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# Small Angle X-Ray Scattering of Neutron- and Electron-Irradiated $Pd_{80}Si_{20}$ Amorphous Alloy*

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## Synopsis

Small angle X-ray scatterig (SAXS) was measured for neutron- and electron-irradiated $Pd_{80}Si_{20}$ amorphous alloy. The experimental SAXS intensity curves are well approximated by the Guinier formula below h=0.04 $\mathring{A}^{-1}$. The radii of gyration are almost same between electron-irradiated and aged sample, while neutron-irradiated sample shows a small radius of gyration.

## I. Introduction

Small angle X-ray scattering is a well suited technique for investigating the atomic density fluctuation over the region from about 10 to 1000 Å. As amorphous alloys are in the non-equilibrium state with disordered atomic arrangement, it is expected that the atomic density fluctuation in amorphous alloys produced by electron- and/or neutron-irradiation shows a characteristic behaviour different from that in crystalline alloys.

The neutron-irradiation effect for $Pd_{80}Si_{20}$amorphous alloy has been so far investigated by using various kinds of experimental technique1),2). Itoh et al.1) found from positron annihilation experiment that discrete voids as observed in crystalline metals were never created in $Pd_{80}Si_{20}$ amorphous alloy. Concerning X-ray structure factor S(Q) for $Pd_{80}Si_{20}$ amorphous alloy, however both the height and the width of the first peak in S(Q) suffer no appreciable change due to neutron-irradiation1). In the experiments mentioned above, the temperature during irradiating $Pd_{80}Si_{20}$ amorphous alloy has reached about 150 °C. Therefore, it is not elucidated whether the structural change observed is caused by irradiation or due to the rise of temperature.

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Doi et al.[2)] measured SAXS of $Pd_{80}Si_{20}$ amorphous alloy which was irradiated with fast neutrons to a fluence of $5 \times 10^{20}$ neutrons/$cm^2$. Based on the analysis of scattering curve near h=0.3 $Å^{-1}$($h=4\pi\sin\theta/\lambda$, $2\theta$:scattering angle), they concluded that structural inhomogeneities with the coherent region of about 8 Å diameter separated from each other by a mean distance of about 20 Å were produced.

In this study it is aimed at measuring SAXS of $Pd_{80}Si_{20}$ amorphous alloys neutron-irradiated at ambient temperature and electron-irradiated under liquid nitrogen temperature. In order to characterize large scale density fluctuation, particular attension is paid to the observation of the scattering curve below h=0.1 $Å^{-1}$. For comparison we measure SAXS of as-prepared and thermal annealed $Pd_{80}Si_{20}$ amorphous alloys, too.

## II. Experimental

$Pd_{80}Si_{20}$ amorphous alloy sample was prepared by rapid quenching from melt under Ar-gas atmosphere of 100 Torr into a thin plate form of 10 mm×10 mm×0.02mm. Several sheets of the sample were irradiated by fast neutrons up to a fluence of $9 \times 10^{18}$ n/$cm^2$ (>1MeV) using Japan Material Testing Reactor, Oarai Research Establishment, Japan Atomic Energy Reserch Institute (JAERI). The sample temperature was kept below 150 °C during the neutron-irradiation. Another several sheets of the sample were irradiated by 2.5 MeV electron up to a fluence of $1 \times 10^{18}$ e/$cm^2$ in liquid nitrogen with the electron accelerator located at Takasaki Radiation Chemistory Research Establishment, JAERI. One sheet of the sample was aged at 290 °C for 460 min in a vacuum of $10^{-6}$ mmHg to result in the formation of MS-I metastable phase[3)].

SAXS intensity curve were measured using a conventional long-slit SAXS spectrometer (Rigaku, 12 KW rotor unit), where a thick Pb-metal shield was set in front of an X-ray detecting counter to prevent the induced radiation of the irradiated sample from striking the detector. The spectrometer used may be regarded as equipping a infinitely long-slit system, if no SAXS is observed above the scattering angle of $2\theta=2.13°$. All the measurements were carried out with Mo-target at 50 KV and 140 mA in a room temperature.

## III. Results

The experimental scattering intensity J(h) was calculated using equation (1) as follows:

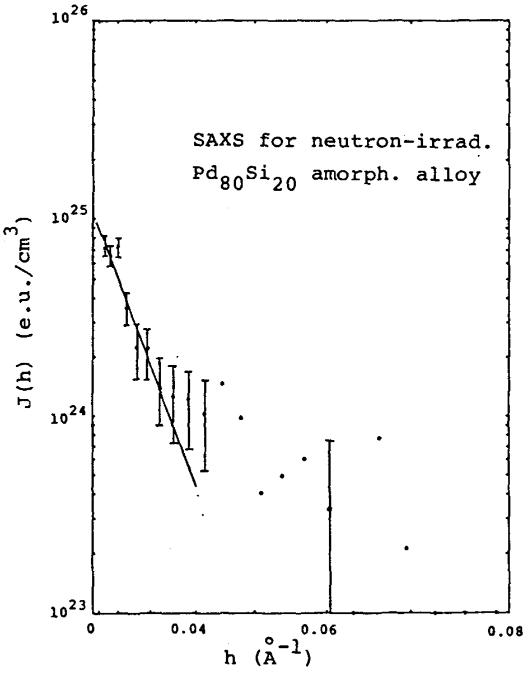

Fig.1. The Guinier plot for neutron-irradiated $Pd_{80}Si_{20}$ amorphous alloy

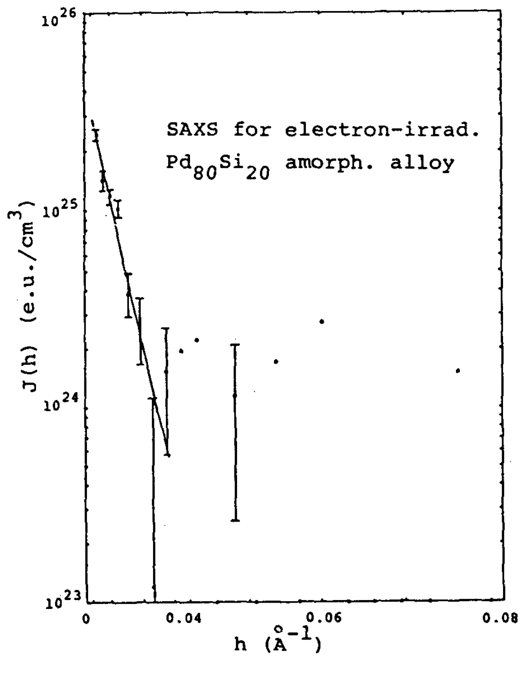

Fig.2. The Guinier plot for electron-irradiated $Pd_{80}Si_{20}$ amorphous alloy

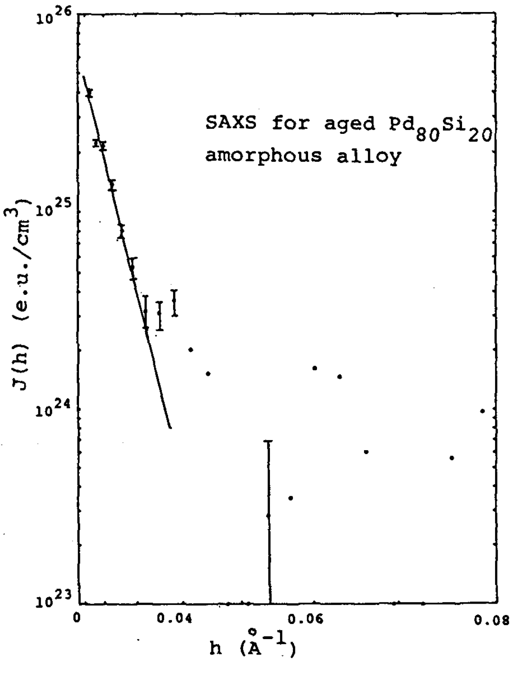

Fig.3. The Guinier plot for aged $Pd_{80}Si_{20}$ amorphous alloy

$$J(h)=\frac{\tilde{P}_{obs}}{(\tilde{P}_{obs})_{Lupolen,150\mathring{A}}}\times\frac{1}{t\times e^{-\mu t}}\times 0.0307\ (cm^{-1}) \qquad (1)$$

where $h(=4\pi\sin\theta/\lambda)$ is the scattering vector ($2\theta$:scattering angle, $\lambda$: wave length of incident X-ray). $\tilde{P}_{obs}$ is the photon count from sample . $(\tilde{P}_{obs})_{Lupolen,150\mathring{A}}$ is the photon count from Lupolen at a Bragg angle corresponding to d=150 Å, t is the sample thickness (cm) and $\mu$ is the absorption coefficient of sample.

The experimental results thus obtained for neutron-, electron-irradiated and aged sample are shown in Figs. 1 to 3 respectively. The experimental errors indicated by vertical bars in these figures mean the square-root of the sum of statistical variances of photon counts from the sample and background. The absolute values of the scattering intensity are of order of $10^{24}$ e.u./cm$^3$ in the irradisted and aged sample, which cannot be neglected but are relatively small. However we cannot observe the scattering intensity greater than $1\times10^{23}$ e.u./cm$^3$ for the as-prepared sample before irradiation. The observed SAXS intensity, therefore, corresponds to the effect of the irradiations and/or the thermal annealing.

Over the higher scattering vector range above h=0.06 Å$^{-1}$, it is not possible to distinguish the photon counts scattered by the sample from that by the background. Therefore we discard Porod plot.

Below h=0.04 Å$^{-1}$, the scattered intensities are well approximated by the Guinier formula as evidently shown in Figs 1 to 3. The values of radius of gyration Rg obtained from the Guinier plot combined with weighted least squares fitting are given as follows:

Rg=78.2±9.4 Å for neutron-irradiated sample
Rg=93.9±7.7 Å for electron-irradiated sample
Rg=94.0±4.9 Å for annealed sample.

## IV. Discussion

According to Masumoto et al.$^{3)}$, the globular metastable phase so called MS-I starts to precipitate in $Pd_{80}Si_{20}$ amorphous alloy aged at 290 °C for 460 minutes. By measuring the diameter of the globular precipitates in the transmission electron micrograph in their work, the average diameter of the MS-I precipitates can be estimated to be about 250 Å. In the present SAXS measurements, the diameter d of the globular particle is given by $2\sqrt{5/3}$ Rg using the radius of gyration Rg. Therefore the diameter 243±13 Å is obtained from the estimated value of Rg=94.0±4.9 Å. The both experiments give the nearly same values for the diameter of the annealing precipitate in $Pd_{80}Si_{20}$

amorphous alloy.

As well known, only one or two pairs of Frenkel-type defect are produced in the crystalline metal irradiated by electron beam of about 1 MeV. Therefore the value of Rg in irradiated metals must be the order of several Å. The experimental value of Rg is quite larger than the representative value of Frenkel-type defect. Furthermore the scattering intensity of the electron-irradiated sample has a nearly same pattern as that of the aged sample. These facts suggest that some crystalline precipitates such as MS-I may be accelerated in $Pd_{80}Si_{20}$ amorphous alloy even at liquid nitrogen temperature by electron beam irradiation. The acceleration of crystallization by room temperature electron-irradiation has already been found for Ni-B-Si, Ni-P-B and Ni-P amorphous alloys$^{4)}$.

As for the fast neutron-irradiated $Pd_{80}Si_{20}$ amorphous alloy, Itoh et al.$^{1)}$ concluded from their experiments of both positron annihilation and X-ray diffraction that the voids larger than single vacancy were not produced by neutron-irradiation without any sign of crystalline precipitation.

The average energy of neutrons used for irradiating $Pd_{80}Si_{20}$ amorphous alloy is about 2 MeV. Using the Kinchin-Pease model, the approximated number of atoms displaced by 2 MeV neutron collision is given $(1/A)\times(En/Ed)\sim(1/100)\times(2\times10^6/25)=800$, where A is the atomic number, $E_n$ is the neutron energy and $E_d$ is the atomic displacement energy. Since the volume per $Pd_{0.8}Si_{0.2}$ molecular formula is 14.3 $Å^3$ in $Pd_{80}Si_{20}$ amorphous alloy, the spatial fluctuation extending over $14.3 \times 800 = 1.14\times10^4$ $Å^3$ can be brought about by one neutron. If the shape of the fluctuation induced by neutron-irradiation is supposed to be spherical, its volume is $(4\pi/3)\times(5Rg/3)^3=(4.3\pm1.7)\times10^6$ $Å^3$ using the radius of gyration Rg=78.2 9.4 Å estimated in Fig.1. This value is much larger than the value estimated above. Therefore, the shape of the fluctuation brought about into $Pd_{80}Si_{20}$ amorphous alloy by neutron-irradiation can not be approximated by the sphere. When the shape is approximated by an ellipsoid of revolution (a,a,va), of which volume is $(4\pi/3)va^3\sim1.14\times10^4$ $Å^3$ and radius of gyration is $\surd(2+v^2)/5\times a\sim78.3$ Å, we obtain two different types of the shape, a prolate of v=43, a=4 Å and an oblate of $v=1.5\times10^{-3}$, a=122 Å. A prolate (4 Å,4 Å,170 Å) may be more realistic than an oblate (122 Å, 122 Å,0.18 Å).

## V. Conclusion

(1) From the results of SAXS experiments, it is found that the larger region of spatial fluctuation is produced by the low temperature electron irradiation compared with the neutron irradiation in $Pd_{80}$-$Si_{20}$ amorphous alloy.

(2) The similarity of the SAXS results between the electron-irradiated and the aged $Pd_{80}Si_{20}$ amorphous alloy suggests that the electron irradiation may accelerate the crystallization of $Pd_{80}Si_{20}$ amorphous alloy such as metastable phases like MS-I state even at liquid nitrogen temperature.

(3) On the contrary, the neutron irradiation gives the spatial fluctuation with the radius of gyration of Rg=78.2±9.4 Å in $Pd_{80}Si_{20}$ amorphous alloy. Consideration of the number of displaced atoms suggests that this spatial fluctuation has non-spherical shape (i.e., prolate or oblate) which still preserves the amorphous state.

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