An Experimental Derivation of Partial Structure Functions of Amorphous Pd_<80>Si_<20> Alloy Using Combination of X-ray, Electron and Neutron Diffraction Experiments

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(Received January 31, 1980)

Synopsis

Three partial interference functions corresponding to Pd-Pd, Pd-Si and Si-Si correlations have been separated using the combination of three total interference functions observed by neutron, X-ray and electron diffraction experiments respectively. The number-concentration correlation functions were calculated from the partial Pd-Pd, Pd-Si and Si-Si correlation functions.

I. Introduction

In metal-metalloid amorphous alloys metalloid atoms play an important role to stabilize the amorphous structure. However, it is not easy to obtain experimentally the structural information concerning metalloid atoms in metal-metalloid amorphous alloys even by neutron diffraction as well as conventional X-ray diffraction, because the scattering factor and atomic fraction of metalloid atoms are usually small in these alloys.

Recently, we[1,2] have observed well resolved RDF's of amorphous Pd-Si alloys which show distinct separation between two first-neighbor peaks associated with Pd-Si and Pd-Pd correlations respectively, using a time-of-flight pulsed neutron total scattering technique based on electron LINAC. Unfortunately, no reliable information of Si-Si correlation could be found out with that experiment.

In this paper, three partial structure functions related to Pd-Pd , Pd-Si and Si-Si correlations in amorphous $Pd_{80}Si_{20}$ alloy are sepa-

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rated using combination of X-ray, electron and neutron diffraction experiments and then number-concentration correlation functions are derived.

II. Experimental

Amorphous Pd-19.8at%Si alloy was prepared in a form of thin ribbon with about 2 mm in width and less than 30 μm in thickness by splat quenching from the molten state using a single roll technique. Silicon content in the alloy was determined by conventional chemical analysis. Three total interference functions of the alloy were measured by neutron, X-ray and electron diffraction respectively. Neutron total interference function was obtained by pulsed neutron total scattering experiment[3]. X-ray[4] and electron[5] total interference functions were measured by conventional methods. Details of these measurements have been described elsewhere[3-5]. Three total interference functions observed for amorphous Pd-19.8at%Si alloy are shown in Figure 1.
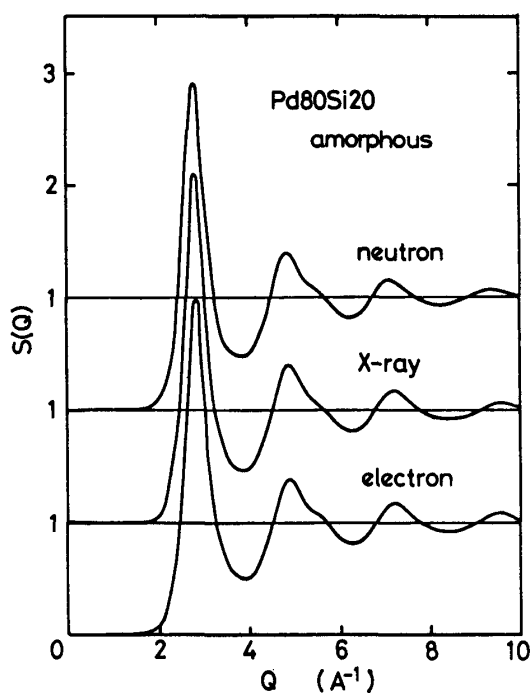

Fig. 1. Total interference functions of amorphous Pd-19.8 at%Si alloy observed by neutron, X-ray and electron diffraction.

III. Partial pair Structure Functions

The measured total interference function $S(Q)$ for an amorphous A-B binary alloy can be written as a weighted sum of partial pair interference functions $S_{AA}(Q)$, $S_{AB}(Q)$ and $S_{BB}(Q)$ corresponding to A-A, A-B and B-B correlations in the alloy as follows

$$S(Q) = W_{AA}S_{AA}(Q) + 2W_{AB}S_{AB}(Q) + W_{BB}S_{BB}(Q) \ , \tag{1}$$

where

$$\left. \begin{array}{l} W_{AA} = c_A^2 f_A^2 / (c_A f_A + c_B f_B)^2 \ , \\[2mm] W_{AB} = c_A c_B f_A f_B / (c_A f_A + c_B f_B)^2 \\[2mm] W_{BB} = c_B^2 f_B^2 / (c_A f_A + c_B f_B)^2 \ , \end{array} \right\} \tag{2}$$

and

c_A and c_B are the concentration fractions of A and B atoms in the alloy, and f_A and f_B are the atomic scattering factors of A and B atoms respectively.

Since three total interference functions $S(Q)$'s of amorphous Pd-19.8at%Si alloy observed by neutron, X-ray and electron diffraction experiments have different weighting factors W_{PdPd}, W_{PdSi} and W_{SiSi} one another, three partial pair interference functions $S_{PdPd}(Q)$, $S_{PdSi}(Q)$ and $S_{SiSi}(Q)$ can be solved from the simultaneous linear equation

$$\begin{pmatrix} S^N(Q) \\ S^X(Q) \\ S^E(Q) \end{pmatrix} = \begin{pmatrix} W^N_{PdPd} & 2W^N_{PdSi} & W^N_{SiSi} \\ W^X_{PdPd} & 2W^X_{PdSi} & W^X_{SiSi} \\ W^E_{PdPd} & 2W^E_{PdSi} & W^E_{SiSi} \end{pmatrix} \begin{pmatrix} S_{PdPd}(Q) \\ S_{PdSi}(Q) \\ S_{SiSi}(Q) \end{pmatrix} , \tag{3}$$

where the superscripts N, X and E mean neutron, X-ray and electron diffraction respectively. The weighting factors W_{ij} (i,j=Pd or Si) in neutron, X-ray and electron total interference functions for amorphous Pd-19.8at%Si alloy are listed in Table 1.

Table 1. Weighting factors of amorphous Pd-19.8at%Si alloy in neutron, X-ray and electron diffraction experiments.

	W_{PdPd}	$2W_{PdSi}$	W_{SiSi}
neutron	0.730	0.249	0.021
X-ray	0.895	0.101	0.003
electron	0.835	0.158	0.007

It is difficult to determine three partial pair interference functions by solving directly equation (3), because values of the weighting factor of Si-Si correlation for X-ray and electron diffraction are very small compared with those of Pd-Pd and Pd-Si correlations.

In this work, therefore, three partial pair interference functions were derived with two steps iterative procedure. First, trial $S_{PdPd}(Q)$ and $S_{PdSi}(Q)$ are calculated from combination of X-ray and electron total interference functions

$$\left. \begin{array}{l} S^X(Q)=W^X_{PdPd}S^X_{PdPd}(Q)+2W^X_{PdSi}S^X_{PdSi}(Q)+W^X_{SiSi}S^X_{SiSi}(Q) \\[2mm] S^E(Q)=W^E_{PdPd}S^E_{PdPd}(Q)+2W^E_{PdSi}S^E_{PdSi}(Q)+W^E_{SiSi}S^E_{SiSi}(Q) \ , \end{array} \right\} \quad (4)$$

where an initial requirement of $W^X_{SiSi}=W^E_{SiSi}=0$ is used. Second, $S_{SiSi}(Q)$ is obtained using trial partial interference functions $S_{PdPd}(Q)$ and $S_{PdSi}(Q)$ and neutron total interference function as follows

$$S_{SiSi}(Q) = \frac{S^N(Q)-W^N_{PdPd}S_{PdPd}(Q)-W^N_{PdSi}S_{PdSi}(Q)}{W^N_{SiSi}} \quad (5)$$

The $S_{SiSi}(Q)$ obtained is substituted into equation (4) and then $S_{PdPd}(Q)$ and $S_{PdSi}(Q)$ are again calculated. Such an iterative calculation is continued until three partial pair interference functions $S_{PdPd}(Q)$, $S_{PdSi}(Q)$ and $S_{SiSi}(Q)$ are converged to reasonable solutions within experimental errors. Finally, the physical reliability of obtained partial pair interference functions was examined by the following criteria used by Enderby et al.[6] and Edwards et al[7].

(1) Solutions are found in the range defined by the dashed line in Figure 2.

(2) A smooth curve is drawn such that the sum rule is satisfied.

$$\int (S_{PdPd}(Q)-1)Q^2 \ dQ = \int (S_{PdSi}(Q)-1)Q^2 \ dQ$$

$$= \int (S_{SiSi}(Q)-1)Q^2 \ dQ = -2\pi^2\rho \ . \quad (6)$$

Figure 3 shows final pair interference functions $S_{PdPd}(Q)$, $S_{PdSi}(Q)$ and $S_{SiSi}(Q)$ for amorphous Pd-19.8at%Si alloy. Error bands in $S_{PdPd}(Q)$, $S_{PdSi}(Q)$ and $S_{SiSi}(Q)$ result from the statistical
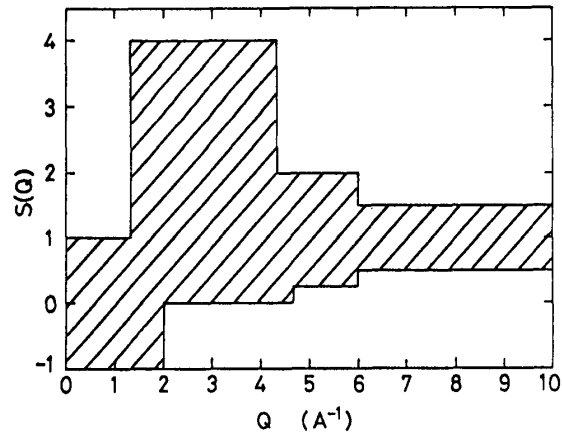
Fig. 2. A region allowed empirically for interference
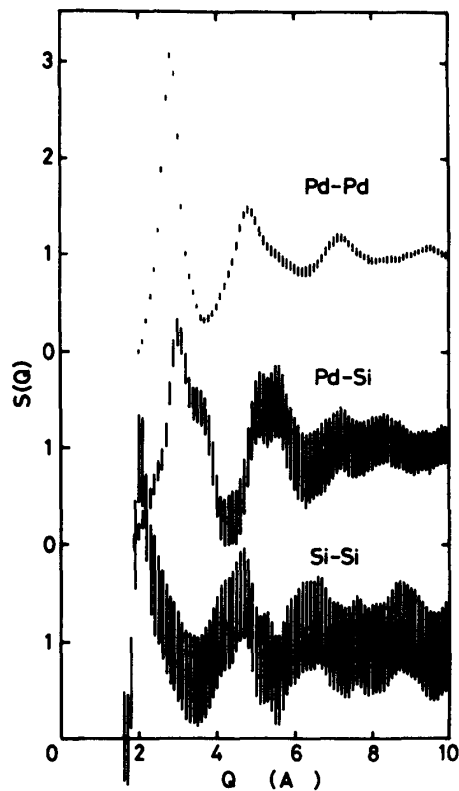function of amorphous Pd-19.8at%Si alloy.

Fig. 3. Partial pair interference functions for Pd-Pd,
Pd-Si and Si-Si correlations. Error bands originate
from 2 % uncertainties in experimental total
interference functions.

uncertainty in experimental total interference functions which is less than 2 % in each experiment.

The partial pair distribution functions $g_{ij}(r)$ (i,j=Pd or Si) are defined as Fourier transforms of $S_{ij}(Q)$ (i,j=Pd or Si)

$$g_{ij}(r) = 1 + \int_0^\infty \frac{1}{2\pi^2 \rho r} \, Q(S_{ij}(Q)-1)\sin Qr \, dQ \ . \tag{7}$$

Figure 4 shows $g_{PdPd}(r)$, $g_{PdSi}(r)$ and $g_{SiSi}(r)$ of amorphous Pd-19.8at%Si alloy, where the integration of equation (7) is truncated at $Q_{max}=10$ A^{-1} in case of Pd-Pd correlation and at $Q_{max}=7$ A^{-1} in case of Pd-Si and Si-Si correlations because of increasing uncertainty included in $S_{ij}(Q)$ at higher Q region.
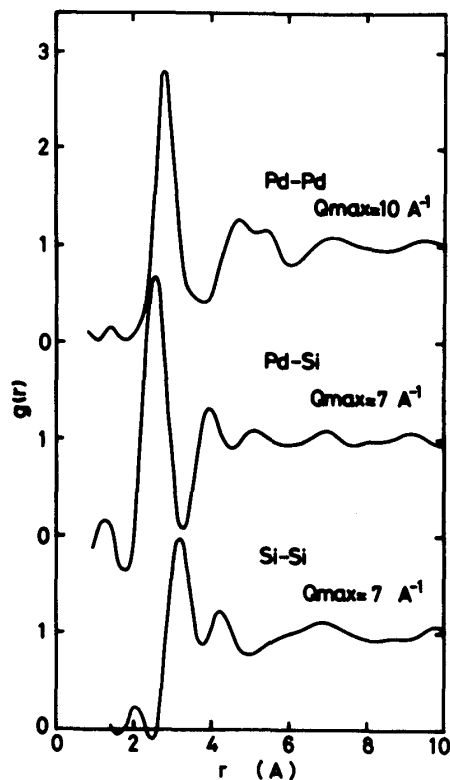

Fig. 4. Partial pair distribution functions for
Pd-Pd, Pd-Si and Si-Si correlations.

IV. Number-Concentration Structure Functions

Bhatia and Thornton[8] have shown that total interference function S(Q) is divided into another set of the three partial interference

functions which correspond to number-number $S_{NN}(Q)$, number-concentration $S_{NC}(Q)$ and concentration-concentration $S_{CC}(Q)$ correlations

$$S(Q) = \frac{1}{<f^2>} \{ <f>^2 S_{NN}(Q) + 2\Delta f<f>S_{NC}(Q) + <\Delta f>^2 S_{CC}(Q) \} , \quad (8)$$

where $<f>=c_A f_A + c_B f_B$ and $\Delta f = |f_A - f_B|$.

There number-concentration partial interference functions $S_{NN}(Q)$, $S_{NC}(Q)$ and $S_{CC}(Q)$ are written as a linear combination of partial pair interference functions as follows

$$\left. \begin{array}{l} S_{NN}(Q) = c_A^2 S_{AA}(Q) + c_B^2 S_{BB}(Q) + 2c_A c_B S_{AB}(Q) , \\[2mm] S_{CC}(Q) = c_A^2 c_B^2 \{ S_{AA}(Q) + S_{BB}(Q) - 2S_{AB}(Q) \} + c_A c_B , \\[2mm] S_{NC}(Q) = c_A c_B \{ c_A S_{AA}(Q) - c_B S_{BB}(Q) + (c_B - c_A) S_{AB}(Q) \} . \end{array} \right\} \quad (9)$$

The same relationships are maintained between $\{ g_{NN}(r), g_{NC}(r), g_{CC}(r) \}$ and $\{ g_{AA}(r), g_{AB}(r), g_{BB}(r) \}$. Figures 5 and 6 show the results of number-concentration structure functions obtained for amorphous Pd-19.8at%Si alloy.
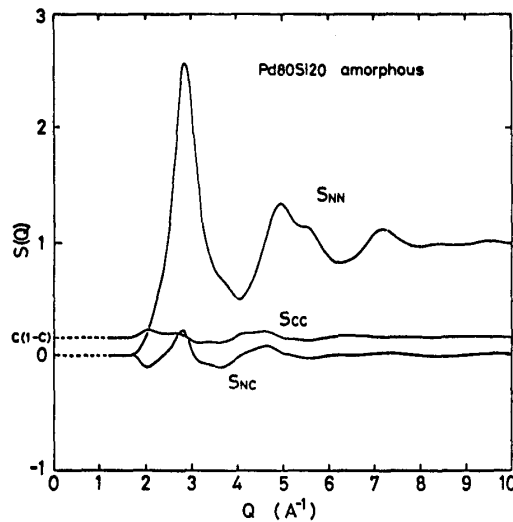

Fig. 5. Number-concentration interference functions
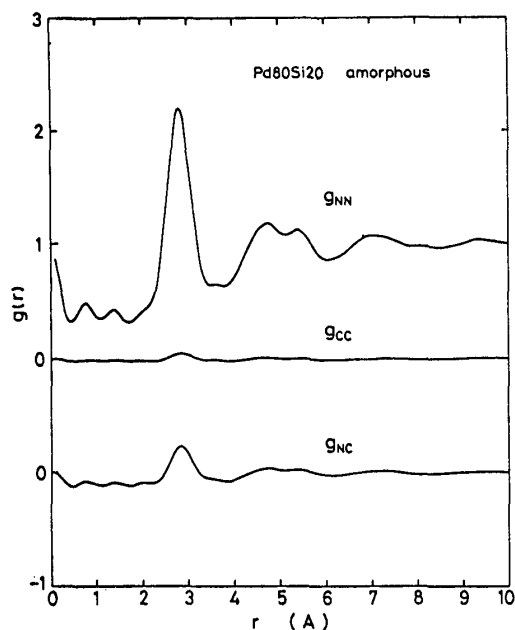for amorphous Pd-19.8at%Si alloy.

Fig. 6. Number-concentration pair distribution
functions for amorphous Pd-19.8at%Si alloy.

V. Results and Discussion

The overall behavior of $S_{PdPd}(Q)$ in Figure 3 is quite analogous
to that of each experimental total $S(Q)$. This confirms that the total
$S(Q)$ of amorphous Pd-19.8at%Si alloy is predominantly dominated by
Pd-Pd correlation even in neutron diffraction.

The $S_{PdSi}(Q)$ has a shoulder at high Q side of the first peak.
Such a shoulder has been found in $S_{FeP}(Q)$ of Fe-P and $S_{NiP}(Q)$ of Ni-P
amorphous alloys obtained by Waseda et al.[9,10] using anomalous X-ray
scattering technique. However, the first peak of $S_{CoP}(Q)$ of amorphous
Co-P alloy reported by Sadoc and Dixmier[11] does not show a well-
defined shoulder but an asymmetric profile extended to high Q region.
These characteristic behaviors of partial metal-metalloid pair inter-
ference functions are definitely originated from the well-defined
local coordination of metal atoms surrounding a metalloid atom.

The first peak of $S_{SiSi}(Q)$ appears at low Q region compared with
those of $S_{PdPd}(Q)$ and $S_{PdSi}(Q)$. This result is in good agreement with
the behavior of $S_{PP}(Q)$ in amorphous Ni-P and Fe-P alloys observed by
Waseda et al.[9,10] and in amorphous Co-P alloy by Sadoc and Dixmier[11].

As shown in Figure 4, the characteristic splitting of the second

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peak remains in $g_{PdPd}(r)$. The first-neighbor position for Pd-Pd correlation is 2.85 A which is a little larger than the value(2.80 A) observed by high resolution neutron total pair distribution function of amorphous Pd-Si alloy[1,2]. The first peak of $g_{PdSi}(r)$ is located at 2.60 A. This distance is fairly larger than the value(2.41 A) in high resolution neutron total pair distribution function[1,2]. These discrepancies are usually caused due to the truncation effect of Fourier transformation. Misawa and Suzuki[12] have demonstrated that the position of narrow first peak in pair distribution function converges gradually with increasing truncation value Q_{max} in inter-ference function. Therefore, Q_{max} values adopted in this work are too small to obtain exact values of the first peak positions particu-larly for narrow Pd-Si correlation. The first peak position in $g_{SiSi}(r)$ is about 3.2 A and the second peak is located closely to the first peak. The oscillation of subsequent peaks in $g_{SiSi}(r)$ is broader than those in $g_{PdPd}(r)$ and $g_{PdSi}(r)$. It can be said that Si atoms never be at the nearest neighbor position in amorphous Pd-Si alloy.

As shown in Figures 5 and 6, both of $S_{NN}(Q)$ and $g_{NN}(r)$ vary in a manner similar with $S_{PdPd}(Q)$ and $g_{PdPd}(r)$. This can be understood from equation (9) because of predominant content of Pd atoms with large scattering factor in amorphous Pd-19.8at%Si alloy. When the concentration fluctuation in A-B binary alloy is uncorrelated, i.e. $S_{AA}(Q)=S_{AB}(Q)=S_{BB}(Q)$, the relations of $S_{CC}(Q)=c_A c_B$ and $g_{CC}(r)=0$ are realized. On the other hand, $S_{CC}(Q)<c_A c_B$ and $g_{CC}(r)<0$ if unlike-atom A-B correlation predominantly exists, and $S_{CC}(Q)>c_A c_B$ and $g_{CC}(r)>0$ if like-atom A-A and B-B correlations are prefered. Although the accuracy of partial structure functions obtained in this work is much limited, the spatial fluctuation and segregation of constituent atoms are concluded to be very small in amorphous Pd-19.8at%Si alloy.

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