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Partial structure of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ bulk metallic glass

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Abstract. In order to study local structure in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent bulk metallic glass-former, an anomalous x-ray scattering (AXS) experiment was performed at energies close to the Pd, Ni and Cu K absorption edges together with the reference $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Cu_{40}P_{20}$ glasses at the beamline BM02 of the ESRF. The differential structure factors, $\Delta_i S(Q)$, were obtained with a good statistical quality. A small shoulder observed at about 19 nm⁻¹ in S(Q) becomes prominent in $\Delta_{Pd}S(Q)$, indicating a Pd-Pd atomic correlation of 0.32 nm. This pre-shoulder was not observed in $Pd_{40}Ni_{40}P_{20}$ bulk glass having a slightly worse critical-cooling-rate, but in $Pd_{40}Cu_{40}P_{20}$ glass ribbon available by only ultrafast quenching. It is suggested that covalently bonded Pd-P-Pd connection with an almost right bond angle would be formed by replacing the Ni with the Cu atoms. From the obtaining differential pair distribution function around the Pd K edge, $\Delta_{Pd}g(r)$, the first peak position in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ shows a longest atomic distance among the glasses and the width of the first peak is slightly narrower than that in $Pd_{40}Cu_{40}P_{20}$. Thus, a more uniform atomic arrangement around Pd atoms with a loose packing, i.e., a longer and uniform Pd sublattice, is expected for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ compared to the other two reference glasses.

1. Introduction

Bulk metallic glasses of Pd-Ni-Cu-P alloys, discovered by Nishiyama and Inoue [1], have been intensively investigated due to their excellent glass-forming abilities (GFA). They optimized the concentration dependence of the critical-cooling-rate (CCR), and found that $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ has at present the slowest CCR value of 0.067 K/s among metallic glasses and can form a massive bulk glass with a diameter of more than 40 mm by a simple water-quenching [2]. Although several thermodynamic and mechanical properties have been studied in detail in the Pd-Ni-Cu-P alloy glasses [2], only a few fundamental attempts have been made from view points of the structural and electronic properties to understand why it has the excellent GFA.

An anomalous x-ray scattering (AXS) was performed by Park et al. [4] at the beamline BL7C of the Photon Factory, KEK for the similar quadruple alloy of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ and the

Table 1. The large contributions of $S_{ij}(Q)$ (more than 0.05) to the $\Delta_{\text{Pd}}S(Q)$ and S(Q) in the Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ alloy at the first maximum in S(Q) around 29 nm⁻¹.

	Pd-Pd	Pd-Cu	Pd-P	Pd-Ni	Cu-Cu
S(Q)	0.38	0.31	0.10	0.07	0.06
$\Delta_{\mathrm{Pd}}S(Q)$	0.56	0.29	0.08	0.07	

reference ternary $Pd_{40}Ni_{40}P_{20}$ glass at energies close to the Ni and Cu K absorption edges. From the features of the differential data, they concluded that the effect of the elemental substitution with Cu for Ni induces the particular atomic association related to the Cu atoms. However a recent electronic study [5] revealed that the Pd atoms play an important role for the stability of the glassy states, i.e., only the Pd 4d partial density of states becomes localized and largely decreases at the Fermi energy by replacing Ni with Cu. Thus, it is essential to investigate the local structure around the Pd atoms.

We have preliminarily performed AXS experiments on this $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent metallic glass close to the Pd K absorption edge, and the differential structure factor, $\Delta_i S(Q)$, and the differential pair distribution function, $\Delta_i g(r)$ were obtained close to the Pd edge [6]. By comparing to the total structure factors, S(Q), and the total pair distribution functions, g(r), of Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ and Pd₄₀Ni₄₀P₂₀ glasses, it was found that a pre-shoulder observed at about 20 nm⁻¹ in only the Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ glass, originates from the Pd-Pd atomic correlation, and the first peak in $\Delta_{Pd}g(r)$ shows an interatomic length around the Pd atoms longer than the average value.

For the further study we have carried out AXS experiments on $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Cu_{40}P_{20}$ glasses. In the present paper, we discuss the local environment around the Pd atoms in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent glass former by comparing to those in the reference $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Cu_{40}P_{20}$ glasses in detail.

2. Experimental procedure

The AXS experiments were carried out at the beamline BM02 of the European Synchrotron Radiation Facility (ESRF). For obtaining the $\Delta_i S(Q)$ spectra close to the Pd, Ni and Cu atoms, two x-ray scattering experiments were performed at energies below each K absorption edge, i.e., 30 eV below the Pd K edge (24350 eV) or 20 eV below the Ni K (8333 eV) and Cu K (8979 eV) edges, and 200 eV below each K edge, using a standard $\omega - 2\theta$ diffractometer installed at the beamline. Due to the high energy of the Pd K edge, the Q range measurable was up to 180 nm⁻¹, which is effective to suppress the truncation errors on calculating the pair distribution functions. The experimental setup, in particular on the new detecting system, is in detail given elsewhere [7].

Following the analyzing procedure given in Ref. [8], $\Delta_i S(Q)$ were calculated from the scattering data. For each $\Delta_i S(Q)$, the corresponding *i*-th edge element related partial structure factors, $S_{ij}(Q)$, dominates $\Delta_i S(Q)$. For example, Table 1 shows the large contributions of $S_{ij}(Q)$ (more than 0.05) to the $\Delta_{\rm Pd} S(Q)$ and S(Q) in the Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ alloy at the Q value of the first maximum in S(Q) around 29 nm⁻¹. The values change slightly with Q. As clearly seen in the table, a large difference between the $\Delta_{\rm Pd} S(Q)$ and S(Q) is realized mainly in $S_{\rm PdPd}(Q)$, and the others are very small.

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3. Results and discussion

The crosses, triangles and circles in figure 1 show $\Delta_i S(Q)$ functions close to the Ni, Cu and Pd K edges, respectively, for (a) Pd₄₀Ni₄₀P₂₀, (b) Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ and (c) Pd₄₀Cu₄₀P₂₀ glasses. The solid curves at the bottom of each figure indicate S(Q) measured at 24150 eV, 200 eV below the Pd K edge. Although there spectra look very similar to each other, small differences are found by a detailed observation. The first peak position in $\Delta_{Pd}S(Q)$ in each glass is slightly smaller than that in the corresponding S(Q), while that in $\Delta_{Ni}S(Q)$ or $\Delta_{Cu}S(Q)$ is slightly larger than that in S(Q). The oscillations in $\Delta_{Pd}S(Q)$ in each glass clearly shift towards the low Q side compared to the corresponding S(Q).



Figure 1. The crosses, triangles and circles show $\Delta_i S(Q)$ functions close to the Ni, Cu and Pd K edges, respectively, for (a) Pd₄₀Ni₄₀P₂₀, (b) Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ and (c) Pd₄₀Cu₄₀P₂₀ glasses. The solid curves at the bottom of each figure indicate S(Q) spectra. (Color online)

The most interesting result in this figure is that even in S(Q), a pre-shoulder is observed at the lower Q value (0.19 nm⁻¹) of the first peak in the Cu-including Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ and Pd₄₀Cu₄₀P₂₀ glasses, indicating the existence of an intermediate-range order (IRO), but not in the Pd₄₀Ni₄₀P₂₀ glass. It should be noted that this pre-shoulder becomes much clearer in the $\Delta_{Pd}S(Q)$ spectra. Due to the contributions of $S_{ij}(Q)$ to these spectra as shown in Table 1, it is easily concluded that the pre-shoulder originates from the Pd-Pd atomic correlations induced by replacing the Ni atoms with Cu atoms in these metallic glasses. On the other hand, this result indicates that the existence of the Pd-Pd intermediate correlations is not related directly to the GFA as expected in the previous paper [6], and the Cu atoms may induce this peculiar correlation in the Pd-based metallic glasses.

The $\Delta_i g(r)$ functions were obtained by the Fourier-transforms of the corresponding $\Delta_i S(Q)$ spectra. Figure 2 shows the $\Delta_i g(r)$ close to the Ni, Cu and Pd K edges given by the crosses, triangles and circles, respectively, for (a) Pd₄₀Ni₄₀P₂₀, (b) Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ and (c) Pd₄₀Cu₄₀P₂₀ glasses. The solid curves at the bottom of each figure indicate the g(r) functions. Because of the limited Q range measurable for the Ni and Cu K edges, important spatial information in $\Delta_{\rm Ni}g(r)$ and $\Delta_{\rm Cu}g(r)$ may hinder behind the blurred peaks and the serious truncation errors. Due to the wide Q range measurable, however, the truncation errors are relatively small in the $\Delta_{\rm Pd}g(r)$ and g(r) functions, which mainly appear below 0.2 nm, calculated even without any special handling in the data analysis.

The first peak positions in g(r) for all glasses is about 0.275 nm, and those in $\Delta_{\text{Pd}}g(r)$ locate slightly longer positions of about 0.28 nm, indicating a longer inter-atomic distance around the Pd atoms than the average values. This value is consistent with the estimation by Park et al. [4],



Figure 2. The crosses, triangles and circles show $\Delta_i g(r)$ functions close to the Ni, Cu and Pd K edges, respectively, for (a) Pd₄₀Ni₄₀P₂₀, (b) Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ and (c) Pd₄₀Cu₄₀P₂₀ glasses. The solid curves at the bottom of each figure indicate g(r). (Color online)

0.280 nm, for the atomic distance between Pd-M (M:Pd, Ni and Cu) in Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀based on topological short-range order (TSRO) model using polyhedra clusters (a trigonal prism capped with three half octahedra and a transformed tetragonal dodecahedron). On the other hand, the first peak in $\Delta_{\text{Ni}g}(r)$ and $\Delta_{\text{Cu}g}(r)$ locate at the shorter positions as also expected from the TSRO model although the data qualities are not sufficient due to the limited Q ranges.

Figure 3 shows The first peaks in $\Delta_{Pd}g(r)$ for $Pd_{40}Ni_{40}P_{20}$ (dashed), $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ (solid) and $Pd_{40}Cu_{40}P_{20}$ (dotted) glasses in an enlarged scale. A shoulder is seen at the lower rvalue of the first maximum, about 0.230 nm, in each $\Delta_{Pd}g(r)$ and g(r), which is considered as M-P correlations in the TSRO model, but shorter than the TSRO model of more than 0.24 nm. From the pre-shoulder in $\Delta_{Pd}S(Q)$ spectra in the Cu-contained glasses, the correlation length between the Pd atoms is estimated to be $2\pi/19 \sim 0.32$ nm. If the Pd-P covalent-like bonds exist as expected by the electronic study [5], the Pd-P-Pd bond angle can be calculated to be $85^{\circ}-92^{\circ}$, almost the right angle, which is plausible to form the TSRO model cluster.



Figure 3. The first peaks in $\Delta_{Pd}g(r)$ for $Pd_{40}Ni_{40}P_{20}$ (dashed), $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ (solid) and $Pd_{40}Cu_{40}P_{20}$ (dotted) glasses shown in an enlarged scale. (Color online)

Finally, it should be pointed out a clear relation between the excellent GFA and the atomic structure of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$. The first peak in $\Delta_{Pd}g(r)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ shows the longest atomic distance (0.282 nm) among the glasses (0.278 nm for $Pd_{40}Ni_{40}P_{20}$ and

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0.279 nm for $Pd_{40}Cu_{40}P_{20}$), as well as the highest peak height. The Pd concentration of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ is 2.5% larger than the other glasses. From a simple calculation of the $S_{PdPd}(Q)$ as in Table 1, the Pd-Pd partials in $\Delta_{Pd}S(Q)$ increases by 2-4% with increasing the Pd concentration by 2.5%, which gives the increase of the average bond length of 0.0002-3 nm. This value is almost one order of magnitude smaller than the differences of the first neighbor distance observed in the present AXS study. Thus such an increase in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ is not the concentration effect. Moreover, the width of the first peak is slightly narrower than that in $Pd_{40}Cu_{40}P_{20}$. Thus, a more uniform atomic arrangement around the Pd atoms with a longer packing diameter, i.e., a longer and uniform Pd sublattice, is expected for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ compared to other two reference glasses.

Inoue [9] discussed the structures of bulk metallic glasses with high GFA. Based on the previously reported experimental data obtained for multicomponent amorphous alloys, it has been clarified that amorphous alloys can have (a) higher degrees of dense randomly packed atomic configurations, (b) new local atomic configurations different from those of the corresponding crystalline phases, and (c) a homogeneous atomic configuration of the multicomponents on a long-range scale. Although his discussion was intuitive, the present results seem to be largely supported by his predictions, in particular by (b) and (c) for the Pd sublattice. The longer and higher first neighboring peak with a narrow width in $\Delta_{Pd}g(r)$ may also be an indication of (a) the higher degrees of dense randomly packed atomic configurations of the Pd sublattice.

In summary, in order to study local structure in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent bulk metallic glass-former, an AXS experiment was performed at energies close to the Pd, Ni and Cu K absorption edges together with the reference $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Cu_{40}P_{20}$ glasses at BM02/ESRF. The $\Delta_i S(Q)$ spectra were obtained with a good statistical quality. A small shoulder observed at about 19 nm⁻¹ in S(Q) becomes prominent in $\Delta_{Pd}S(Q)$, indicating a Pd-Pd atomic correlation of 0.32 nm. This pre-shoulder was not observed in $Pd_{40}Ni_{40}P_{20}$ bulk glass having a slightly worse critical-cooling-rate, but in $Pd_{40}Cu_{40}P_{20}$ glass ribbon available by only ultra-fast quenching. It is suggested that covalently bonded Pd-P-Pd connection with an almost right bond angle would be formed by replacing the Ni with the Cu atoms. From the obtained $\Delta_{Pd}g(r)$ functions, the first peak position in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ shows a longest atomic distance among the glasses and the width of the first peak is slightly narrower than that in $Pd_{40}Cu_{40}P_{20}$. Thus, a more uniform atomic arrangement around Pd atoms with a larger packing diameter, i.e., a longer and uniform Pd sublattice, is expected for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ compared to other two reference glasses.

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