Structural Study of Pd-Based Amorphous Alloys with Wide Supercooled Liquid Region by Anomalous X-ray Scattering

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The anomalous X-ray scattering (AXS) measurements have been made to determine the local ordering structures around Ni and Cu in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys in both the liquid and amorphous state using the synchrotron radiation at incident X-ray energies close to the K -absorption edges of Ni and Cu. A characteristic small hump was clearly found at $r=0.37$ nm in the environmental radial distribution function (RDF) around Cu in liquid and amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy. Such peak was not detected in the environmental RDF around Ni, and the local atomic arrangement around Ni was found to be similar to the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ case. These experimental facts can be described when considering the trigonal prismatic packing related to Ni and the tetragonal dodecahedral packing related to Cu. This is in a sense a necessary condition at best, although it might not be the sufficient condition. However, the effect of elemental substitution with Cu for Ni in the Pd-Ni-Cu-P alloy is thought to induce the particular atomic association related to Cu, which is an important factor for exhibiting its wide supercooled liquid region and high reduced glass transition temperature.

(Received January 12, 1999)

Keywords: palladium-nickel-copper-phosphorus system, liquid and amorphous alloys, local structure, anomalous X-ray scattering measurement, short-range order

I. Introduction

The Pd-Ni-P system has been well known to exhibit wide temperature interval (about 60 K) of supercooled liquid region since the first report by Chen⁽¹⁾. An alternative system showing similar thermodynamic behaviors of Pd-Cu-P system was suggested by Saunders and Miodownik⁽²⁾. Nishiyama and Inoue⁽³⁾ reported in 1996 that the glass forming ability of the Pd-Ni-P system could be extremely improved by substituting Ni with Cu. At the composition of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, the widest temperature interval (about 100 K) of supercooled liquid region was obtained with exhibiting the lowest melting point and the highest reduced glass transition temperature. This new finding made the production of bulk amorphous ingot alloy as large as up to 72 mm in diameter and 75 mm in length possible⁽⁴⁾. On the other hand, the simple mixing of Ni and Cu is known not to improve the glass forming ability at all to destabilize the liquid phase effectively⁽²⁾. This prompts us to investigate the local ordering structure around Ni and Cu in these particular Pd-based amorphous alloys with special respect to "how Ni and Cu can coexist in the stable liquid phase of this particular composition".

In this paper, the local ordering structures around Ni and Cu in both liquid and as-quenched amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloys are estimated from the environmental structural functions obtained by the anomalous

X-ray scattering (AXS) method. The results are discussed by comparing the reference structure of liquid and as-quenched amorphous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys within the framework of topological short-range order around P.

II. Fundamentals of the AXS Method

Atomic scattering factor shows distinct energy dependence due to the anomalous dispersion effect when the energy of the incident X-ray is close to the absorption edge relevant to K or L -shell electrons of a constituent, and is expressed by

$$f(Q, E) = f^0(Q) + f'(E) + if''(E) \quad (1)$$

where $f^0(Q)$ corresponds to the scattering factor of the atom at the energy sufficiently far from the absorption edge, and $f'(E)$ and $f''(E)$ are the real and imaginary parts of the anomalous dispersion terms. If we define the reduced interference function as $I(Q, E) \equiv \{a(Q, E) - 1\} \langle f(Q, E) \rangle^2$ for a system of n different atomic species, where $a(Q, E)$ is the Faber-Ziman type structure factor⁽⁵⁾ and the angle bracket means the average of the contents, it is promptly reduced to the following form;

$$I(Q, E) = I_{\text{obs.}}(Q, E) - \sum_{i=1}^n c_i f_i^2(Q, E) \\ = \sum_{i=1}^n \sum_{j=1}^n c_i c_j f_i(Q, E) f_j(Q, E) \{a_{ij}(Q) - 1\} \quad (2)$$

where $I_{\text{obs.}}(Q, E)$ is the observed intensity of the coherent X-ray scattering per atom, Q and E the wave vector and the incident X-ray energy, respectively, and c_i is the atomic fraction. This form includes the partial structure factor $a_{ij}(Q)$, which is related to the partial pair distribution function $g_{ij}(r)$ by the following relationships;

$$a_{ij}(Q) - 1 = \frac{1}{Q} \int_0^\infty 4\pi r \rho_0 [g_{ij}(r) - 1] \sin(Qr) dr \quad (3)$$

where ρ_0 is the average number density in the system, and $g_{ij}(r)$ is defined as $\rho_{ij}(r)/(c_j \rho_0)$, where $\rho_{ij}(r)$ is the par-

tial number density distribution function.

When the incident energy is set to the close vicinity below the absorption edge E_{abs} of a specific element A , the anomalous dispersion phenomena become significant, and thereby the variation between the reduced interference functions, $\Delta I_A(Q, E_1, E_2) = I_A(Q, E_1) - I_A(Q, E_2)$, measured at the incident energies of E_1 and E_2 , is attributed to the change in real part of anomalous dispersion term f' of A . Straightforwardly, the following relation can be obtained.

$$\begin{aligned} \Delta i_A(Q, E_1, E_2) &\equiv \frac{\{I_{\text{obs.}}(Q, E_1) - \langle f^2(Q, E_1) \rangle\} - \{I_{\text{obs.}}(Q, E_2) - \langle f^2(Q, E_2) \rangle\}}{\langle f(Q, E_1) \rangle^2 - \langle f(Q, E_2) \rangle^2} \\ &\approx \frac{\{I_{\text{obs.}}(Q, E_1) - \langle f^2(Q, E_1) \rangle\} - \{I_{\text{obs.}}(Q, E_2) - \langle f^2(Q, E_2) \rangle\}}{c_A \{f'_A(E_1) - f'_A(E_2)\} W(Q, E_1, E_2)} \\ &= \sum_k \frac{c_k \Re \{f_k(Q, E_1) + f_k(Q, E_2)\}}{W(Q, E_1, E_2)} \{a_{Ak}(Q) - 1\} \end{aligned} \quad (4)$$

in which

$$W(Q, E_1, E_2) = \sum_k c_k \Re \{f_k(Q, E_1) + f_k(Q, E_2)\} \quad (5)$$

where $E_{\text{abs}} > E_2 > E_1$ and $\Re$ denotes the real part of the values in the brackets. $\Delta i_A(Q, E_1, E_2)$ is the environmental interference function that presents the contribution of the structure related only to the element A . The terms in the front of $\{a_{Ak}(Q) - 1\}$ are the effective weighting factors. The environmental interference function is related to the pair distribution function as follows;

$$\begin{aligned} \Delta i_A(Q, E_1, E_2) &= \sum_k \frac{c_k \Re \{f_k(Q, E_1) + f_k(Q, E_2)\}}{W(Q, E_1, E_2)} \left(\frac{1}{Q} \right) \\ &\quad \times \int_0^\infty 4\pi r \rho_0 \{g_{Ak}(r) - 1\} \sin(Qr) dr \end{aligned} \quad (6)$$

Thus, the reduced environmental radial distribution function $G_A(r)$ that presents the atomic environment around a specific element A is obtained in the following form.

$$\begin{aligned} G_A(r) &= \sum_k \frac{c_k \Re \{f_k(Q, E_1) + f_k(Q, E_2)\}}{W(Q, E_1, E_2)} \\ &\quad \times 4\pi r \rho_0 \{g_{Ak}(r) - 1\} \\ &= \frac{2}{\pi} \int_0^\infty Q \Delta i_A(Q) \sin(Qr) dQ \end{aligned} \quad (7)$$

The effective weighting factors for the radial distribution function are usually approximated to an average value in the range of Q space, and then the environmental radial distribution function can be written as follows.

$$4\pi r^2 \rho_A(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q \Delta i_A(Q) \sin(Qr) dQ \quad (8)$$

III. Experimental

1. Amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys

As-quenched amorphous samples of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys with about 1 mm width and about 0.020–0.025 mm thickness were obtained by the single-roller melt-spinning technique in argon atmosphere. For the X-ray diffraction experiment, the ribbons were cut into small pieces of about 20 mm long and closely arranged on aluminum frame with a window of 15 mm wide and 10 mm high. In order to obtain enough scattering intensity from the sample, a few layers were

Fig. 1 Energy dependence of anomalous dispersion terms for isolated Ni and Cu near K absorption edges. ($E_1=8.0317$, $E_2=8.3067$, $E_3=8.6803$, and $E_4=8.9553$ keV).

stacked upon the frame. The ordinary X-ray diffraction experiment was done using monochromatic MoK_α radiation (17.447 keV). The AXS measurements were carried out at a beam line (7C station) in the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan with incident energies of 8.0317, 8.3067, 8.6803, and 8.9553 keV, which are 300 eV and 25 eV below NiK (8.3317 keV) and CuK (8.9803 keV) absorption edges, respectively, as illustrated in Fig. 1. The sample was mounted on a double-axis goniometer that was placed vertically to eliminate the polarization effect. The scattered intensities were detected by intrinsic Ge solid state detector. The sample densities were measured by the Archimedeian method. The number densities of amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys were estimated at 78 nm^{-3} and 76 nm^{-3} , respectively.

2. Liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys

In order to maintain the free surface of a liquid sample, the diffractometer requires asymmetrical reflection optics, where the incident beam of the synchrotron radiation should be irradiated to the horizontal surface with a fixed and small glancing angle. The details of the experimental apparatus and its setting have been described elsewhere⁽⁶⁾⁽⁷⁾ and not described here. The alloy samples were prepared by the same procedure described by Kimura *et al.*⁽⁸⁾. The samples were heated up to 860 K for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and 1170 K for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ in a rectangular graphite crucible ($18 \times 35 \text{ mm}^2 \times 4 \text{ mm}$ depth) by a Mo wire heater wound around an alumina supporter under a highly-purified Ar atmosphere. The temperatures were monitored by Pt-Pt13%Rh thermocouple inserted in a hole at the side of the support just below the sample. The uncertainty in the surface temperature was estimated as about $\pm 15 \text{ K}$. The AXS measurements were carried out at the same incident energies of the as-quenched alloy cases. But, the ordinary diffraction experiment was undertaken at incident energy of 13 keV.

After corrections for air scattering, polarization and

absorption, the measured intensity is converted to electron units per atom with the generalized Krogh-Moe-Norman method⁽⁹⁾. The Compton scattering is corrected using the theoretical values⁽¹⁰⁾⁽¹¹⁾ for a free atom with the so-called Breit-Dirac recoil factor. The atomic scattering factors are taken from the compilation of *International Tables for X-ray Crystallography*⁽¹²⁾, including their theoretical anomalous dispersion terms⁽¹³⁾ (data base of SCM-AXS: <http://www.iamp.tohoku.ac.jp>) using the Cromer-Liberman scheme⁽¹⁴⁾. The values for anomalous dispersion factors of constituents used in this work are listed in Table 1. The atomic number densities of liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys were approximated to values of the amorphous alloys.

IV. Results and Discussion

Solid lines in Fig. 2 show the ordinary and environmental interference functions of amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys. The fundamental structural features of amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ are similar to those of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, except for $Q\Delta i_{\text{Cu}}(Q)$. This simply suggests that the local ordering structure around Ni in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ may not be different from the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ case largely. On the other hand, the amplitude of the first peak in $Q\Delta i_{\text{Ni}}(Q)$ for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ is rather distinct than that of $Q\Delta i_{\text{Cu}}(Q)$ even though the content of Ni is smaller than Cu in this alloy. In other words, this appreciable difference detected in the present work proves the usefulness of AXS method for separating the local ordering structure around a specific element in multi-component systems including next neighboring elements in the periodic table, such as Ni and Cu. Obviously, next neighboring elements in the periodic table cannot be distinguished with the conventional X-ray diffraction method.

Solid lines in Fig. 3 give the ordinary and environmental RDFs for Ni and Cu obtained by Fourier transformation of the interference functions in Fig. 2. It is worth mentioning the following points. Since the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy contains four elements, the struc-

Table 1 Anomalous dispersion terms $f'(E)$ and $f''(E)$ used in the present study for isolated Ni, Cu, Pd and P atoms.

Energy	$f'_{\text{Ni}}(E)$	$f''_{\text{Ni}}(E)$	$f'_{\text{Cu}}(E)$	$f''_{\text{Cu}}(E)$	$f'_{\text{Pd}}(E)$	$f''_{\text{Pd}}(E)$	$f'_{\text{P}}(E)$	$f''_{\text{P}}(E)$
8.0317 keV (Ni K-300 eV)	-3.00	0.511	-2.01	0.591	-0.0718	3.95	0.284	0.437
8.3067 keV (Ni K-25 eV)	-5.48	0.481	-2.31	0.556	-0.0881	3.73	0.274	0.408
8.6803 keV (Cu K-300 eV)	-2.51	3.61	-3.07	0.513	-0.117	3.46	0.261	0.376
8.9553 keV (Cu K-25 eV)	-1.83	3.44	-5.63	0.485	-0.143	3.28	0.251	0.354
13.0 keV	0.110	1.87	-0.0235	2.11	-0.626	1.71	0.150	0.171
17.447 keV (Mo K_α)	0.285	1.11	0.263	1.27	-1.18	1.01	0.090	0.095

Fig. 2 Ordinary and environmental interference functions of amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys (solid lines) with the calculated functions based on the polyhedra in Fig. 6 (dotted lines).

Fig. 3 Ordinary and environmental radial distribution functions of amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys (solid lines) with the calculated functions based on the polyhedra in Fig. 6 (dotted lines).

ture is essentially decomposed into ten possible atomic pairs; Pd-Pd, Pd-Ni, Pd-Cu, Pd-P, Ni-Ni, Ni-Cu, Ni-P, Cu-Cu, Cu-P and P-P. The atomic pairs of Ni-Ni, Ni-P, Cu-P and P-P can be ignored in the interpretation of the RDFs because the atomic fraction of Ni is much

less than the other three elements (Pd, Cu and P) and the scattering factor of P is considerably less than metallic elements (Pd, Ni and Cu). In spite of this assumption, the remaining six partial structures still overlap in the ordinary RDF. However, the environmental RDF around Ni contains only four partials of Ni-Pd, Ni-Ni, Ni-Cu, and Ni-P. Similarly, the environmental RDF around Cu consists of four partials of Cu-Cu, Cu-Pd, Cu-Ni, and Cu-P. It should also be stressed that the vertical scale in the environmental RDF differs from the ordinary RDF case due to the difference in weighting factors described by eqs. (2) and (4).

As expected in the interference functions, the environmental RDFs for Ni are found quite similar in both alloys, although there are differences in detail mainly arising from weighting factors of eqs. (2) and (4). In contrast, a small hump between the first and the second peak is clearly observed at $r=0.37$ nm in the environmental RDF for Cu in amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy. Such particular feature is obtained only from the AXS measurements for Cu. It is quite likely to be rather different local atomic arrangement around Cu from the average structure.

Solid lines in Fig. 4 and Fig. 5 give the interference functions and their RDFs of liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys, respectively. General features on the structure of amorphous alloys appear to remain in the liquid state, although a characteristic shoulder or the separation of the second peak of structural functions, usually detected in various amorphous alloys including metalloid elements, becomes obscure when melted. Particularly, it would rather be noticed that the particular small hump between the first and the second peak in the environmental RDF for Cu in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ are clearly observed at $r=0.36$ nm in the liquid state.

Differences in the structural functions between liquid and amorphous alloys should be attributed to the degree of mobility and thermal vibration at given state. Nevertheless, the present authors maintain the view that the local ordering structure of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy in both the liquid and amorphous state deviates from that of the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloy, when substituting Ni for Cu.

Refinement of the structural parameters in near neighbors, in addition to the nearest neighbor correlation, is quite useful for discussing the local ordering structure in disordered systems. For this purpose, the non-linear least square fitting method, originally proposed by Narten and Levy⁽¹⁵⁾, enables us to provide one way when applied to both the ordinary and the environmental functions. This method is known to be convenient in cases where only restricted Q -range data are available. By representing interference functions as a summation of Gaussian-like distribution and approximating the atomic distribution beyond a certain distance to the average number density distribution, the interference function can be given as follows⁽¹⁶⁾.

Fig. 4 Ordinary and environmental interference functions of liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys (solid lines) with the calculated functions based on the polyhedra in Fig. 6 (dotted lines).

$$\begin{aligned}
 Qi(Q) = & \sum_{j=1} \sum_k c_j \frac{f_j f_k}{\langle f \rangle^2} \frac{N_{jk}}{r_{jk}} \exp(-b_{jk} Q^2) \sin(Qr_{jk}) \\
 & + \sum_{\alpha} \sum_{\beta} \frac{c_{\alpha} c_{\beta} f_{\alpha} f_{\beta}}{\langle f \rangle^2} 4\pi\rho_0 \exp(-b'_{\alpha\beta} Q^2) \\
 & \times \frac{Qr'_{\alpha\beta} \cos(Qr'_{\alpha\beta}) - \sin(Qr'_{\alpha\beta})}{Q^2}
 \end{aligned} \quad (9)$$

Here, N_{jk} is the number of k atom around origin j atom, r_{jk} the average separation between j and k , and b_{jk} the half of the mean-square variation of Gaussian distribution. The first term in this equation represents the summation of Gaussian distributions within a certain distance of interest $r'_{\alpha\beta}$, and the second term corresponds to the average distribution beyond the boundary region $r'_{\alpha\beta}$ which need not be sharp.

Figure 6 illustrates two typical polyhedra for describing the local ordering around P frequently employed for discussing on the structure of amorphous alloys including metalloid elements. The trigonal prism capped with three half octahedra is thought proper to describe the atomic environment around Ni, and close to the average structure as expected for most metal-metalloid amorphous alloys^{(17)–(20)}. On the other hand, the transformed tetragonal dodecahedron found as a basic structural unit of $\text{Pd}_{1.5}\text{Cu}_{2.5}\text{P}^{(21)}$ appears to be recognized for reproducing the particular small hump at $r=0.37$ nm in the environmental RDFs for Cu in Fig. 3 and Fig. 5.

Taking accounts of these polyhedra and the experimental facts, the calculation was done with eq. (9) so as to reproduce the ordinary and environmental interference functions simultaneously. In this calculation,

Fig. 5 Ordinary and environmental radial distribution functions of liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys (solid lines) with the calculated functions based on the polyhedra in Fig. 6 (dotted lines).

Fig. 6 Polyhedra for topological short range order around P atom without distinction of Cu from Ni and Pd; (a) trigonal prism capped with three half octahedra and (b) transformed tetragonal dodecahedron found in $\text{Pd}_{1.5}\text{Cu}_{2.5}\text{P}^{(21)}$.

equal probability for metal atom occupying vertices in these polyhedra was assumed. The dotted lines in Figs. 2~5 represent the calculated results. The resultant structural parameters are listed in **Table 2**. The present results are again acceptable at least in a sense of the necessary condition at best, although they might not be the sufficient condition.

The first coordination number of metal atoms around Ni in the amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy is 12.6 and this is comparable to a value (11.4) of metal atoms around Ni in the amorphous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloy, which is close to the coordination number of metallic glasses frequently reported⁽²²⁾. The value of 11.4 for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ can be described basically by the trigonal prism capped with three half octahedra packing which exhibits the simple dense random packing of hard spheres⁽²³⁾⁽²⁴⁾. In other words, the particular packing related to Cu for

Table 2 Structural parameters of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloys based on the TSRO models.

(unit: nm)

	$r_{\text{P-M}}$ $N_{\text{P-M}}$	$r_{\text{Pd-M}}$ $N_{\text{Pd-M}}$	$r_{\text{Ni-M}}$ $N_{\text{Ni-M}}$			$r_{\text{Ni-P}}$ $N_{\text{Ni-P}}$
Liquid $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$	0.241 9.0	0.279 9.5	0.272 9.3	0.388 5.5	0.475 11.8	0.428 4.1
Amorphous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$	0.241 8.7	0.268 11.1	0.265 11.4	0.409 5.2	0.440 15.3	0.424 4.0
	$r_{\text{P-M}^*}$ $N_{\text{P-M}^*}$	$r_{\text{Pd-M}^*}$ $N_{\text{Pd-M}^*}$	$r_{\text{Cu-M}^*}$ $N_{\text{Cu-M}^*}$			$r_{\text{Cu-P}}$ $N_{\text{Cu-P}}$
Liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	0.240 8.4	0.279 9.1	0.272 7.9	0.359 6.7	0.474 18.8	0.431 5.3
Amorphous $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	0.248 8.1	0.280 11.5	0.271 7.7	0.368 6.8	0.450 11.1	0.422 5.0
			$r_{\text{Ni-M}^*}$ $N_{\text{Ni-M}^*}$			$r_{\text{Ni-P}}$ $N_{\text{Ni-P}}$
			0.271 12.6		0.410 4.4 0.448 12.5	0.427 4.7

M: Pd and Ni, M*: Pd, Ni, and Cu

$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ may suggest a certain chemical association effect on the local atomic arrangement, relevant to the atomic species correlations. However, the present authors take the view that the particular Cu-related atomic arrangement is thought rather homogeneously distributed in the average structure, so as not to distinguish the Cu-related tetragonal dodecahedron structure with the Ni-related trigonal prism arrangement, in both amorphous and liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy. This is also consistent with the following results.

The nearest coordination numbers around Pd show almost same values both for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$. In addition, the relationships of correlation distances were found not so sharp as expected from the model polyhedra. The ratios of correlation distances to the first coordination distance were found slightly larger than those of ideal polyhedra, which is thought as the size effect of constituents or the distortion of polyhedron to form the higher packing⁽²⁵⁾.

The number of metal atoms around P is close to 9 for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and close to 8 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$. It is difficult to say about some specific comments from these values alone, because the equal probability assumption for Pd, Ni, and Cu atoms could sufficiently reproduce the experimental structural functions of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{40}\text{P}_{20}$.

In Fig. 7, the vertical lines are denoted by the representative metal-metal and phosphorous-metal correlation distances obtained by the topological short-range order models. The severe distortion of polyhedra or the drastic change in inter-relationship of constituent atoms from the particular topological short-range order is not identified in the present experimental data. Considering these experimental results with the help of model polyhedra, the particular topological short-range order around Cu found in the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy can be

Fig. 7 Radial distribution functions of amorphous and liquid $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloys with the representative pair correlation distances assessed by topological short range order model. —: P-metals, ·····: metal-metals.

attributed to the characteristic feature of the transformed tetragonal dodecahedral topology. However, there is no sharp boundary between the atomic association induced by the Cu substitution and the residual Ni-related atomic arrangement. The average structure of metallic elements rather maintains their dense random packing.

V. Concluding Remarks

The AXS measurements have been carried out to obtain the local ordering structures around Ni and Cu in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ in both the amorphous and liquid states. The characteristic small hump between the first and the second peak is clearly found in the environmental RDFs for Cu in the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy. Such hump is not detected in both the ordinary RDFs and environmental RDFs for Ni. This particular structural feature for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{10}$ can be described when employing the tetragonal dodecahedral packing related to Cu, slightly different from the typical prismatic packing of metal atoms for various amorphous alloys including $\text{Pd}_{40}\text{Ni}_{40}\text{Pd}_{20}$. The characteristic structural feature around Cu firstly detected in the present AXS measurements may be an important factor for exhibiting the wide super cooled liquid region and high reduced glass transition temperature of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ alloy. However, some further systematic structural studies are strongly required for alloys showing good glass forming ability before the full potential of this remark can be assessed.

Acknowledgement

The authors wish to express their gratitude to Prof. M. Nomura, Photon Factory, for his help on the AXS measurements (Proposal No. 98G266). One of the authors (C.P.) wishes to express his gratitude to the Ministry of Education, Science and Culture, Japan for its financial support.

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