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

L. Yang
International Center for New-Structured Materials (ICNSM) and Laboratory of New-Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People’s Republic of China

S. Yin, X. D. Wang, Q. P. Cao, and J. Z. Jiang$^a$
International Center for New-Structured Materials (ICNSM) and Laboratory of New-Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People’s Republic of China

K. Saksl and H. Franz
HASYLAB am DESY, Notekstrasse 85, D-22603 Hamburg, Germany

(Received 2 August 2007; accepted 23 August 2007; published online 17 October 2007)

Atomic structure of Zr$_{70}$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 Zr$_{70}$Ni$_{30}$ MG. The discrepancy in atomic structure between Zr$_{70}$Ni$_{30}$ MG and its corresponding crystalline (or quasicrystalline) phases can explain the fact that Zr$_{70}$Ni$_{30}$ MG does not transform to neither icosahedral nor fcc Zr$_2$Ni 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 Zr$_{70}$Cu$_{30}$Pd$_4$ MG,$^{10,11}$ which leads to primary phase transition by forming icosahedral quasicrystal$^{12,13}$ after annealing, while Zr$_{70}$Ni$_{30}$Pd$_{10}$ (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 Zr$_{70}$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

Zr$_{70}$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 × 2 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 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 Zr$_{70}$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 equation$^{23}$ 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
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 Zr$_{70}$Ni$_{30}$ MG, respectively. It is found that the first main peak and long-range oscillations up to about 15 Å$^{-1}$ 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 Å$^{-1}$, 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 Å, respectively, which are similar with those of ideal interatomic distances based on HSDP model. Distributions of atomic coordination number (CN) around Zr and Ni are plotted in Fig. 2 together with the average atom-atom CNs for Zr$_{70}$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.\(^{18,19}\), obtained from RMC simulation of neutron (electron) diffraction data for Zr$_{66.7}$Ni$_{33.3}$ MG.

Atomic structure of as-prepared Zr$_{70}$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 $\langle n_3, n_4, n_5, n_6, \ldots \rangle$, $n_i$ 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 3.5 Å. It is found that various VCs around Zr and Ni atoms exist in the Zr$_{70}$Ni$_{30}$ MG, plotted in Fig. 3 together with data reported for the Zr$_{66.7}$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 Zr$_{70}$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 $\langle 0,3,6,3 \rangle$.
(one of distorted icosahedra 9.82%), while the ideal icosahedron (standard Z12 Kasper one) indexed by \((0,0,12,0)\) has a concentration of 3.58%. Around Ni atoms, the most popular VCs are \((0,2,8,1)\) (9.42%), \((0,4,4,3)\) (one of distorted Z11 Kasper polyhedron 8.42%), and \((0,3,6,1)\) (one of distorted Z10 Kasper polyhedron 7.23%), while the distorted icosahedra \((0,3,6,3,0,2,8,2,0,4,4,4)\) have a total concentration of 14.66% together with 1.39% the ideal icosahedron \((0,0,12,0)\). These results reveal that Z11 Kasper polyhedron and distorted icosahedra are favored atomic structures in this Zr\(_{70}\)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 Zr\(_{66.7}\)Ni\(_{33.3}\) MG. The average CN of Ni atoms was estimated to be 10.6 for Zr\(_{70}\)Ni\(_{30}\) MG obtained here and 10 for Zr\(_{66.7}\)Ni\(_{33.3}\) MG. 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 Zr\(_{70}\)Ni\(_{30}\) and Zr\(_{66.7}\)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.\(^{8}\) 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 Zr\(_{70}\)Ni\(_{30}\) MG, thus, might be higher than those, in which only one XRD data\(^{8}\) or one neutron (electron) diffraction data\(^{15,16}\) was used (Table I).

We further compared the atomic structure of Zr\(_{70}\)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\(_{2}\)Ni phase, three clusters exist, in which Zr\(_{11}\)Ni\(_{4}\) clusters have a Zr atom at center with CN=14 atoms and Zr\(_{2}\)Ni\(_{1}\) (Ni center) and Zr\(_{7}\)Ni\(_{6}\) (Zr center) clusters are icosahedra with index of \((0,0,12,0)\) (the ideal icosahedron), which differs from distorted icosahedra \((0,2,8,2,0,3,6,3,0,4,4,4)\) for bond angles and structural symmetry. In comparison, the atomic structure of Zr\(_{70}\)Ni\(_{30}\) MG largely differs from the three clusters in fcc Zr\(_{2}\)Ni phase and also from the ideal icosahedron. On the other hand, in the tetragonal Zr\(_{2}\)Ni phase, Ni-centered Zr\(_{8}\)Ni\(_{3}\) cluster has a CN=10, indexed as \((0,2,8,0)\), which exists also in Zr\(_{70}\)Ni\(_{30}\) MG with a relative high fraction. The cluster \((0,2,8,0)\) is very similar with \((0,2,8,1)\) (CN=11) for structural symmetry, which can be both regarded as Zr\(_{8}\)Ni\(_{3}\)-like clusters here, with a total fraction of 13.73%. The Zr-centered Zr\(_{12}\)Ni\(_{4}\) cluster has CN=15, which is rare in Zr\(_{70}\)Ni\(_{30}\) MG. These discrepancies and similarity in atomic structure between Zr\(_{70}\)Ni\(_{30}\) MG and the corresponding intermetallic compounds could be the possible reason why neither fcc Zr\(_{2}\)Ni phase nor icosahedral phase was formed during annealing treatment of Zr\(_{70}\)Ni\(_{30}\) MG, whereas only the tetragonal Zr\(_{2}\)Ni phase is detected experimentally.
CONCLUSIONS

In summary, atomic structure of Zr70Ni30 MG was investigated by RMC simulation 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 for 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 Zr70Ni30 MG. The fact that Zr70Ni30 MG does not transform to icosahedral or fcc Zr2Ni phase during crystallization process could be reflected by the discrepancy in atomic structure between Zr70Ni30 MG and its corresponding crystalline (or quasicrystalline) phases.

ACKNOWLEDGMENTS

The authors would like to thank HASYLAB in Germany, KEK and SPring-8 in Japan, BSRF in Beijing, NSRL in Hefei, and APS in USA for use of the synchrotron radiation facilities. Financial support from the National Natural Science Foundation of China (Grants Nos. 50341032, 50425102, 50601021, 5070138 and 60776014), the Zhejiang University-Helmholtz cooperation fund, the Ministry of Education of China (Program for Changjiang Scholars), the Zhejiang University, and the Nanjing University of Aeronautics and Astronautics is gratefully acknowledged.

12J. Saida, M. Matsushita, and A. Inoue, Intermetallics 10, 1089 (2002).

TABLE I. Local atomic structure obtained from RMC simulation for Zr70Ni30 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.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>8.8</td>
<td>3.0</td>
<td>2.1</td>
<td>8.4</td>
<td>11.8</td>
<td>10.5</td>
<td>11.4</td>
</tr>
<tr>
<td>R by RMC (Å)</td>
<td>3.15</td>
<td>2.79</td>
<td>2.51</td>
<td>2.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R by HSDP (Å)</td>
<td>3.20</td>
<td>2.85</td>
<td>2.50</td>
<td>2.85</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>