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Local structure characterization in quasicrystal-forming $Zr_{80}Pt_{20}$ binary amorphous alloy

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The local structure of melt-spun $Zr_{80}Pt_{20}$ alloy was investigated in the amorphous and icosahedral quasicrystal (QC)-formed states by x-ray diffraction and extended x-ray absorption fine structure measurements. While the local environment around the Zr atom in the amorphous state is considerably different from that in the QC-formed state, it remains during the quasicrystallization around the Pt atom. It is suggested that the stable icosahedral local structure is mainly formed in the center of the Pt atom in the amorphous state. © 2007 American Institute of Physics.

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Recent discoveries of nanoquasicrystallization in Zr–Al–Ni–Cu multicomponent metallic glasses with high glass-forming ability^{1–5} have led us to new aspects of local structure investigation in the glassy state. The formation of a nanoicosahedral quasicrystalline phase (I phase) suggests the possibility of a common structure between the I phase and local atomic configuration in the glassy state.⁶ We have already reported the local structural similarity between the glassy and quasicrystal-formed states in the Zr–Al–Ni metallic glass.⁷ In recent series of local structural studies, the authors obtained the conclusion that the stability of a supercooled liquid state is strongly correlated with the icosahedral local structure.^{8,9}

I-phase formation has also been reported in Zr–Pd and Zr–Pt binary alloys.^{10–13} These results lead us to another hypothesis that the icosahedral local structure may be formed in the corresponding binary systems. Takagi *et al.* reported local structural studies of the $Zr_{70}Pd_{30}$ metallic glass in both amorphous and QC phase-precipitated states.¹⁴ They concluded that the I phase can be precipitated easily from the quenched-in icosahedral clusters around the Zr atom. However, no significant studies of local structure analysis have been reported for the QC-forming Zr–Pt binary alloy. In this letter, we investigate the detailed structure and local environment around Zr and Pt atoms in the nano QC-forming $Zr_{80}Pt_{20}$ amorphous alloy by radial distribution function (RDF) analysis and x-ray absorption fine structure (EXAFS) measurement.

The amorphous ribbon was prepared by single-roller melt quenching with the Cu roll speed of 60 m/s. The oxygen content in the prepared ribbon sample was approximately 400 mass % ppm. The local atomic structure was studied by ordinary x-ray diffraction (XRD) measurements with monochromatic Mo $K\alpha$ radiation of 50 kV, 30 mA pro-

duced by a rotating anode x-ray generator. The coordination number N and interatomic distance r between the constituent elements were calculated by fitting an interference function $Qi(Q)$ and RDF. EXAFS measurements were performed at the SPring-8 synchrotron radiation facility on beam line BL01B1. All measurements were done in transmission geometry at room temperature. The mean-square fluctuation parameter σ^2 appearing in the Debye-Waller (DW) factor $\exp(-2k^2\sigma^2)$ in the EXAFS formula was obtained by least-squares fitting in k space, using the structural parameters of r and N and theoretical phase shifts and backscattered amplitude functions calculated by the FEFF-8 code.

We previously reported that the $Zr_{80}Pt_{20}$ amorphous alloy has a two-stage crystallization process, where the first exothermic reaction with an onset temperature of 717 K corresponds to the precipitation of the nano-I phase.¹⁵ The second reaction, of which the peak temperature is 923 K, corresponds to the decomposition of the I phase into Zr+ZrPt + Zr_5Pt_3 + Zr_9Pt_{11} phases. In this study, we have fixed the annealing condition as 820 K for 300 s for the evaluation of QC-formed state. A homogeneous amorphous structure in the as-quenched state and the precipitation of nano-I phase in the annealed state were confirmed by transmission electron microscopy. However, some residual amorphous regions were simultaneously observed in the annealed sample. Figure 1(a)

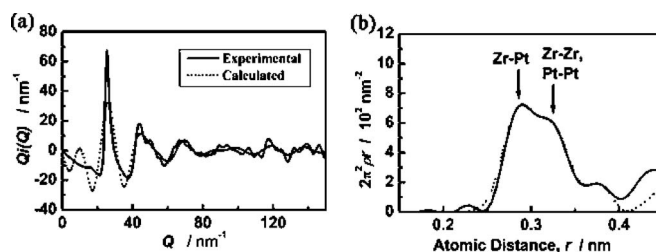


FIG. 1. (a) $Qi(Q)$ of the $Zr_{80}Pt_{20}$ amorphous alloy. The solid and dotted curves are the experimental and calculated ones, respectively. (b) RDF curve obtained from the FT of $Qi(Q)$.

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TABLE I. Nearest-neighbor atomic distances (r) and coordination numbers (N) calculated from RDF results.

Pairs	r (nm)	N
Zr–Zr	0.326 ± 0.002	8.8 ± 0.3
Zr–Pt	0.286 ± 0.001	2.3 ± 0.2
(Pt–Zr)		(9.3 ± 0.2)
Pt–Pt	0.326 ± 0.002	1.8 ± 0.2

shows the $Q_i(Q)$ of the $Zr_{80}Pt_{20}$ amorphous alloy as the solid curve.¹⁶ The dotted curve represents the calculated result. The calculated curve agrees with the experimental result in the first nearest-neighboring shell. The RDF curve is shown in Fig. 1(b). The fitted positions of the Zr–Zr, Zr–Pt, and Pt–Pt pairs are indicated in the figure. Based on the RDF curve, we calculated r and N , as shown in Table I. The r of Zr–Zr can be fitted by 0.326 nm, which is close to the calculated value of 0.320 nm. On the other hand, the r of the Pt–Pt pair (0.326 nm) is significantly longer than the value expected from its atomic radius (approximately 0.278 nm), which implies that the Pt atom forms a different local structure. The total coordination numbers around Zr and Pt are both 11.1. Since they are close to 12.0, it suggests the possibility of the existence of an icosahedral-like local environment around both atoms. The authors have already reported the RDF analysis in the QC-precipitated $Zr_{80}Pt_{20}$ alloy prepared by lower quenching rate.¹⁷ The total coordination numbers around Zr and Pt atoms are 14.2 and 12.4, respectively. Considering the similar total coordination numbers around the Pt atom in the amorphous and QC-precipitated alloys, we speculate that the icosahedral-like local environment around the Pt atom is more stable than that around the Zr atom.

The k^3 -weighted EXAFS spectra of the Zr K edge (a) and Pt K edge (b) in the as-quenched and QC-formed states are shown in Fig. 2. The calculated results of the icosahedral cluster model and Zr_5Pt_3 structure, which is one of the major precipitated phases after the decomposition of the I phase, of the both edges are also shown. The corresponding atomic

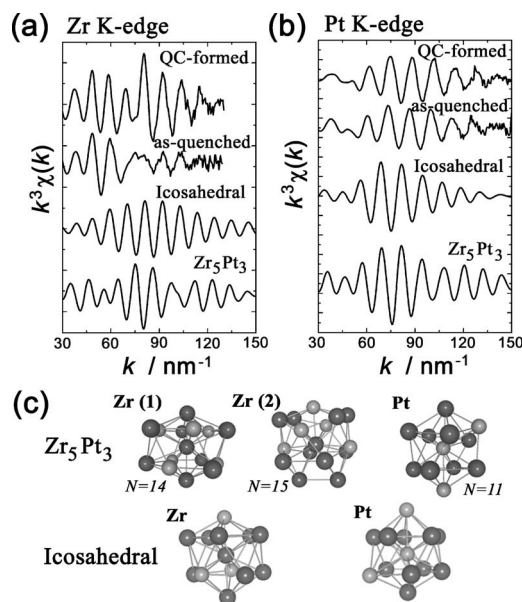


FIG. 2. k^3 -weighted EXAFS spectra of the Zr K edge (a) and Pt K edge (b) in the as-quenched and QC-formed states. The corresponding atomic structures of the icosahedral cluster and Zr_5Pt_3 are schematically denoted in (c).

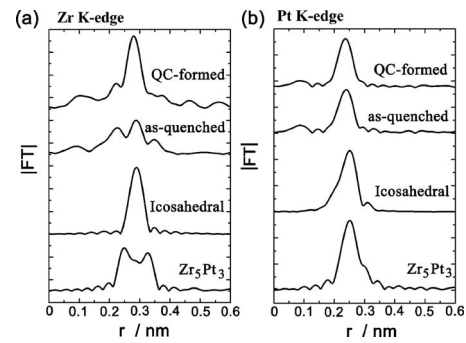


FIG. 3. FT curves of EXAFS measurements of the Zr K edge (a) and Pt K edge (b) in the as-quenched and QC-formed states.

structures of the icosahedral cluster and Zr_5Pt_3 are schematically denoted in Fig. 2(c). Here, the icosahedral cluster model is constructed based on the fitting results of r and N in Table I. For example, it has nine Zr and three Pt atoms around Zr, which is basically defined by the coordination numbers of Zr–Zr (8.8 ± 0.3) and Zr–Pt (2.3 ± 0.2). The pair distance is also reflected. The calculated result of the Zr K edge of the Zr_5Pt_3 structure is combined with those of two kinds of Zr atomic sites. The EXAFS spectrum around the Zr K edge in the as-quenched state has a significantly different periodic oscillation compared with that of the icosahedral cluster model as well as the Zr_5Pt_3 structure. In the QC-formed state, it is the same as that of the icosahedral cluster model rather than that of the Zr_5Pt_3 structure. On the other hand, the oscillations of measured results in the both states are very similar to each other around the Pt K edge and they have a similar period to that of the icosahedral cluster model.

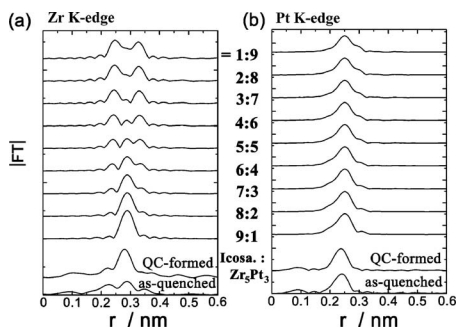
Figure 3 shows Fourier transformation (FT) curves of EXAFS measurements of the Zr K edge (a) and Pt K edge (b) in the as-quenched and QC-formed states together with those of the icosahedral and Zr_5Pt_3 structure models. The atomic distribution changes during the precipitation of the QC phase around the Zr K edge, as shown in Fig. 3(a), implying that the rearrangement of Zr atoms is necessary for quasicrystallization. While the QC-formed state has a significantly different local environment from that of the Zr_5Pt_3 structure, the sharp peak at around $r=0.32$ nm in the measured curve is similar to that of the icosahedral cluster model. However, the shoulder peak in the lower distance at around $r=0.22$ nm cannot be fitted to the icosahedral cluster model. In contrast, the FT curves of the Pt K edge in the as-quenched and QC-formed states resemble each other. The curves can be fitted by the icosahedral cluster model well rather than by the Zr_5Pt_3 structure model. Here, the shoulder peak around $r=0.2$ nm in the icosahedral cluster model corresponds to that of the experimental ones. Moreover, the shoulder peak appeared around $r=0.3$ nm in the Zr_5Pt_3 model does not fit in the experimental curves. These results indicate the existence of the stable icosahedral local structure around the Pt atom in the $Zr_{80}Pt_{20}$ amorphous alloy. The result is also consistent with that of RDF fitting. However, the experimental results for the two states cannot be fitted perfectly by the single icosahedral model, indicating the possibility of the existence of another local environment. Meanwhile, it is noted that the tendency is different from that revealed in the previous study in the $Zr_{70}Pd_{30}$ metallic glass, where the icosahedral local structure is formed around the Zr atom.¹⁴ The reason of different conclusions in the two binary alloys is still unclear, but

TABLE II. Structural parameter fitting results of EXAFS measurements in the as-quenched and QC-formed states.

	Pairs	r (nm)	N (fixed)	DW (nm)
As quenched	Zr–Zr	0.311 ± 0.007	8.3	0.0155 ± 0.003
	Zr–Pt	0.276 ± 0.007	2.3	0.0114 ± 0.006
	(Pt–Zr)		(9.3)	0.0106 ± 0.001
	Pt–Pt	0.311 ± 0.003	1.8	0.0120 ± 0.006
QC formed	Zr–Zr	0.316 ± 0.004	8.8	0.0141 ± 0.002
	Zr–Pt	0.273 ± 0.005	2.3	0.0105 ± 0.005
	(Pt–Zr)		(9.5)	0.0100 ± 0.001
	Pt–Pt	0.315 ± 0.003	2.9	0.0131 ± 0.010

it may be due to the difference in the chemical affinity between Zr–Pd and Zr–Pt. Table II summarizes the results of structural parameter fitting of EXAFS measurements in the as-quenched and QC-formed states. In these analyses, we fixed the coordination numbers of Zr–Pt (Pt–Zr), Zr–Zr, and Pt–Pt pairs, which were determined by RDF analysis.^{16,17} The distance of each pair remains almost constant during the precipitation of the QC phase. All of distances are also consistent with those in the RDF parameter fitting results. The DW factors of the Zr–Zr pair in both states are significantly larger than those of other pairs, which indicates that the Zr–Zr pair is in the more disordered state, i.e., it has several kinds of local environments. The decrease of the DW factor of the Zr–Zr pair during quasicrystallization implies the occurrence of rearrangement by ordering. Other pairs have low DW factors and they have comparatively small reductions during quasicrystallization. This result indicates the existence of a stable local structure especially around the Pt atom, which does not change upon QC formation. This is highly consistent with the results of the formation of the icosahedral local structure around Pt by RDF and EXAFS measurements.

In order to characterize the detailed local environments, we applied the mixed local structure model of the icosahedral and Zr_5Pt_3 structures. Figure 4 shows the calculation results of FT curves around the Zr K edge (a) and Pt K edge (b) for various ratios of the icosahedral and Zr_5Pt_3 local structure models. The curve of the ratio of the icosahedral cluster to the Zr_5Pt_3 structure of 6:4 well corresponds to the measured result around the Zr atom for the as-quenched state. The well-fitted curve changes the ratio of 8:2 for the experimental curve of the QC-formed state. The increase of the ratio of the icosahedral cluster during quasicrystallization

FIG. 4. Calculation results of FT curves around Zr K edge (a) and Pt K edge (b) for various ratios of icosahedral and Zr_5Pt_3 local structure models.

is very reasonable. However, the Zr_5Pt_3 local structure of approximately 20% can be estimated even in the QC-formed state, which suggests that the Zr atom has the Zr_5Pt_3 local structure in the residual amorphous region. The local environment around the Pt atom in the as-quenched state as well as in the QC-formed state can be characterized as having a higher ratio of the icosahedral local structure (80%–90%), which is clearly identified by the disappearance of the shoulder peak around $r=0.3$ nm observed in the curve of a lower ratio of the icosahedral cluster. This is due to the contribution of most Pt atoms to the formation of icosahedral local structures. Therefore, it is concluded that the two kinds of local environments of the icosahedral and Zr_5Pt_3 local structures can be applied around Zr and Pt atoms in the $Zr_{80}Pt_{20}$ amorphous alloy. The fraction of the icosahedral local structure around the Pt atom is more than that around the Zr atom.

In the present study, we described the results of the local structural investigation of QC-forming $Zr_{80}Pt_{20}$ amorphous alloy. We obtained evidence of the existence of the stable icosahedral local structure around the Pt atom as the dominant structure with a minor fraction (10%–20%) of a Zr_5Pt_3 -like structure. This feature does not change very much upon the precipitation of quasicrystal. In contrast, a mixture environment of the icosahedral and Zr_5Pt_3 local structures around the Zr atom was suggested. We estimated the fraction of the Zr_5Pt_3 local structure to be approximately 40%. Moreover, about 20% of the Zr_5Pt_3 local structure still remained after quasicrystallization.

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