Partial structure of Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ bulk metallic glass: Comparison to the reference Pd$_{40}$Ni$_{40}$P$_{20}$ glass

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Abstract. In order to study local structure around the Pd atoms in Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ excellent metallic glass-former, an anomalous X-ray scattering (AXS) experiment was performed at energies close to the Pd K absorption edge. The differential structure factor, $\Delta_PdS(Q)$, was obtained with a good statistical quality, which demonstrates that a pre-shoulder at about 20 nm$^{-1}$, indicating the existence of an intermediate-range order, originates from the Pd-Pd atomic correlation. The first peak in the differential pair correlation function, $\Delta_Pdg(r)$, shows a longer inter-atomic length around the Pd atoms than the average value. The local structure is discussed in detail by comparing to the previous experiments of AXS and electronic structure.

1. Introduction

Bulk metallic glasses of Pd-Ni-Cu-P alloys, discovered by Nishiyama and Inoue [1], have been intensively investigated due to their good glass-forming abilities (GFA). They have 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 lowest CCR of 0.067 K/s among metallic glasses and can form a massive bulk glass with a diameter of more than 40 mm by simple water-quenching [2]. Although several thermodynamic and mechanical properties have been studied in detail in the Pd-Ni-Cu-P alloys [2], only a few basic attempts have been made from the viewpoints of their structural and electronic properties to understand why it has such an excellent GFA.

In order to clarify the role of electronic structure in the Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ glass by comparing the Pd$_{40}$Ni$_{40}$P$_{20}$ glass, having a worse CCR of about 1.6 K/s [3], several measurements of electronic spectroscopies were carried out using synchrotron radiation, and partial density of states (DOS) of Pd 4d, Ni 3d, and Cu 3d electrons were estimated [4]. It was found that the Pd 4d partial DOS largely decreases near the Fermi energy, and its feature seems to become located by replacing the Ni atoms with Cu atoms, while that of Ni 3d partial DOS remains...
The large contributions of $S_{ij}(Q)$ (more than 0.05) to the $\Delta_{Pd}S(Q)$ and $S(Q)$ in the Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ alloy at the first maximum in $S(Q)$ around 29 nm$^{-1}$.

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

almost unchanged. Thus, these data demonstrate that they are closely related to the excellent GFA of the Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ glass through a selective formation of Pd-P covalent bonds.

For the atomic structure, an anomalous X-ray scattering (AXS) experiment was performed by Park et al. [5] at the beamline BL7C of the Photon Factory for the similar alloys of Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ and the Pd$_{40}$Ni$_{40}$P$_{20}$ reference 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 in the Pd-Ni-Cu-P alloys induces the particular atomic association related to the Cu atoms. Although the electronic study revealed that the Pd atoms play an important role for the stability of the glassy states, the local structure around the Pd atoms has not yet been examined due to the limited energy range of older generation synchrotron radiation facilities. In this paper, the authors report AXS results close to the Pd K absorption edge, and discuss the local structure around the Pd atoms in the Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ excellent glass-former.

### 2. Experimental procedure

The AXS experiments were carried out at the beamline BM02 of the European Synchrotron Radiation Facility (ESRF). For obtaining the differential structure factor close to the Pd K edge, $\Delta_{Pd}S(Q)$, two scattering experiments were performed at energies 30 eV and 200 eV below the Pd K absorption edge (24.350 keV) using a standard $\omega$–$2\theta$ diffractometer installed at the beamline. Due to the high energies close to the Pd K edge, the $Q$ range measurable is up to 180 nm, much wider than that of the previous AXS measurement [5], which is effective to suppress the truncation errors on calculating the radial distribution functions. The experimental setup, in particular on the new detecting system, is indetail given elsewhere [6]. Following the procedure given in Ref. [7], $\Delta_{Pd}S(Q)$ was calculated from the scattering data. The large contribution of $S_{ij}(Q)$ (more than 0.05) to the $\Delta_{Pd}S(Q)$ and $S(Q)$ in the Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ alloy at the first maximum in $S(Q)$ around 29 nm$^{-1}$ are tabulated in Table 1. The values change slightly with $Q$. The large difference between the $\Delta_{Pd}S(Q)$ and $S(Q)$ is seen in mainly $S_{PdPd}(Q)$, and the others change very small.

### 3. Results and discussion

The open and closed circles in figure 1 respectively show the $\Delta_{Pd}S(Q)$ and $S(Q)$ spectra of Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ alloy, $S(Q)$ being measured at 24.150 keV, 200 eV below the Pd K edge. Also given by the dotted curve is the $S(Q)$ of Pd$_{40}$Ni$_{40}$P$_{20}$ reference alloy. Because of the good statistic quality, An excellent quality of the $\Delta_{Pd}S(Q)$ data were able to be obtained although the contrast of the spectra between two energies far from and very close to the Pd K edge is only several %.

Although these three spectra look similar to each other, small differences are found by a detailed observation of the spectra. The oscillation in Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ glass clearly shifts towards the low $Q$ side compared to $S(Q)$. The first peak position in $\Delta_{Pd}S(Q)$ of Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$ alloy is 28.4 nm$^{-1}$, which is larger than those in $S(Q)$ of 28.8 and 29.1
nm\(^{-1}\) for Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) and Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) alloys, respectively. The most interesting result in this figure is that a pre-shoulder is observed at about 20 nm\(^{-1}\) in the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) glass, indicating the existence of an intermediate-range order (IRO), but not in the Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) reference alloy. This result was not reported in the previous AXS paper [5] and other papers. It should be noted that this pre-shoulder becomes much clearer in the \(\Delta g(r)\) spectrum of Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) alloy.

The differential and ordinary pair-correlation functions, \(\Delta g(r)\) and \(g(r)\), are respectively obtained from the \(\Delta g(r)\) and \(g(r)\) spectra in these alloys, which are given in figure 2. Due to the wide Q range measurable, the truncation errors are relatively small even in the \(\Delta g(r)\) spectrum. The first peak positions of \(g(r)\) in the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) and Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) reference alloys are respectively 0.275 and 0.273 nm, similar to each other. On the other hand, that in the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) glass locates at 0.282 nm, indicating a longer inter-atomic distance around the Pd atoms than the average value. This value is in consistent with the estimation by Park et al. [5], 0.280 nm, for the atomic distance between Pd-M (M: Pd, Ni, and Cu) in the Pd\(_{40}\)Ni\(_{10}\)Cu\(_{30}\)P\(_{20}\) alloy based on topological short-range order (TSRO) model using polyhedra clusters (a trigonal prism capped with three half octahedra and a transformed tetragonal dodecahedron), which are expected to exist in metallic glasses.

**Figure 1.** The \(\Delta g(r)\) and \(g(r)\) spectra of Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) alloy are shown by open and closed circles, respectively. Also given by the dotted curve is the \(g(r)\) of Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) reference alloy.

**Figure 2.** The \(\Delta g(r)\) and \(g(r)\) spectra of Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) alloy are shown by open and closed circles, respectively. Also given by the dotted curve is the \(g(r)\) of Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) reference alloy.
A shoulder is seen at the lower \( Q \) value of about 0.230 nm of the first maximum in each \( \Delta Pd g(r) \) and \( g(r) \), which was considered as M-P correlations in the TSRO model, but was not directly observed in the previous AXS experiment [5]. This finding demonstrates the advantage of high-energy AXS experiment. Due to the wide \( Q \) range up to 180 nm\(^{-1}\) used for the Fourier analysis, the first peak can be well separated into the long M-M and short M-P contributions, while the previous AXS measured in the limited \( Q \) range up to 80 or 100 nm\(^{-1}\), and thus the obtained first peak looks a broad single peak [5]. The shoulders in the present measurement locate about 0.23 nm, which is much shorter than the results of the TSRO model, 0.248 nm for the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) glass and 0.241 nm for the Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) reference alloy. This difference may be originate from the fact that the M-P correlates much stronger than expected from the model, and the clusters would be highly distorted from the model cluster. The recet study of electronic structure [4] demonstrates that the PD atoms selectively form covalent bonds with the P atoms by replacing the Ni atoms with Cu atoms, and thus the distortion may happen in the Pd-P bonds. The present AXS , however, cannot conclude it because the contrast of the Pd-P contributions between the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) and the Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) reference alloys is very small as given in table 1.

Finally, we discuss the IRO in the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) excellent glass-former. As seen in figure 1, a pre-shoulder is observed in each of the \( S(Q) \) and \( \Delta Pd S(Q) \), originating the Pd-Pd interatomic correlation. It was believed for a long time that a prepeak or pre-shoulder at \( Q_p \sim 20 \) nm\(^{-1}\) reflects the existence of an IRO with a correlation length of \( r = 2\pi/Q_p \sim 0.31 \) nm in real space. Since the pre-shoulder is not a sharp peak, the Pd-Pd correlation has a large distribution of the correlation length. In fact, a small shoulder around 0.33 nm is visible in the \( \Delta Pd g(r) \) spectrum. Moreover, since there seems to be no structure in the \( g(r) \), it is plausible that this shoulder originates from the Pd-Pd correlation. If this shoulder really exists and the Pd-Pd correlation is made of Pd-P-Pd connections, the bond angle can be calculated to be \( 85^\circ - 92^\circ \), almost the right angle, which is plausible to form in the TSRO model cluster using polyhedra. It should be, however, noted that since the truncation error would appear in the same range as the small 0.33-nm shoulder in the \( \Delta Pd g(r) \) spectrum, the existence of the Pd-Pd connections with the right bond angle cannot be concluded at present for the model of the IRO in the Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) excellent glass-former.

4. Conclusion
In order to study local structure around the Pd atoms in Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) excellent metallic glass-former, an AXS experiment was performed at energies close to the Pd K edge. The \( \Delta Pd S(Q) \) spectrum was obtained with a good statistical quality, which demonstrates that a pre-shoulder at about 20 nm\(^{-1}\), indicating the existence of an IRO, originates from the Pd-Pd correlation. The local structure around the Pd atoms is discussed in detail.

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