

Anomalous small-angle scattering from nanoquasicrystalline precipitates in $\text{Zr}_{80}\text{Pt}_{20}$ ribbons

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Synopsis Anomalous small-angle scattering of quasicrystals in a Zr-Pt binary alloy was examined at Zr K absorption edge. Small differences in both density and composition were found between the quasicrystals and the amorphous matrix.

Abstract Anomalous small-angle X-ray scattering (ASAXS) profiles of $\text{Zr}_{80}\text{Pt}_{20}$ ribbons have been measured at Zr K absorption edge. By annealing the melt-spun ribbons at 800 K, a well-defined SAXS patterns from nanoquasicrystals were observed although the compositions of quasicrystals and the amorphous matrix have been reported to be the same. The SAXS intensities were found to show small anomalous effect at the Zr K edge. Contrast analysis suggested that the origin of small-angle scattering is a small compositional fluctuation coupled with a small density difference which enhances SAXS intensity, but reduces the anomalous effect. A constant ASAXS intensity ratio for QC microstructure suggests that the ratio of the composition difference to the density difference between QC and the amorphous is almost constant for the ZrPt ribbons examined here.

Keywords: Zr-Pt, quasicrystal, anomalous small-angle X-ray scattering

1. Introduction

In Zr-Pt and Zr-Pd binary alloys, quasicrystals (QC) with a size of a couple of nanometers have been reported to precipitate on annealing melt-spun ribbon samples at temperatures between 700 K and 840 K (Saida, Matsushita & Inoue 2000a; 2000b; Murty et al., 2001). The mechanism of these nano-quasicrystallization has attracted attention from a viewpoint that it may help understanding the local stabilization mechanism of the glass/amorphous in conjunction to the icosahedral SRO or clusters in the metal-metal type of bulk metallic glass samples (Saida, Matsushita & Inoue 2000b; Xing et al., 2000; Murty et al., 2000).

By examining precipitation processes in Zr-Pt binary alloys using transmission electron microscopy (TEM) with composition analysis by nanobeam fluorescence analysis using an Energy Dispersive X-ray (EDX) detector, Saida et al. (2000b) concluded that the nanoscale QCs appearing on annealing $\text{Zr}_{80}\text{Pt}_{20}$ melt-spun ribbons have no appreciable concentration difference from the amorphous matrix. Their result suggests that the difference between the quasicrystals and the amorphous matrix may be purely the difference in the atomic arrangements, i.e., density. On the

contrary, the composition of nano-quasicrystals was found to be different in Zr-Pd alloys, where precipitation process was analyzed by using conventional Avrami analysis (Murty et al., 2001). Whether the nanocrystallization in the alloy gives a pure density contrast or is associated with a composition modulation is an important question to understand the nature of structure stability and the kinetics of quasicrystallization of the alloy. If there is no composition change during precipitation of quasicrystals, it means that the transformation is congruent and no long-range diffusion is required for nucleation and growth. This model implies that the kinetics of quasicrystallization process in Zr-Pt may be quite different from that of Zr-Pd if the picture of pure density fluctuation holds. However, it is quite difficult to tell whether and how the compositional partitioning is incorporated in the formation of nanoQC, since the difference is below detection limit of experimental techniques for composition evaluation.

In the present work, we measured anomalous small-angle scattering intensities at the K absorption edge of Zr to examine the nature of fluctuation in the annealed Zr-Pt ribbons. Medium angle range of the scattering vector up to 12 nm^{-1} was also measured simultaneously to examine if Bragg peaks for crystalline phases appear (Okuda et al., 2006; 2007).

2. Experimental

Zr-Pt ribbons were prepared by melt-quenching the sample by a copper wheel rotating at 40 m/s at the surface. The size of the ribbons was 1 mm width x 0.02 mm thickness. The initial conditions of the samples were checked by X-ray diffraction measurements of as-quenched samples. The samples were then annealed at 800 K in Ar atmosphere to form QC precipitates. The first halo gradually split to show Bragg peaks corresponding to formation of QC (Saida et al., 2000a).

Small-angle scattering measurements were carried out at beamline 40B2 of Spring8, Hyogo Japan. In order to suppress background, the SAXS camera was fully evacuated and no Kapton windows were left between the guard slits, samples and the direct beam stop. The scattering intensity was normalized by the integrated intensity of delta prime precipitates in an Al-8at%Li binary alloy (Okuda et al, 2006). The photon energies of the incident beam were chosen as 17.995 keV for the near-edge condition, and 17.720 keV for the far-edge condition.

3. Results and Discussion

Figure 1 (a) shows the SAXS profiles of as melt-spun and isothermally annealed samples as a function of the magnitude of the scattering vector, $q=4\pi \sin(\theta)/\lambda$ for the far-edge condition. The SAXS intensity for the as-quenched ribbon is the weakest, with simple power-law component with $I(q)$ proportional to $q^{-3.2}$ at small q , which is quite often seen in the small-angle scattering measurements for metallic glasses (Maret et al., 1989; Okuda et al., 2007). A very small diffuse scattering between $q=0.5$ and 2 nm^{-1} is seen for the as melt-spun sample, suggesting that formation of nano QCs during melt-spinning was quite small. The intensity markedly increases with annealing time. Figure 1 (b) gives the intensity profiles at larger q , showing that a well-defined Bragg peak corresponding to formation of crystalline phase with $d=0.726 \text{ nm}$ appears on annealing for 3.6 ks. The SAXS profiles for the sample with the annealing time up to 1.8 ks, therefore, correspond to the scattering from QCs, and for 3.6 ks, the profile corresponds

to the scattering from a mixture of QCs and large crystalline phases. SAXS profiles for the sample annealed for 0.9 ks at the two photon energies are shown in Fig. 2. The shapes of the scattering intensity agree well each other, and the intensity is slightly stronger for the near edge condition. Therefore, we may use a common form factor to describe the microstructure between the two energies, and the anomalous dispersion effect only concerns the scattering contrast that changes the magnitude of the intensity.

The change of the size of nano QCs during annealing is shown in Fig.3. The radius of gyration, R_g , was 1.2 nm for 0.9 ks and 1.9 nm for 1.8 ks. At 3.6 ks of annealing, well-defined Bragg peak as shown in Fig. 1 suggests that large crystals of metastable phase appears at this stage, whose SAXS should appear at much smaller q , and nanoQCs do not grow any more. Therefore, the SAXS profiles for 0.9 ks and 1.8 ks of annealing represent scattering intensities from the microstructures of nanoQCs and the amorphous matrix. In the following analysis, these two conditions are used to examine the contrast between nanoQCs and the amorphous matrix.

SAXS intensity is given by ;

$$I(q) = A(q)A^*(q)$$

with

$$A(q) = \int \Delta f(r, E) \exp(iqr) dr \quad (1)$$

where

$$\Delta f(r, E) = \Delta \{ f_{Pt} c(r) + f_{Zr} (1 - c(r)) \} n(r) \quad (2)$$

i.e.,

$$\frac{\Delta f}{c_0 n_0} \equiv (f_{Pt} - f_{Zr}) \cdot \Delta \tilde{c}(r) + \frac{\bar{f}}{c_0} \Delta \tilde{n}(r) \quad (3)$$

$\Delta \tilde{c}$ and $\Delta \tilde{n}$ are the composition and density difference normalized by the average composition and density, respectively, and $\bar{f} = c_0 f_{Pt} + (1 - c_0) f_{Zr}$.

In general, SAXS intensity from microstructures having both composition and density fluctuation is given by (Bartia & Thornton, 1970),

$$I(q) = \alpha^2 S_{cc}(q) + 2\alpha\beta S_{cn}(q) + \beta^2 S_{nn}(q) \quad (4)$$

where S_{cc} , S_{cn} , S_{nn} are the Fourier transform of the correlations and cross-correlation of composition, $\Delta \tilde{c}(r)$, and density, $\Delta \tilde{n}(r)$. α and β are the coefficients related to the scattering factors as described below.

Since well-defined spherical nano-quasicrystals are observed after annealing the present samples (Saida, Matsushita & Inoue, 2000b), we may use two-phase model for the analysis. Then the contrast is given by the difference in composition and density between the QCs and the matrix, Δc and Δn , with the form factor for a sphere of a radius R given by

$$\Phi(q) = 3v \frac{(qR \cos qR - \sin qR)}{(qR)^3}.$$

Equation (4) is then simplified as ;

$$I(q, E) = \{\alpha(E)\Delta\tilde{c} + \beta(E)\Delta\tilde{n}\}^2 \Phi^2(qR) \quad (5)$$

with

$$\alpha(E) = c_0 n_0 (f_{Pt}(E) - f_{Zr}(E))$$

and

$$\beta(E) = n_0 \bar{f}(E).$$

The ratio of scattering intensity at the far edge to that at the near edge is then given by

$$R = \frac{I_{far}(q)}{I_{near}(q)} = \frac{\{\alpha(E_{far})\Delta\tilde{c} + \beta(E_{far})\Delta\tilde{n}\}^2}{\{\alpha(E_{near})\Delta\tilde{c} + \beta(E_{near})\Delta\tilde{n}\}^2} \quad (6)$$

If the composition between the QCs and the amorphous matrix is exactly the same, then $\Delta c=0$ and the contrast is given by Δn . The ratio of the scattering intensity between that for the far edge and that for the near edge is then given as:

$$R_n = \frac{I_{far}(q)}{I_{near}(q)} = \frac{\bar{f}(E_{far})^2}{\bar{f}(E_{near})^2} \quad (7)$$

for the pure density fluctuation, and

$$R_c = \frac{I_{far}(q)}{I_{near}(q)} = \frac{(f_{Pt}(E_{far}) - f_{Zr}(E_{far}))^2}{(f_{Pt}(E_{near}) - f_{Zr}(E_{near}))^2} \quad (8)$$

for the opposite case where density is uniform and small difference in the composition, Δc , is the origin of the small-angle scattering. The equations (7) and (8) show that the ratio of the scattering intensity between the two energies depends only on the origin of the contrast, namely, whether it is composition fluctuation or density fluctuation, and does not depend on the amplitude of the fluctuation. This is an important point, since the EDX result (Saida et al, 2000) implies that the difference in the composition between the nano-QC is within experimental error, and it is difficult to discuss whether the compositional modulation is essential for the quasicrystallization of the alloy.

Real part of the atomic scattering factors, $f_0 + f'$, for Zr and Pt (Sasaki, 1988) based on Cromer and Liberman (1970) and that calculated for the sample composition are shown in Table I for the near edge and the far edge conditions. The contrast by compositional fluctuation is proportional to $f_{Pt} - f_{Zr}$, and increases as the incident photon energy comes closer to the absorption edge. R_c calculated from the table was 0.79. On the contrary, the scattering contrast is weaker for the density fluctuation at the near edge condition, giving $R_n = 1.19$. The experimental ratio for the intensities corresponding to the well-defined nanoQCs, i.e., those for 0.9 ks and 1.8 ks of annealing, were 0.96 and 0.94, respectively. This suggests that the origin of the scattering contrast is neither simple compositional partitioning nor density fluctuation alone.

To understand the results, a model is required for a coupled fluctuation of density and composition with very weak amplitude. Considering the XAFS results (Saida et al, 2007) that the interatomic distances for Pt-Pt and Zr-Zr are almost the same, but that for Pt-Zr is smaller, we may write down the change in density induced by a composition change of Δc from the sample composition $c_0=0.2$ as :

$$\frac{\Delta n}{n_0} = 3.6\varepsilon\Delta c$$

where

$$\varepsilon = \frac{d_{Zr-Zr} - d_{Zr-Pt}}{\bar{d}_{Zr0.8Pt0.2}}$$

by assuming that the average interatomic distance is given by an average of Zr-Zr, Pt-Pt and Pt-Zr pairs with random solution approximations. Then the ratio for such coupled intensity is given by ;

$$R_{coupled} = \left(\frac{(f_{Pt}(E_{far}) - f_{Zr}(E_{far})) + 3.6\varepsilon \cdot \bar{f}(E_{far})}{(f_{Pt}(E_{near}) - f_{Zr}(E_{near})) + 3.6\varepsilon \cdot \bar{f}(E_{near})} \right)^2. \quad (9)$$

Substituting the interatomic distances by reported ones (Saida et al, 2007), the calculated ratio of 0.92 was found to be in much better agreement with the experimental results. Therefore, we may conclude that the contrast that gives small-angle scattering for nanoQC particles formed during annealing of melt-spun $Zr_{80}Pt_{20}$ ribbons at 800K is well explained by a small compositional difference and the density change associated with the composition change. Concerning the anomalous effect, whether the contrast is enhanced at the far edge or at the near edge, composition and density have the opposite effect as shown in Table I. Since the ASAXS ratio of 0.95 is slightly larger than the calculated one of 0.92, and eq. (6) has two analytical solutions, there might be some room left for further discussion.

Figure 4 shows the calculated ratio $I(far)/I(near)$ as a function of $\Delta\tilde{c}/\Delta\tilde{n}$. The ratio agrees with R_c at $\Delta\tilde{c}/\Delta\tilde{n} = \pm\infty$.

Substituting R in eq. (6) by the experimental results, one obtains two solutions,

$$\frac{\Delta\tilde{n}}{\Delta\tilde{c}} = \frac{\pm\alpha_{far} - \sqrt{R_{exp}}\alpha_{near}}{\sqrt{R_{exp}}\beta_{near} \mp \beta_{far}} \quad (10)$$

which are shown by the intersections of the calculated ratio and the line of the experimental ratio, R_{exp} in Fig. 4. The two solutions have the opposite sign, meaning that the Pt rich region may denser or sparser in density. However, considering that eq. (7) suggest positive solution, and also the calculated result that the negative solution in (8) gives a very weak contrast resulting in no appreciable SAXS intensity, it is concluded that $\Delta\tilde{c}/\Delta\tilde{n}$ should be positive. Accordingly, we obtain

$$\Delta c = \Delta\tilde{n} \frac{c_0}{0.17} = 1.2\Delta\tilde{n}. \quad (11)$$

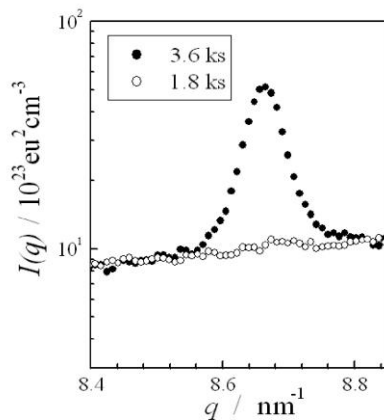
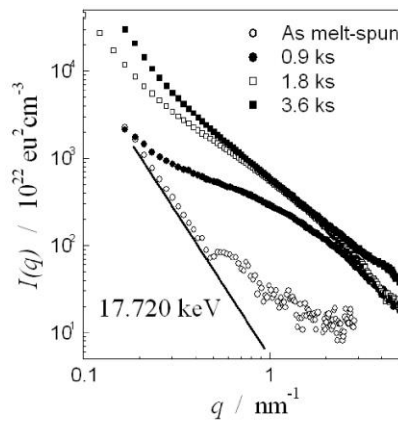
The present results show that the nanoscopic quasicrystals in Zr-Pt alloys have a small but well-defined contrast from the amorphous matrix. The contrast consists of a density and a composition contributions with a same order of magnitude. These two contributions enhance the scattering contrast together, but cancel the anomalous dispersion effect each other.

4. Conclusions

Anomalous small-angle scattering measurements for $Zr_{80}Pt_{20}$ ribbons at Zr K absorption edge have been performed. By annealing at 800 K up to 1.8 ks, nanoquasicrystals with about 1 to 2 nm in radius were formed and grew. At 3.6 ks of aging, nanoquasicrystallization was followed by the formation of large metastable crystals.

The ratio analysis based on the anomalous effect suggested that the quasicrystals precipitated in Zr-Pt ribbons have both a weak composition and a weak density contrast, meaning that the precipitates include small compositional change. The two contrasts increased the scattering intensity, but cancelled the anomalous effect. Experimental results suggest that the local density fluctuation is slightly higher than the one expected from simple calculations estimated from interatomic distances associated with composition change.

(a)



(b)

Figure 1 SAXS profiles (a) and the Bragg peak profiles at higher q (b) for the far-edge condition. A well-defined Bragg peak appeared at 3.6 ks of annealing.

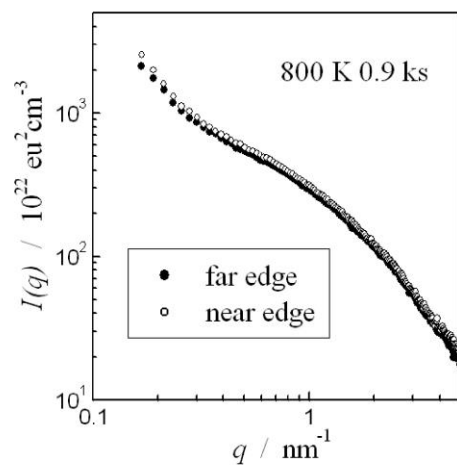


Figure 2 The scattering intensities measured at the near edge and the far edge conditions for the ribbons annealed at 800 K for 0.9 ks.

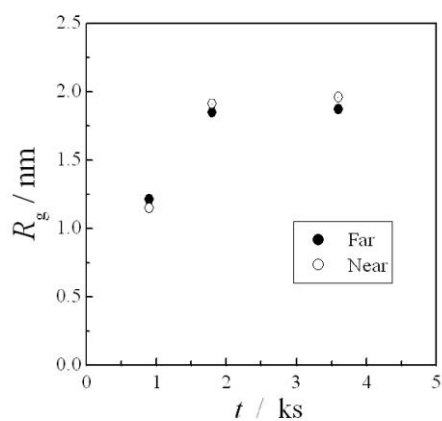


Figure 3 Temporal evolution of gyration radius during annealing.

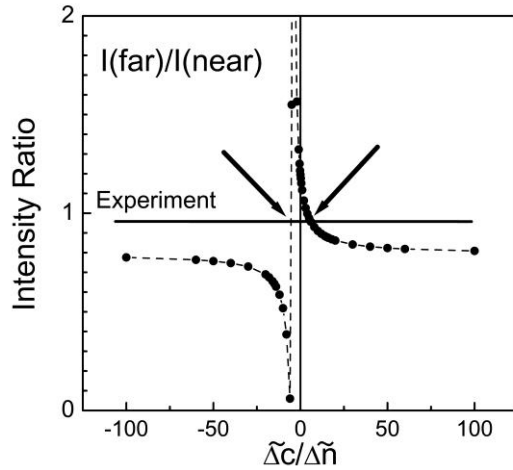


Figure 4 Ratio of scattering intensities calculated as a function of relative compositional difference normalized by relative density difference. The arrows are the two solutions of the equation (8).

Table 1 Real part of the contrast at the near edge and the far edge conditions in electrons (Sasaki, 1988).

	f_{Zr}	f_{Pt}	$(f_{Pt}-f_{Zr})$	$\overline{f}$
near edge	31.56	75.82	44.25	40.42
far edge	36.30	75.71	39.41	44.18

Acknowledgements Present work was financially supported by Grant-in-Aid for Scientific research, Priority Area ‘Materials Science of Metallic Glasses’, under proposal number 15074210.

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