume dependence of Pd₄₀Cu₃₀Ni₁₀P₂₀ glass on pressure. Data points are derived from experimental data $r_1(p)$. Dashed lines are calculated using the fitted analytical functions for r_1 and q_1 . Birch–Murnaghan EOS is given by the solid line.

(dashed lines). From the derivative $(1/V_0)(\delta V/\delta p)|_{p=0} = 1/B_0$, the bulk modulus $B_0 = 178$ GPa is calculated, which is within the error limits in agreement with $B_0 = 166$ GPa obtained from ultra-sound measurement of the bulky Pd₄₀Cu₃₀Ni₁₀P₂₀ glass sample.

The volume-pressure dependence at constant temperature as a thermodynamic function is described by the equation of state of solids in terms of a second-order Birch–Murnaghan (B–M) relation [11]:

$$p = \frac{3}{2}B_0 \left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}} \right] \left\{ 1 - \frac{3}{4}(4 - B'_0) \left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1 \right] \right\}, \quad (7)$$

where B_0 and B'_0 are the bulk modulus and its pressure derivative at zero pressure, respectively. With the values of $B_0 = 178$ GPa and $B'_0 = 3.0$ of the Pd₄₀Cu₃₀Ni₁₀P₂₀ glass, the pressure dependence of the volumetric change was calculated according to Eq. (7). Fig. 8 shows a good agreement between the volume change derived from the diffraction data and the calculation. This also confirms the absence of phase transformation.

5. Conclusions

Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk metallic glass was investigated as a function of hydrostatic pressure by means of in situ high energy synchrotron X-ray diffraction. Structure factor as well as atomic pair correlation functions exhibit monotonic changes upon applied pressure without any indication of a phase transition. All maxima of the atomic pair correlation function including the nearest neighbour distance are lowered and scale with pressure. The volume function can be extracted from the diffraction data. The dependence of volume on pressure of Pd₄₀Cu₃₀Ni₁₀P₂₀ metallic glass can be well described by the Birch–Murnaghan equation of state.

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