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A combination of anomalous x-ray scattering and neutron diffraction for structural characterizations of $Zr_{63}Ni_{25}Al_{12}$ metallic glass

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Abstract. $Zr_{63}Ni_{25}Al_{12}$ bulk metallic glass was investigated using neutron diffraction and anomalous x-ray scattering close to the Zr and Ni K edges. The experimental results were analyzed using reverse Monte Carlo modeling (RMC) to obtain partial structure factors and pair distribution functions. The obtained partial structural results were compared with RMC results when neutron diffraction data are not included in the analysis and the report of $Zr_{60}Ni_{25}Al_{15}$ by Fukunaga et al. using high-energy x-ray and neutron total scattering data.

1. Introduction

In the last two decades, bulk metallic glasses (BMG) with distinct glass transitions have been discovered in various multi-component metallic alloys. They show extremely excellent glass-forming abilities (GFA), where even a very slow cooling rate such as $\sim$ 1 K/s can avoid crystallization. Physical and technological properties of these glasses were well investigated, including glass transition, structural change, phase stability, elastic constants, magnetic properties, etc [1]. Among these BMG's, the alloy studied in this paper, $Zr_{63}Ni_{25}Al_{12}$, has an excellent critical cooling rate of some K/s allowing to form a massive BMG with a diameter of more than 15 mm [2].

To understand the origin of such an excellent GFA in Zr-Ni-Al alloys, partial structural investigations are essential. Fukunaga et al. [3] utilized contrasts between x-ray and neutron diffraction (XD and ND) data of $Zr_{60}Ni_{25}Al_{15}$ BMG for reverse Monte Carlo (RMC) modeling to obtain partial structural information. We have recently performed anomalous x-ray scattering (AXS) on $Zr_{63}Ni_{25}Al_{12}$ BMG close to the Zr and Ni K edges, and the experimental results

were analyzed using RMC modeling [4]. The comparison of our results with those obtained by Fukunaga et al. showed some discrepancies especially in the Ni-Ni pair correlations.

To investigate $Zr_{63}Ni_{25}Al_{12}$ BMG in more detail, we added ND measurements. In this paper, we report results of AXS and ND measurements and subsequent RMC modeling to obtain partial structure factors, $S_{ij}(Q)$, and partial pair distribution functions, $g_{ij}(r)$ in this BMG.

2. Experimental procedure and data analysis

A $Zr_{63}Ni_{25}Al_{12}$ alloy ingot with nominal composition was prepared by arc-melting of mixtures of Zr, Ni, and Al metals with purities of 99.5%, 99.99%, and 99.99%, respectively, in a high-purity Ar atmosphere. From this, a cylindrical rod of ~ 3 mm in diameter and ~ 15 mm in length was manufactured by tilt casting with a Cu mold.

AXS experiments were conducted at the beamline BM02 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. To obtain differential structure factors, $\Delta_k S(Q)$, close to the Zr and Ni K edges, two scattering experiments were performed at two incident x-ray energies 30 eV and 200 eV below the Zr K edge (17.998 keV), and 20 eV and 200 eV below the Ni K edge (8.333 keV), using a standard $\omega - 2\theta$ diffractometer installed at the beamline. The experimental details, in particular, on a high-resolution high-intensity detecting system, is given elsewhere [5]. Following procedures given in Ref. [6], $\Delta_k S(Q)$'s were calculated from the scattering data. For the analysis, the ordinary and anomalous terms of the atomic form factors were taken from literatures [7, 8].

ND measurements were performed using the High Intensity Total Diffractometer (NOVA) installed at the beamline BL21 of Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC). The rod sample was put into a thin-walled vanadium cylindrical can with a thickness of 0.1 mm and an inner diameter of 6 mm, and set at the center of the diffractometer. A ND total structure factor, $S_{\mathrm{N}}(Q)$, was obtained from the scattered intensity after correcting background,container scattering, absorption, and multiple scattering, and normalizing to a reference sample of a vanadium rod.

RMC modeling [9] is a useful tool to construct 3D atomic configurations of disordered materials using experimental diffraction data. In the RMC calculations, atoms are moved from an initial configuration so as to minimize deviations from experimental data, e.g., in this study, two $\Delta_k S(Q)$'s, an XD total structure factor measured near the Zr K edge, $S_{\mathrm{X}}(Q)$, and $S_{\mathrm{N}}(Q)$ using a standard Metropolis Monte Carlo algorithm [10].

A starting configuration of a system containing totally 10,000 atoms with the measured number density of 46.73 nm^{-3} was generated using a hard-sphere Monte Carlo simulation (a random configuration except short bonds). To avoid unphysical atomic configurations, only a constraint of shortest atomic distances of 0.20 nm was applied to all the atomic pairs in the RMC calculations. The RMC calculations were performed using the RMC++ program package coded by Gereben et al. [11].

3. Results

Circles in Fig. 1 show experimental data of $\Delta_{\mathrm{Zr}} S(Q)$, $\Delta_{\mathrm{Ni}} S(Q)$, $S_{\mathrm{X}}(Q)$, and $S_{\mathrm{N}}(Q)$, of which the x-ray results were already published elsewhere [4]. The Q range in $\Delta_{\mathrm{Ni}} S(Q)$ is limited to about 70 nm^{-1}, owing to the low energy of incident x-rays near the Ni K edge. As shown in the figure, $\Delta_{\mathrm{Ni}} S(Q)$ has spectral features very different from $\Delta_{\mathrm{Zr}} S(Q)$, $S_{\mathrm{X}}(Q)$, and $S_{\mathrm{N}}(Q)$. In particular, out-phases are seen in the oscillations beyond 30 nm^{-1}.

Although $\Delta_{\mathrm{Zr}} S(Q)$ looks similar to $S_{\mathrm{X}}(Q)$, small differences are identified by inspecting the spectra, i.e., the amplitude of oscillations in $\Delta_{\mathrm{Zr}} S(Q)$ is larger than in $S_{\mathrm{X}}(Q)$, and a slight phase shift is realized towards smaller Q values.

Solid curves in Fig. 1 represent best fits of the RMC modeling. Although the experimental results show very different scattering features from each other, the RMC modeling reproduce

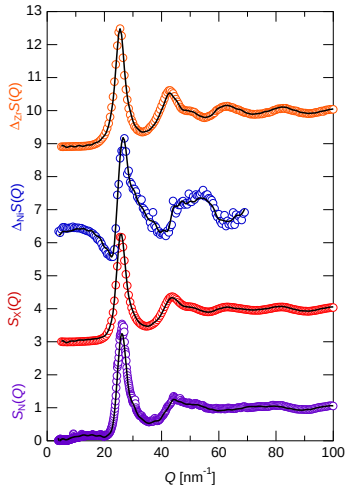

Figure 1. (Color online.) From top to bottom: $\Delta_k S(Q)$'s close to the Zr and Ni K edges, $S_{\rm X}(Q)$, and $S_{\rm N}(Q)$. Circles indicate those obtained from the experiments, and solid curves denote best fits of the RMC modeling. For clarity, the spectra are displaced upwards by 3 each.

well all of the experimental data within the experimental errors.

4. Discussion

Figures 2(a) and (b) show the $g_{ij}(r)$ and $S_{ij}(Q)$ functions, respectively, obtained from the present RMC modeling. The $g_{ij}(r)$ functions show sharp first peaks at different interatomic distances. Compared with the previous results [4], the first peaks in the Al-related partials become sharper and the unphysical peaks near the cutoff length disappear, while the other correlations remain mostly unchanged. The difference in the Al-related partials may be due to the addition of the ND data which has different weighting factors for the partial correlations as given in Table 1 of Ref. [4] to the RMC modeling.

Some interesting features in the local structures are observed: 1) The atomic distances of Zr-related partials are in good agreement with the XAFS data for $Zr_{70}Ni_{20}Al_{10}$ [12], and it is confirmed that the Zr-Ni distance is much smaller than the average of the Zr-Zr and Ni-Ni

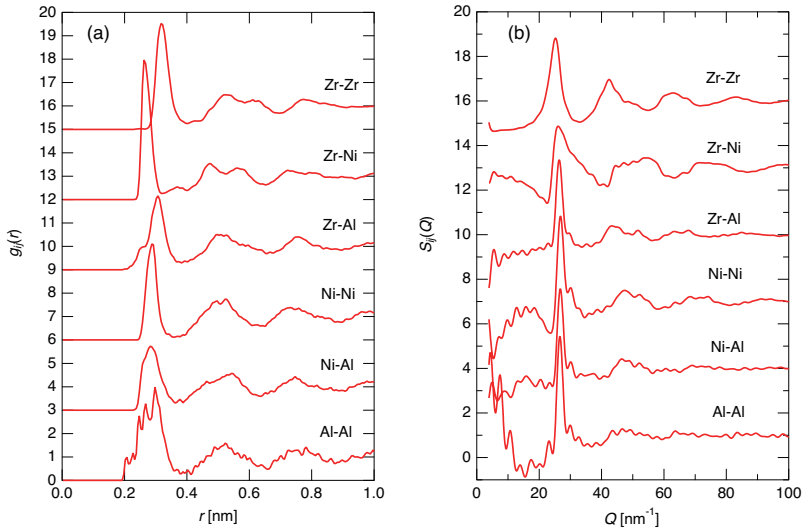

Figure 2. (Color online.) (a) $g_{ij}(r)$ and (b) $S_{ij}(Q)$ functions obtained from the RMC fits. For clarity, the spectra are displaced upwards by 3 each.

distances. 2) The difference in the atomic diameters of Zr and Ni atoms is approximately 18 %, which matches well Inoue's empirical rule [13]. 3) The width of the first peak in the Zr-Zr correlation (0.045 nm) is wider than those in the Zr-Ni (0.034 nm) and Ni-Ni (0.032 nm) ones. The $g_{\mathrm{AlAl}}(r)$ function is still noisy even in the first peak, which may be owing to the small weighting factor of 0.3 % even for the ND data.

As regards the $S_{ij}(Q)$ functions, $S_{\mathrm{ZrZr}}(Q)$ resembles that of a typical dense-packed monatomic configuration. The first peak in $S_{\mathrm{ZrNi}}(Q)$, however, has a large shoulder at the higher Q side, indicating a non-hard-sphere Zr-Ni correlation. Of special interest is that the Ni-related partials have broad prepeaks at about 15 nm^{-1}, and the Ni-Ni partial shows the most prominent one, indicating the existence of weak intermediate-range correlations around the Ni atoms, in particular, in the Ni-Ni correlations. The existence of the prepeak in $S_{\mathrm{NiNi}}(Q)$ was the large discrepancy between our previous results without ND [4] and the report by Fukunaga et al. on the $\mathrm{Zr_{60}Ni_{25}Al_{15}}$ BMG [3], and the confirmation of the prepeak in $S_{\mathrm{NiNi}}(Q)$ is an important progress by adding the ND data. However, the prepeak in our results is much smaller in height and broader compared with the report by Fukunaga et al. [3].

$S_{\mathrm{AlAl}}(Q)$ shows a large increase in the small Q range. This feature in this region resembles well the initial spectrum of random configuration of the RMC modeling, and highly depends on the initial configuration. Thus, the reliability of the Al-Al correlations in the large r range is still doubtful even after adding the ND data in the RMC modeling.

5. Conclusion

To investigate the local structural origin of good GFA of $\mathrm{Zr_{63}Ni_{25}Al_{12}}$ bulk metallic glass, an ND measurement was performed, and the result was included in the RMC modeling together with previous AXS data close to the Zr and Ni K edges and XD results. The qualities of the $g_{ij}(r)$ and $S_{ij}(Q)$ functions was highly improved except the enhancement of the $S_{\mathrm{AlAl}}(Q)$ in the low Q region. Although a prepeak was observed in the Ni-Ni correlation as previously reported by Fukunaga et al. [3], the prepeak width is much broader than their result. By improving the partial data we made an important step towards helping to understand the good GFA in the BMG.

Acknowledgments

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