Atomic structure in $\text{Zr}_{70}\text{Ni}_{30}$ metallic glass

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Atomic structure of $\text{Zr}_{70}\text{Ni}_{30}$ metallic glass (MG) was investigated by reverse Monte Carlo simulation combining with x-ray diffraction and Ni and Zr K -edge extended x-ray absorption of fine structure measurements. Distributions of coordination number (CN) and Voronoi clusters were analyzed by Voronoi tessellation method. The average CN of atoms was obtained to be 11.4 together with the average CN of Zr and Ni atoms of about 11.8 and 10.6, respectively. It is found that Z11 Kasper polyhedron and distorted icosahedra are mainly favored structural units in $\text{Zr}_{70}\text{Ni}_{30}$ MG. The discrepancy in atomic structure between $\text{Zr}_{70}\text{Ni}_{30}$ MG and its corresponding crystalline (or quasicrystalline) phases can explain the fact that $\text{Zr}_{70}\text{Ni}_{30}$ MG does not transform to neither icosahedral nor fcc Zr_2Ni phase during crystallization process. © 2007 American Institute of Physics. [DOI: 10.1063/1.2798386]

INTRODUCTION

Atomic structure of metallic glasses (MGs) has been studied experimentally and theoretically^{1–4} because their extraordinary mechanical and magnetic properties strongly depend on their atomic structures. Gaskell proposed that atomic structure of MG is similar with that of corresponding crystalline phases.⁵ Stability of MG is linked with its atomic structure,^{6,7} which correlates with atomic structure of the corresponding crystalline phase by annealing.^{8,9} For example, icosahedral clusters are found to be dominant atomic structure in $\text{Zr}_{70}\text{Cu}_{29}\text{Pd}_1$ MG,^{10,11} which leads to primary phase transition by forming icosahedral quasicrystal^{12,13} after annealing, while $\text{Zr}_{70}\text{Ni}_{30-x}\text{Pd}_x$ ($x < 10$ at. %) MGs do not exhibit such primary precipitation.⁸ Furthermore, Zr–Cu binary MGs exhibit a glass transition event, whereas Zr–Ni binary MGs do not,¹⁴ which might be due to their different atomic structures.⁸ Thus, studies of atomic structure in such simple MGs are strongly demanded, which will promote our understanding to multicomponent bulk metallic glasses. However, structure of Zr–Ni MGs is still not completely understood^{15–18} in spite of its wide amorphous-forming compositional range.¹⁹ In the present work, we report the atomic structure of a $\text{Zr}_{70}\text{Ni}_{30}$ MG by reverse Monte Carlo (RMC) simulation combining with x-ray diffraction (XRD) and extended x-ray absorption of fine structure (EXAFS) as well as Voronoi tessellation method.

EXPERIMENT

$\text{Zr}_{70}\text{Ni}_{30}$ ingot was prepared by arc melting high-purity metals (99.8% Zr and 99.9% Ni). Amorphous ribbons with a cross section of $0.03 \times 2 \text{ mm}^2$ were obtained from these alloys by single-roller melt spinning at a wheel surface velocity of 30 m/s in purified Ar atmosphere. The oxygen content of the as-prepared ribbon samples was analyzed to be less than 800 mass ppm by inductively coupled plasma spectroscopy. The influence of oxygen on the transformation behavior can thus be disregarded.^{20,21}

Room-temperature high resolution XRD measurements were carried out for as-prepared $\text{Zr}_{70}\text{Ni}_{30}$ sample with high energy x-ray (100 keV) at beamline BW5, Hasylab in Germany. Diffraction patterns were recorded by a Mar2300 image plate. Beamstop was located away from the center to record data with larger Q (wave vector transfer) range, resulting in high resolution in real-space reduced pair distribution function $G(r)$. XRD patterns were integrated to Q -space data file after subtracting its background by the program FIT2D.²² Data were then normalized by the program PDFGETX to remove the effect of polarization, sample self-absorption, fluorescence contribution, and inelastic scattering. Finally, structure factor $S(Q)$ was obtained by using the Faber-Ziman equation²³ and truncated its two ends, leaving the region with reliable oscillation signal. The corresponding $G(r)$ was obtained by Fourier transformation (FT) of $S(Q)$. EXAFS measurements were performed at beamline A1, Hasylab in Germany. Zr and Ni K -edge spectra were measured by transmission method. To obtain high quality data, more than ten times measurements were performed for each sample and

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then averaged to have data with high value of signal-to-noise ratio. Measured spectra were analyzed by standard procedures of data reduction, using the program WINXAS.²⁴ The EXAFS signal, $\chi(k)$, was extracted, followed by FT to get radial distribution function (RDF).²⁵ The main peak of RDF was selected and reversely transformed into k space and truncated to be 4–10 $\text{\AA}^{-1}$, which is the most reliable information from experiments. Its corresponding amplitude and phase were calculated by the program FEFF.²⁶ We performed RMC simulation^{27–30} simultaneously for three experimental data (one $S(Q)$ and two EXAFS Zr and Ni K -edge [$\chi(k)$] spectra) to get the atomic configuration of $\text{Zr}_{70}\text{Ni}_{30}$ MG as reliable as possible. Before the simulation, a box, containing 5000 atoms following its composition and hard sphere dense-packed (HSDP) model, was built. Least-square fitting for $S(Q)$ and $\chi(k)$ data as carried out under the constraint of atomic density calculated from experimental $G(r)$,³¹ which is about 0.0518 $\text{\AA}^{-3}$ for $\text{Zr}_{70}\text{Ni}_{30}$. The minimum atomic distances were set to be 2.8, 2.5, and 2.2 $\text{\AA}$ for Zr–Zr, Zr–Ni, and Ni–Ni pairs, respectively.

RESULTS AND DISCUSSION

Figures 1(a)–1(c) show experimental and simulated data of $S(Q)$ and Zr and Ni K -edge $\chi(k)$ for as-prepared $\text{Zr}_{70}\text{Ni}_{30}$ MG, respectively. It is found that the first main peak and long-range oscillations up to about 15 $\text{\AA}^{-1}$ in Fig. 1(a) are well fitted, indicating good convergence for $S(Q)$. Experimental Zr K -edge $\chi(k)$, weighted by k^3 in Fig. 1(b), shows two spindlelike regions at 5.1 and 8.2 $\text{\AA}^{-1}$, which are in good agreement with those of simulated ones although slight phase deviation is detected in other peaks. For Ni K -edge $\chi(k)$, weighted by k^3 in Fig. 1(c), a good fit is also obtained except for small mismatches at its two ends. Average Zr–Zr, Zr–Ni, and Ni–Ni bond lengths are found to be 3.15, 2.79, and 2.51 $\text{\AA}$, respectively, which are similar with those of ideal interatomic distances based on HSDP model.³² Distributions of atomic coordination number (CN) around Zr and Ni are plotted in Fig. 2 together with the average atom-atom CNs for $\text{Zr}_{70}\text{Ni}_{30}$ MG. It is found that CN ranges from 9–14, while the highest probabilities for Zr and Ni atoms are found to be CN=12 and 11, respectively. The average values around Zr and Ni atoms are 11.8 and 10.5, respectively, resulting in the total average CN value of about 11.4. The difference in average CNs of Zr and Ni atoms is plausible due to the difference of their atom sizes. The average CN for Zr atoms, 11.8, obtained here is rather close to 12, obtained from XRD data alone for the same MG by Saida *et al.*,¹⁷ while it is smaller than that (12–14) reported by Fukunaga *et al.*,^{15,18} obtained from RMC simulation of neutron (electron) diffraction data for $\text{Zr}_{66.7}\text{Ni}_{33.3}$ MG.

Atomic structure of as-prepared $\text{Zr}_{70}\text{Ni}_{30}$ MG was further analyzed by Voronoi tessellation method.^{33,34} Voronoi clusters (VCs) are defined as closed polyhedra with one center atom, piled up with tetrahedra. Various VCs can be indexed as $\langle n_3, n_4, n_5, n_6, \dots \rangle$, n_i is the number of shell atoms which are connected with other i th shell atoms. Various VCs could be extracted from the 5000-atom box after the RMC simulation by setting the maximum atomic distance to be

FIG. 1. Structure factor $S(Q)$, Zr and Ni K -edge spectra obtained from measurements (solid line), and RMC simulated (dotted line) for $\text{Zr}_{70}\text{Ni}_{30}$ metallic glass.

3.5 $\text{\AA}$. It is found that various VCs around Zr and Ni atoms exist in the $\text{Zr}_{70}\text{Ni}_{30}$ MG, plotted in Fig. 3 together with data reported for the $\text{Zr}_{66.7}\text{Ni}_{33.3}$ MG.¹⁵ We found that the dominant VCs (over 60%) around Zr and Ni atoms are CN = 11, 12 and CN = 10, 11, respectively, in the as-prepared $\text{Zr}_{70}\text{Ni}_{30}$ MG. The most popular VCs around Zr atom are $\langle 0, 2, 8, 1 \rangle$ (standard Z11 Kasper polyhedron 11.24%), $\langle 0, 2, 8, 2 \rangle$ (one of distorted icosahedra 11.78%), and $\langle 0, 3, 6, 3 \rangle$

FIG. 2. Distribution of coordination number (CN) of Ni and Zr atoms for $\text{Zr}_{70}\text{Ni}_{30}$ metallic glass together with the average CN for atoms.

(one of distorted icosahedra 9.82%), while the ideal icosahedron (standard Z12 Kasper one) indexed by $\langle 0,0,12,0 \rangle$ has a concentration of 3.58%. Around Ni atoms, the most popular VCs are $\langle 0,2,8,1 \rangle$ (9.42%), $\langle 0,4,4,3 \rangle$ (one of distorted Z11 Kasper polyhedron 8.42%), and $\langle 0,3,6,1 \rangle$ (one of distorted Z10 Kasper polyhedron 7.23%), while the distorted icosahedra ($\langle 0,3,6,3 \rangle$, $\langle 0,2,8,2 \rangle$, and $\langle 0,4,4,4 \rangle$) have a total concentration of 14.66% together with 1.39% the ideal icosahedron $\langle 0,0,12,0 \rangle$. These results reveal that Z11 Kasper polyhedron and distorted icosahedra are favored atomic structures in this $\text{Zr}_{70}\text{Ni}_{30}$ MG. Furthermore, it is also found that our results obtained here largely differ from those reported in Ref. 15, in which relative larger VCs around Zr atoms with CN = 12–14 and smaller VCs centered with Ni atoms with CN = 9–10 are dominant in the $\text{Zr}_{66.7}\text{Ni}_{33.3}$ MG.¹⁵ The average CN of Ni atoms was estimated to be 10.6 for $\text{Zr}_{70}\text{Ni}_{30}$ MG obtained here and <10 for $\text{Zr}_{66.7}\text{Ni}_{33.3}$ MG.¹⁵ According to the Miracle model,^{1,2} R^* values (the optical radius ratio of center to average shell atoms) should be over 0.8 by considering Ni as the solute atom for both $\text{Zr}_{70}\text{Ni}_{30}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ MGs, which results in the average CN of Ni atoms to be 10–11.³² This is in agreement with 10.5 obtained from RMC and 10.6 from VCs in the present work for $\text{Zr}_{70}\text{Ni}_{30}$ MG. In addition, three experimental data (XRD and Zr and Ni K-edge EXAFS) were simultaneously used for RMC simulation in the present work. The reliability to uncover complex atomic structure of $\text{Zr}_{70}\text{Ni}_{30}$ MG, thus, might be higher than those, in which only one XRD data⁸ or one neutron (electron) diffraction data^{15,16} was used (Table I).

We further compared the atomic structure of $\text{Zr}_{70}\text{Ni}_{30}$ MG with possible intermetallic ZrNi compounds, as shown in Fig. 4, in which all polyhedra were selected by the program ATOMS including all nearest atoms from each Wyckoff-site atom.³⁵ In fcc Zr_2Ni phase, three clusters exist, in which $\text{Zr}_{11}\text{Ni}_4$ cluster has a Zr atom at center with CN=14 atoms and Zr_9Ni_4 (Ni center) and Zr_7Ni_6 (Zr center) clusters are icosahedra with index of $\langle 0,0,12,0 \rangle$ (the ideal icosahedron), which differs from distorted icosahedra ($\langle 0,2,8,2 \rangle$, $\langle 0,3,6,3 \rangle$, and $\langle 0,4,4,4 \rangle$) for bond angles and structural symmetry. In

FIG. 3. Distribution of Voronoi clusters around Zr and Ni atoms in $\text{Zr}_{70}\text{Ni}_{30}$ metallic glass together with data reported for the $\text{Zr}_{66.7}\text{Ni}_{33.3}$ metallic glass (Ref. 15).

comparison, the atomic structure of $\text{Zr}_{70}\text{Ni}_{30}$ MG largely differs from the three clusters in fcc Zr_2Ni phase and also from the ideal icosahedron. On the other hand, in the tetragonal Zr_2Ni phase, Ni-centered Zr_8Ni_3 cluster has a CN=10, indexed as $\langle 0,2,8,0 \rangle$, which exists also in $\text{Zr}_{70}\text{Ni}_{30}$ MG with a relative high fraction. The cluster $\langle 0,2,8,0 \rangle$ is very similar with $\langle 0,2,8,1 \rangle$ (CN=11) for structural symmetry, which can be both regarded as Zr_8Ni_3 -like clusters here, with a total fraction of 13.73%. The Zr-centered $\text{Zr}_{12}\text{Ni}_4$ cluster has CN=15, which is rare in $\text{Zr}_{70}\text{Ni}_{30}$ MG. These discrepancies and similarity in atomic structure between $\text{Zr}_{70}\text{Ni}_{30}$ MG and the corresponding intermetallic compounds could be the possible reason why neither fcc Zr_2Ni phase nor icosahedral phase was formed during annealing treatment of $\text{Zr}_{70}\text{Ni}_{30}$ MG, whereas only the tetragonal Zr_2Ni phase is detected experimentally.

TABLE I. Local atomic structure obtained from RMC simulation for $Zr_{70}Ni_{30}$ metallic glass. R , CN, and HSDP stand for the nearest atomic distance, coordination number, and hard sphere dense packing, respectively. M = Zr and Ni atoms.

	Atomic pairs						
	Zr–Zr	Zr–Ni	Ni–Ni	Ni–Zr	Zr–M	Ni–M	M–M
CN	8.8	3.0	2.1	8.4	11.8	10.5	11.4
R by RMC (Å)	3.15	2.79	2.51	2.79			
R by HSDP (Å)	3.20	2.85	2.50	2.85			

CONCLUSIONS

In summary, atomic structure of $Zr_{70}Ni_{30}$ MG was investigated by RMC simulation combining with XRD and Ni and Zr K-edge EXAFS data. Distributions of CN and VCs were analyzed by Voronoi tessellation method. The average CN of atoms was obtained to be 11.4 together with the average CNs of Zr and Ni atoms of about 11.8 and 10.6, respectively. It is

found that Z11 Kasper polyhedron and distorted icosahedra are mainly favored structural units in $Zr_{70}Ni_{30}$ MG. The fact that $Zr_{70}Ni_{30}$ MG does not transform to icosahedral or fcc Zr_2Ni phase during crystallization process could be reflected by the discrepancy in atomic structure between $Zr_{70}Ni_{30}$ MG and its corresponding crystalline (or quasicrystalline) phases.

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FIG. 4. (Color online) Clusters extracted from crystalline Zr–Ni phases, (a) Zr_9Ni_4 , (b) Zr_7Ni_6 , and (c) $Zr_{11}Ni_4$ from fcc Zr_2Ni phase; (d) $Zr_{10}Ni_3$ from ideal icosahedral phase (roughly close to $Zr_{70}Ni_{30}$ composition); (e) Zr_8Ni_3 and (f) $Zr_{12}Ni_4$ from tetragonal Zr_2Ni phase.

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