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Evaluation of the local environment for nanoscale quasicrystal formation in $Zr_{80}Pt_{20}$ glassy alloy using Voronoi analysis

Junji Saida^{1,7}, Keiji Itoh², Shigeo Sato³, Muneyuki Imafuku⁴, Takashi Sanada⁵ and Akihisa Inoue⁶

¹ Center for Interdisciplinary Research, Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

² Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan

³ Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

⁴ Materials Characterization Center, Nippon Steel Technoresearch Corporation, Futtsu, Chiba 293-0011, Japan

⁵ Research Department, Nissan ARC Ltd, Natsushima, Yokosuka 237-0061, Japan

⁶ WPI-AIMR, Tohoku University, Sendai 980-8577, Japan

E-mail: jsaida@cir.tohoku.ac.jp

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Abstract

The local atomic structure of nano-quasicrystal-forming $Zr_{80}Pt_{20}$ binary glassy alloy was investigated by reverse Monte Carlo modeling based on the results of x-ray diffraction. A prepeak at $Q \sim 17 \text{ nm}^{-1}$ originating from the unique bonding between the Pt–Pt pair is observed in the structure factor. Voronoi analysis indicates that an icosahedral-like polyhedron is formed around Pt. It is also found that icosahedral-like polyhedra exist around Zr; however, the fraction of perfect icosahedra is considerably lower than that in the nano-quasicrystal-forming $Zr_{70}Pd_{30}$ glassy alloy. A difference in the local environment between the two binary quasicrystal-forming glassy alloys is suggested.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is well known that Zr-based metallic glasses have a high glass-forming ability (GFA) [1, 2]. Because nano-quasicrystallization is observed in various Zr-based metallic glasses such as Zr–Al–Ni–Cu, the existence of an icosahedral local structure in the glassy state has been investigated [3–6]. Many studies based on x-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS) measurements and computer simulations have reported that GFA strongly depends on the stability and number of icosahedral local structures in the glassy state [7–11]. On the basis of these studies, icosahedral quasicrystalline (QC) phase (I-phase) formation

has attracted attention from the viewpoint of local structure identification in metallic glasses and/or amorphous alloys as well as for using as reinforcing particles to improve the mechanical properties of bulk metallic glasses (BMGs).

It has also been reported that a nanoscale I-phase is formed in binary Zr–Pd and Zr–Pt alloys [12–14]. The results of these studies lead to another hypothesis of the existence of an icosahedral local structure in the corresponding binary alloys. In particular, it is noted that the nanoscale I-phase can be precipitated by directly quenching a melt of the Zr–Pt alloy [15–17]. We have reported a preliminary investigation of the local environment around Zr and Pt atoms in the glassy and nano-QC-formed states in $Zr_{80}Pt_{20}$ (near eutectic) alloy by radial distribution function (RDF) analysis and EXAFS measurement [18]. In the study, we speculated that the

⁷ Author to whom any correspondence should be addressed.

stable icosahedral local structure around the Pt atom is the dominant structure with a minor fraction (approximately 10%) of a Zr_5Pt_3 -like structure in the amorphous state. In contrast, an environment of a mixture of icosahedral and Zr_5Pt_3 local structures around the Zr atom in the amorphous state was also proposed. Sordelet *et al* investigated the structure and devitrification process of hyper-eutectic Zr_xPt_{100-x} ($73 \leq x \leq 77$) metallic glasses in 2008 [19]. They pointed out that QC formation strongly depends on the Pt content, which is attributed to the Pt-centered clusters in the glassy state. However, identification of the local environment around Zr and Pt atoms in relation to QC formation was not performed in these previous studies. In this paper, we examine the local environment around the constituent elements by Voronoi polyhedral analysis based on a reverse Monte Carlo (RMC) simulation result for the $Zr_{80}Pt_{20}$ glassy alloy to identify the key clusters involved in QC formation.

2. Experimental procedure

A master ingot of the $Zr_{80}Pt_{20}$ alloy was produced by arc-melting high-purity Zr (99.9 mass%) and Pt (99.98 mass%) in a purified argon atmosphere. A glassy ribbon was prepared by single-roller melt spinning with a roll speed of 60 m s^{-1} . The oxygen content in the prepared ribbon sample was approximately 400 ppm. The structure was examined by field-emission transmission electron microscopy (TEM) with an accelerating voltage of 300 kV (JEOL JEM-3000F) and ordinary x-ray diffraction measurements using monochromatic $Mo K\alpha$ radiation of 50 kV–300 mA produced by a rotating-anode x-ray generator. The scattered x-ray intensities were corrected for the effects of air-scattering, absorption, polarization and Compton scattering, and converted to electron units per atom by the generalized Krogh-Moe–Norman method [20] to obtain the structure factor, $S(Q)$. $S(Q)$ was analyzed using the Faber–Ziman definition [21] as follows:

$$S(Q) = \frac{I(Q) - \{\langle f^2 \rangle - \langle f \rangle^2\}}{\langle f \rangle^2}, \quad (1)$$

and

$$\langle f^2 \rangle = \sum_i c_i f_i^2, \quad \langle f \rangle = \sum_i c_i f_i, \quad (2)$$

where c_i and f_i are the concentration and atomic scattering factor, respectively, for the x-ray diffraction of component atom i . The pair distribution function, $g(r)$, can be derived from the Fourier transformation of the structure factor when Q is less than 150 nm^{-1} as follows:

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_0^\infty Q(S(Q) - 1) \sin Qr \, dQ, \quad (3)$$

where ρ is the average number density of atoms. The structure factor $S(Q)$ for a Zr–Pt binary mixture can be obtained as a weighted sum of three partial structure factors in accordance with the Faber–Ziman definition:

$$S(Q) = \sum_{i,j} w_{i-j} S_{i-j}(Q). \quad (4)$$

Here w_{i-j} is the weighting factor, defined as

$$w_{i-j} = \frac{c_i c_j f_i f_j}{\langle f \rangle^2}. \quad (5)$$

EXAFS measurements to analyze the local environment around Zr and Pt atoms in the as-quenched and QC-formed (annealed for 300 s at 820 K) states were performed at the SPring-8 synchrotron radiation facility on beamline BL01B1. All measurements were carried out in transmission geometry at room temperature. Measured spectra were analyzed using the REX 2000 program (Rigaku Corp.). Theoretical phase shifts and backscattered amplitude functions were calculated using the FEFF-8 code [22].

An RMC simulation was carried out by fitting to the x-ray structure factor in the range of $Q = 10\text{--}150 \text{ nm}^{-1}$. A starting configuration of 5000 atoms with an appropriate composition, randomly distributed in a cubic box of length 4.7689 nm, was used. The r -spacing of the partial pair correlation functions was set to 0.01 nm. To ensure a physically realistic configuration, the closest distances between two atoms were determined to be 0.28 nm for Zr–Zr, 0.25 nm for Zr–Pt and 0.28 nm for Pt–Pt based on the results of our preliminary study [18]. Atoms were randomly moved so as to minimize the sum of χ^2 values for respective data sets, where χ is the difference between the experimental structure factor, $S_{\text{exp}}(Q)$, and the calculated one, $S_{\text{cal}}(Q)$:

$$\chi^2 = \sum_i [S_{\text{exp}}(Q) - S_{\text{cal}}(Q)]^2 / \sigma_i^2, \quad (6)$$

where σ is the experimental error. The value of σ used in this work was 0.01.

Voronoi polyhedral analysis was performed on the RMC configuration. First-coordination-shell distances were determined from the minimum positions in the partial pair correlation functions. Similar RMC modeling and Voronoi analysis were applied for the $Zr_{70}Pd_{30}$ glassy alloy, in which a nanoscale QC phase is also formed from the glassy state by annealing, to compare the local environment for QC formation between the two binary alloys.

3. Results and discussion

We have previously reported that the $Zr_{80}Pt_{20}$ alloy readily undergoes a structural change from glassy to I-phase with a decrease in the cooling rate [15]. In this study, we have confirmed the existence of a nanoscale homogeneous glassy structure in $Zr_{80}Pt_{20}$ by high-resolution TEM (HREM) observation prior to XRD measurement. Figure 1 shows an HREM image and the selected-area electron diffraction (SAED) pattern of the as-quenched $Zr_{80}Pt_{20}$ melt-spun ribbon. No significant contrast corresponding to an ordered region such as a nanocrystalline particle is observed in the HREM image, indicating a homogeneous glassy structure. Also, the SAED pattern contains only a halo ring, which is consistent with the HREM image. Figure 2 shows Fourier transformation curves of the EXAFS measurements of the Zr K-edge (a) and Pt L3-edge (b) in the as-quenched and QC-formed states [18].

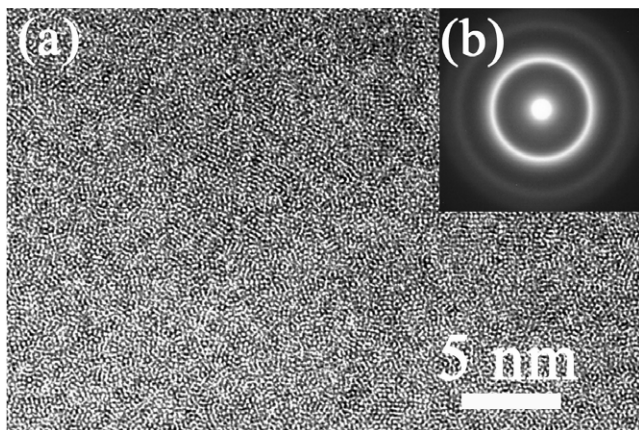


Figure 1. High-resolution TEM (HREM) image (a) and selected-area electron diffraction (SAED) pattern (b) of the as-quenched $Zr_{80}Pt_{20}$ glassy alloy.

The atomic distribution changes during the precipitation of the QC phase around the Zr K-edge, as shown in figure 2(a), implying that the rearrangement of Zr atoms is necessary for quasicrystallization. In contrast, the Fourier transformation curves of the Pt L3-edge in the as-quenched and QC-formed states resemble each other (figure 2(b)), indicating that the local environment does not change during quasicrystallization.

Figure 3(a) shows the experimental structure factor, $S(Q)$, obtained by XRD measurements (solid line) and RMC fitting (broken line) for the $Zr_{80}Pt_{20}$ glassy alloy. Partial structure factors, $S_{ij}(Q)$, derived from the RMC model are also shown in the figure. Since $S(Q)$ obtained from the RMC model is in excellent agreement with the experimental result of XRD measurements, we can verify the validity of RMC modeling. As shown in figure 3(a), a prepeak at $Q \sim 17 \text{ nm}^{-1}$ is observed in the structure factor, which is denoted by an arrow. We found that the prepeak originates from the unique bonding between the Pt–Pt pair (also shown by an arrow), as can be verified by the corresponding partial structure factors, $S_{ij}(Q)$. This feature suggests the existence of a strong chemical short- or medium-range order around the Pt atom [23]. The total pair distribution function, $g(r)$, calculated from XRD measurements and partial pair distribution functions, $g_{i-j}(r)$, calculated from the RMC model are shown in figure 3(b). The position of the first peak is estimated to be at 0.31 nm for Zr–Zr, 0.28 nm for Zr–Pt and 0.33 nm for Pt–Pt. These results are reasonably consistent with those obtained from the RDF analysis in previous reports [19, 23, 24], implying the success of the simulation. The intensity of the second peak in the Pt–Pt pair is high, which may be reflected by the prepeak observed at $Q \sim 17 \text{ nm}^{-1}$ in $S(Q)$. We speculate that the long-range correlation of the Pt atoms may exhibit a unique medium-range atomic configuration such as an icosahedral cluster. Recently, it has been reported that such Pt-centered clusters may also be related to the Zr_5Pt_3 structure coordinated by nine Zr and two Pt atoms [19, 25].

We examined the local structure around Zr and Pt atoms using Voronoi polyhedra analysis of the preferential structure models obtained. Figure 4 shows the fractions of Voronoi

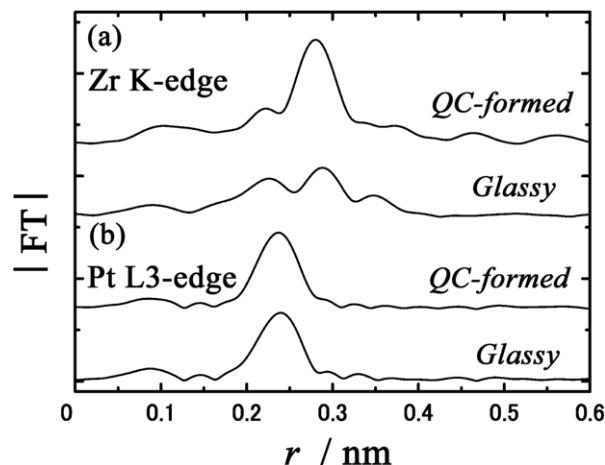


Figure 2. Fourier transformation curves of the EXAFS measurements of the Zr K-edge (a) and Pt L3-edge (b) in the as-quenched and QC-formed states of the $Zr_{80}Pt_{20}$ glassy alloy.

polyhedra around Zr (a) and Pt (b) atoms in the $Zr_{80}Pt_{20}$ glassy alloy. A Voronoi polyhedron is denoted by a set of indices $(n_3 \ n_4 \ n_5 \ n_6 \ n_7 \ n_8)$, where n is the number of faces with i vertices. The fraction of icosahedral-like polyhedra such as $(0, 2, 8, 2, 0, 0)$, $(0, 1, 10, 2, 0, 0)$, $(0, 2, 8, 1, 0, 0)$ and $(0, 3, 6, 3, 0, 0)$, of which the coordination numbers are in the range of 11–13, is high; however, the perfect icosahedron with a Voronoi index of $(0, 0, 12, 0, 0, 0)$ appears less frequently in the local environment around the Zr atom. These results indicate that the distorted icosahedral local structure is mainly formed around the Zr atom. Moreover, polyhedra with higher coordination numbers such as $(0, 2, 8, 4, 0, 0)$, $(0, 1, 10, 3, 0, 0)$ and $(0, 3, 6, 5, 0, 0)$ are simultaneously and frequently observed. We have suggested the existence of a Zr_5Pt_3 crystalline-like local environment around the Zr atom via simulation analysis based on EXAFS measurements [18]. Zr_5Pt_3 is known to be one of the crystalline phases formed by the decomposition of the I-phase [13], and its local atomic configuration is shown in figures 4(c)–(e). There are two atomic configurations around Zr with coordination numbers of 14 (c) and 15 (d) and a single configuration with a coordination number of 11 around Pt (e). It is speculated that these polyhedra with higher coordination numbers may correlate with other local environments such as, for example, a Zr_5Pt_3 -like structure. Actually, the $(0, 1, 10, 3, 0, 0)$ polyhedron has a strong correlation with the Zr_5Pt_3 -like local environment with a coordination number of 15, as shown in figure 4(d). This local environment is related to that of the $(0, 1, 10, 3, 0, 0)$ polyhedron when it is distorted slightly.

In contrast, the Voronoi polygon with an index of $(0, 2, 8, 1, 0, 0)$ with icosahedral-like geometry is dominant around the Pt atom as shown in figure 4(b). This polyhedron has also been investigated by an *ab initio* molecular dynamics simulation [25]. It is known that this polyhedron corresponds to the local environment around Pt in the Zr_5Pt_3 crystalline phase shown in figure 4(e) [24]. These results imply that the cluster can be thermodynamically stable through the entire transformation process from glass to QC and from QC to Zr_5Pt_3 . Actually, the EXAFS measurements

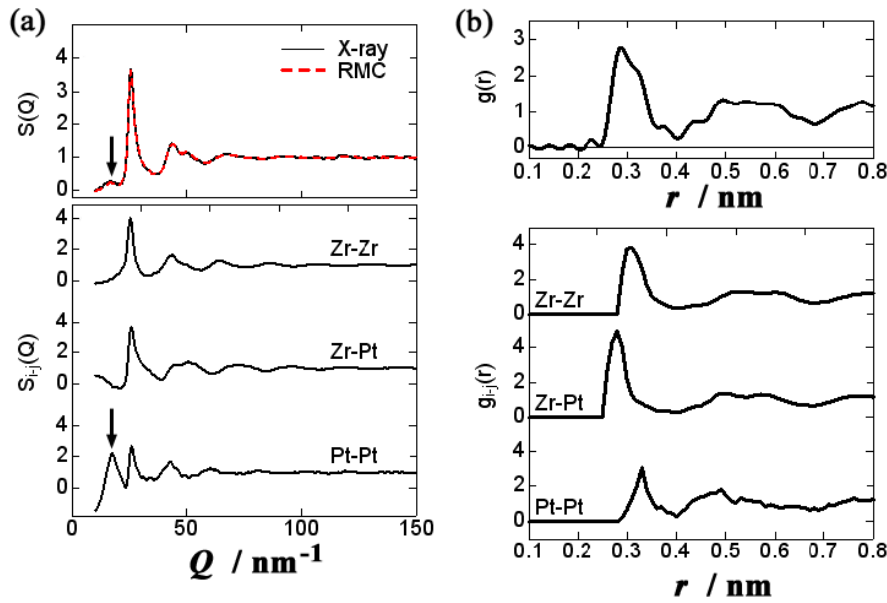


Figure 3. (a) Experimental structure factor, $S(Q)$, of the $\text{Zr}_{80}\text{Pt}_{20}$ glassy alloy obtained by XRD measurements (solid line) and RMC fitting (broken line), and partial structure factors, $S_{ij}(Q)$, derived from the RMC mode. (b) Total pair distribution function, $g(r)$, calculated from XRD measurements and partial pair distribution functions, $g_{i-j}(r)$, calculated from the RMC model.

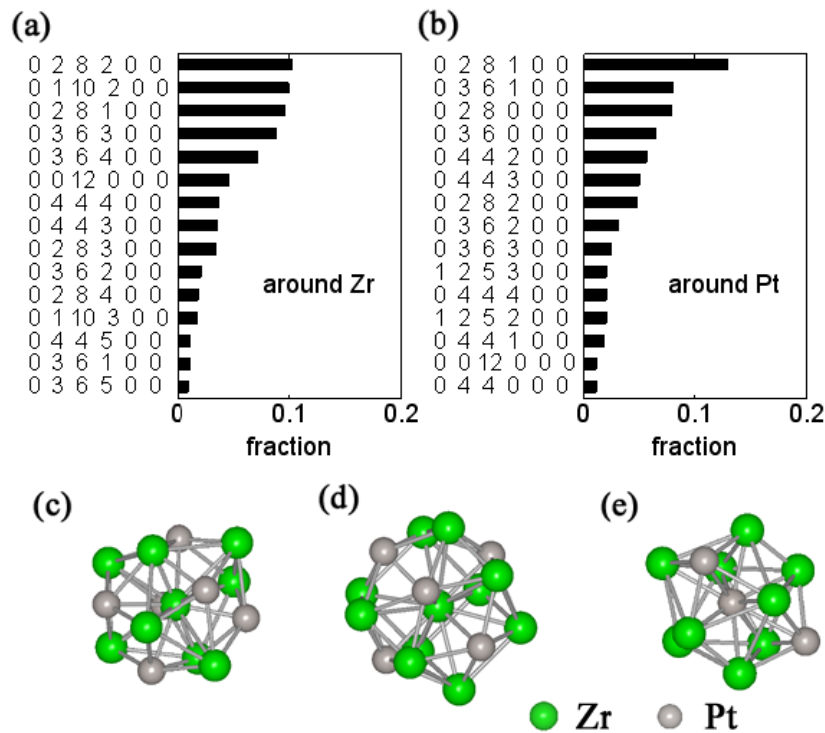


Figure 4. Fractions of Voronoi polyhedra around Zr atom (a) and Pt atom (b) in the $\text{Zr}_{80}\text{Pt}_{20}$ glassy alloy. Local atomic configurations around Zr ((c), (d)) and Pt (e) in Zr_5Pt_3 .

denoted in figure 2 indicate that the local environment changes considerably around the Zr atom but does not change significantly around the Pt atom during the precipitation of the I-phase. We suggest that the non-icosahedral local order existing around the Zr atom contributes to the change in the environment upon quasicrystallization. Meanwhile, no significant rearrangement of atoms is necessary for QC

precipitation owing to a dominant and stable icosahedral-like environment around Pt.

Moreover, a difference in the local atomic environment is observed between the present $\text{Zr}_{80}\text{Pt}_{20}$ alloy and the QC-forming $\text{Zr}_{70}\text{Pd}_{30}$ alloy. Takagi *et al* performed a Voronoi polyhedra analysis for the glassy and QC-formed states in the $\text{Zr}_{70}\text{Pd}_{30}$ alloy by electron diffraction measurement [26]. They

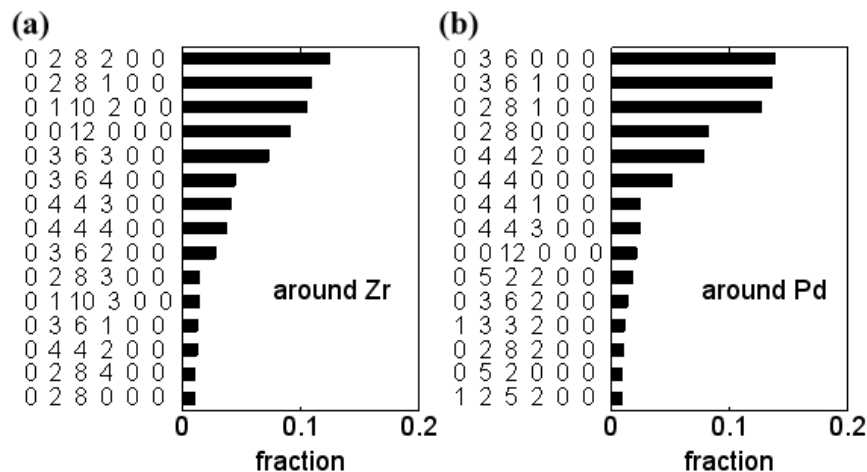


Figure 5. Fractions of Voronoi polyhedra around a Zr atom (a) and a Pd atom (b) in the $Zr_{70}Pd_{30}$ glassy alloy.

clarified that a prism-like environment with Voronoi indices of (0, 2, 8, 0, 0, 0) and (0, 3, 6, 0, 0, 0) is mainly observed and that few icosahedral-like polyhedra appear around the Pd atom, which is clearly different from the polyhedra observed around Pt in the present study. In contrast, the local environment around the Zr atom seems to be the same for both alloys, in which the dominant local environment consists of an icosahedral-like configuration. We also evaluated the local environment by Voronoi analysis based on the XRD results as shown in figure 5. Similar results, i.e. the dominant formation of icosahedral-like polyhedra such as (0, 2, 8, 2, 0, 0), (0, 2, 8, 1, 0, 0), (0, 1, 10, 2, 0, 0) and (0, 3, 6, 3, 0, 0), were observed around the Zr atom as shown in figure 5(a), which are consistent with those in the previous study described above [26]. However, in our study, we found that the perfect icosahedron with a Voronoi index of (0, 0, 12, 0, 0, 0) appears with greater frequency in the $Zr_{70}Pd_{30}$ alloy than in the $Zr_{80}Pt_{20}$ alloy. A prism-like local environment is also observed around the Pd atom in our analysis (figure 5(b)). According to these investigations, it is suggested that there is a different mechanism of QC formation for the two binary alloys. In the Zr–Pd binary alloy, the QC phase may originate from the icosahedral local order with considerably more ordered geometry around the Zr atom. Such icosahedral local order is stabilized thermodynamically with Pd-centered prism-like local order, which is related to the strong chemical affinity between Pd and Zr. Also, icosahedral-like local order around the Pt atom as well as around the Zr atom is thought to contribute to the formation of the QC phase in the $Zr_{80}Pt_{20}$ glassy alloy. It is well known that the QC phase can be formed directly from the melt of $Zr_{80}Pt_{20}$ by cooling at an appropriate rate [15]. Since this phenomenon is not observed in the $Zr_{70}Pd_{30}$ glassy alloy, we can point out the difference between the local structures of the two alloys. The $Zr_{80}Pt_{20}$ glassy alloy has a tendency to form an icosahedral-like environment around both Zr and Pt atoms, leading to the easy growth of the QC phase without any significant rearrangement of the constituent elements [13]. The results of our investigation are also supported by the finding that the QC phase can precipitate from the amorphous state with a low activation energy [27].

4. Conclusion

In the present study we have described the results of the local structural evaluation of QC formation in the $Zr_{80}Pt_{20}$ glassy alloy by XRD measurements and RMC modeling. We observed unique bonding between the Pt–Pt pair, suggesting the formation of specific local ordering around the Pt atom. Actually, Voronoi analysis indicates the formation of an icosahedral-like polyhedron around Pt. We found that the corresponding icosahedral-like cluster has high stability, which remains during the decomposition as well as the precipitation of the I-phase. It was also found that icosahedral-like local order exists around Zr; however, the fraction of perfect icosahedra is low. We conclude that the local environment and the mechanism of QC formation in the $Zr_{80}Pt_{20}$ glassy alloy are different from those in the similar QC-forming $Zr_{70}Pd_{30}$ glassy alloy. In particular, a significant difference in the local environment around the noble metal is observed. This feature results in a different mechanism of QC formation for the two alloys.

Acknowledgments

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