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Atomic configuration of metal atoms in $(Ti_{0.676}Zr_{0.324})D_{0.31}$ metallic glass studied by X-ray, neutron diffraction and reverse Monte Carlo modeling

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Abstract

We have obtained a three-dimensional atomic configuration in $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass using the reverse Monte Carlo (RMC) modeling method with neutron and X-ray diffraction data. Voronoi polyhedral analysis for the RMC configuration of metal atoms revealed the presence of a lot of icosahedral-like clusters.

Keywords: Amorphous materials; Mechanical alloying; Atomic scale structure; X-ray diffraction; Neutron diffraction

1. Introduction

Both Ti and Zr are important elements for hydrogen storage materials because of their strong affinities for hydrogen. A Ti–Zr alloy system is isomorphous and its structure is hexagonal close-packed (h.c.p) [1] where Ti and Zr atoms are distributed randomly [2]. Recently, we have reported neutron and X-ray diffraction results for $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass synthesized by mechanical alloying under deuterium gas atmosphere [3]. In this work, the reverse Monte Carlo (RMC) modeling method was applied to the neutron and X-ray diffraction data in order to determine the atomic configuration of metal atoms in $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass.

It is noteworthy that a neutron zero-scattering alloy can be obtained with composition $Ti_{0.676}Zr_{0.324}$ because of negative and positive coherent scattering length of Ti and Zr, respectively. Additionally, X-ray diffraction has a great advantage in observing the arrangement of Ti and Zr atoms because of much lager scattering factors of Ti and Zr atoms than that of D atom. Therefore, combined use of the neutron and X-ray diffraction data in the RMC modeling will allow us to obtain the three-dimensional atomic configuration of $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass.

2. Experimental procedure

$(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass was synthesized by mechanical alloying under deuterium gas atmosphere. The neutron diffraction measurement was carried out by using the HIT-II spectrometer installed at the pulsed neutron source in the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The X-ray diffraction measurement was carried out by the RIGAKU RINT-Ultima with Mo Kα radiation. After various corrections, the scattering intensity was converted to the total structure factor, $S(Q)$. The pair distribution functions, $g(r)$, can be derived from the Fourier transformation of the $S(Q)$. Details of such experiments were described in the previous paper [3].

3. Reverse Monte Carlo modeling

Reverse Monte Carlo (RMC) simulation [4] was carried out through fitting to the neutron and X-ray $S(Q)$s. A starting configuration of 4000 atoms with appropriate composition, randomly distributed in a cube box of length of 3.95 nm, was used. To ensure a physically realistic configuration, the closest distances between two atoms (D–D, D–Ti, D–Zr, Ti–Ti, Ti–Zr and Zr–Zr) allowed to approach each other were determined from the experimental total distribution functions.

4. Results and discussion

Fig. 1 shows the pair distribution functions, $g(r)$, for $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass observed by neutron and X-ray diffraction [3]. The neutron $g(r)$ shows a negative peak around 0.18 nm and a positive peak around 0.20 nm. Since the X-ray $g(r)$ has no peak in this region, these peaks can be

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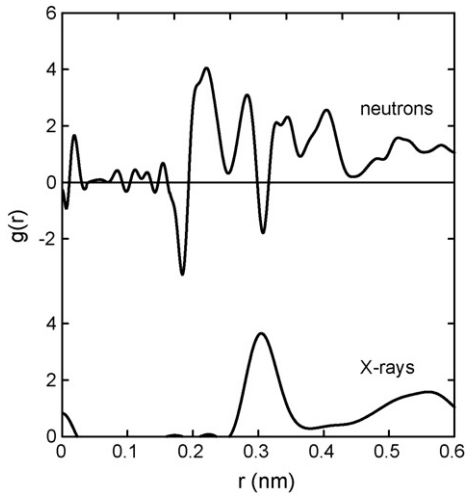

Fig. 1. The pair distribution functions, $g(r)$, for $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass observed by neutron and X-ray diffraction [3].

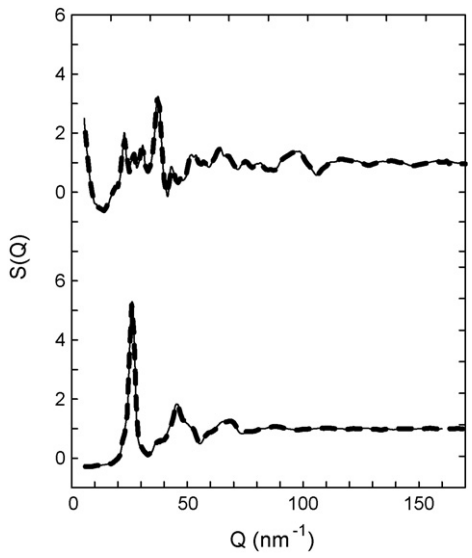

Fig. 2. Neutron and X-ray total structure factors calculated from the RMC model (dashed lines) for $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass, together with the experimental $S(Q)$s (solid lines) [3].

recognized to be metal–D or D–D correlations. Moreover, it is clearly understood that the negative peak is attributed to Ti–D correlations and the positive peak attributed to Zr–D and D–D correlations, respectively, because of the negative coherent neutron scattering length of Ti. A negative peak was again observed in the vicinity of 0.30 nm in the neutron $g(r)$. In the X-ray $g(r)$ a first peak is definitely observed at same distance. Therefore, we can easily recognize that this peak is attributed to Ti–Zr correlations. Positive peaks which locate the left side and the right side of the negative peak in the neutron $g(r)$ can be concluded to be attributed to Ti–Ti and Zr–Zr correlations through the Goldschmidt radii of Ti and Zr atoms, respectively.

Calculated total structure factors from the RMC model (dashed lines) for $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass are shown in Fig. 2, together with the experimental $S(Q)$s (solid lines) [3]. Excellent fits with both neutron and X-ray diffraction data were obtained for Q in the range 6–170 nm^{-1}. A large scattering intensity was observed below 5 nm^{-1} in the neutron $S(Q)$, suggesting atomic density fluctuations about the size of a few nanometers. The low-Q data in the neutron $S(Q)$ could not be used in the RMC calculation because of the limited Q range of X-ray $S(Q)$. However, the RMC model is found to be useful for analysis of the local structure. Voronoi polyhedral analysis has been performed on the RMC configuration of metal atoms. Fig. 3 shows the fraction of Voronoi polyhedra around Ti and Zr atoms. Icosahedral polyhedra (00 12 000) and isosahedron-like polyhedra (028100), (028200), (01 10 200) and (036300) are observed both around Ti and Zr atoms. The sums of the fractions of these polyhe-

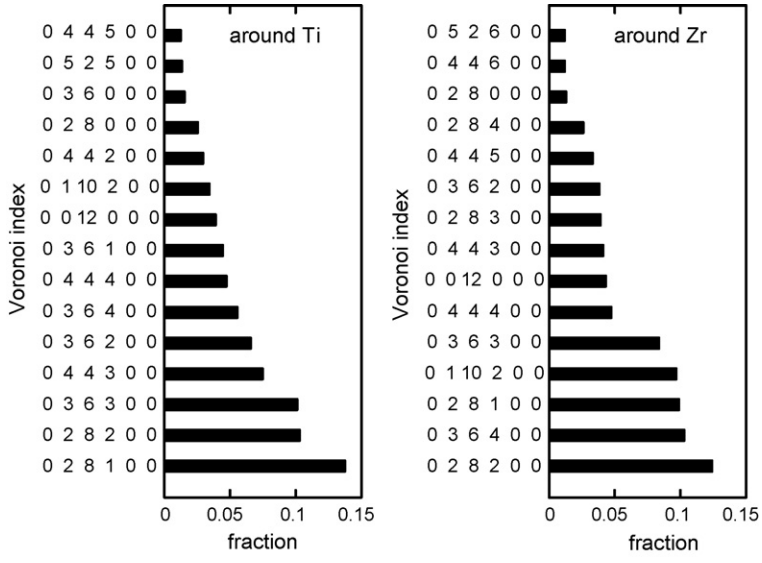

Fig. 3. Fractions of Voronoi polyhedra around Ti and Zr atoms obtained from the RMC configuration of metal atoms for $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass.

dra are more than 40%. The result indicates the presence of a lot of icosahedral-like clusters in the configuration of metal atoms.

5. Conclusion

A three-dimensional atomic configuration in $(Ti_{0.676}Zr_{0.324})$-$D_{0.31}$ glass using the reverse Monte Carlo (RMC) modeling method with neutron and X-ray diffraction data have been obtained. The RMC model shows that a lot of isosahedral-like clusters of metal atoms are presented in $(Ti_{0.676}Zr_{0.324})D_{0.31}$ glass.

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