Structural Study of Amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ ($\text{M} = \text{Cr}, \text{W}, \text{NB}, \text{ZR and HF}$) Alloys by X-ray Diffraction

Takahiro Nakamura$^{1, *}$, Eiichiro Matsubara$^2$, Muneyuki Imafuku$^3$, Hisato Koshiba$^4$, Akihisa Inoue$^2$ and Yoshio Waseda$^5$

$^1$Department of Materials Science, Tohoku University, Sendai 980-8577, Japan
$^2$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
$^3$Inoue Superliquid Glass Project, ERATO, Sendai 982-0807, Japan
$^4$Alps Electric Co., Nagaoka 940-8572, Japan
$^5$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Local atomic structures in amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ ($\text{M} = \text{Cr}, \text{W}, \text{Nb}, \text{Zr}$ and $\text{Hf}$) alloys with different $\Delta T_c$ values were studied by the ordinary X-ray diffraction, anomalous X-ray scattering and EXAFS methods. Their local the atomic structures basically resemble each other, i.e. a random network structure of triangular prisms. Only difference in local atomic structure is a shape of the local structural unit. In the amorphous alloys containing M elements larger than Fe atoms, the prisms show distorted shapes due to a size difference $\Delta r$ between M and Fe. A linear relation between $\Delta r$ and $\Delta T_c$, and a comparison of their crystallization processes suggest us that their thermal stability is attributed to difficulty in rearranging the irregular structural units because of a non-zero $\Delta r$ value.

(Received March 8, 2001; Accepted April 10, 2001)

Keywords: iron-based bulk amorphous alloy, anomalous X-ray scattering method, extended X-ray absorption fine structure (EXAFS) local atomic structure, thermal stability, crystallization

1. Introduction

Zr$^{1,2}$ and lanthanide-based$^3$ amorphous alloys discovered by Inoue et al. show a temperature span of supercooled liquid region more than 100 K, that was larger than the maximum value previously reported in the amorphous alloys containing precious metals, such as Pt–Ni–P and Pd–Ni–P etc.$^4$ These new types of amorphous alloys have been called bulk metallic glasses because of extremely good thermal stability. Inoue pointed out three guiding principles to develop the bulk metallic glasses. Firstly, the system contains more than three elements, secondly the difference of atomic sizes among the main constituent elements is larger than 12%, and thirdly heats of mixing among them are large negative values.$^5$ According to these empirical rules, a Fe-based bulk amorphous alloy with a supercooled liquid region of more than 50 K and a good soft magnetic property has been discovered in Fe-(Al, Ga)-(P, C, B, Si)$^6$ and Fe–Zr–B systems.$^7$ Based upon this Fe–Zr–B system, many other Fe-based bulk metallic glasses were developed.

In the present study, we analyzed the atomic structures of amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ alloys. Their characteristic thermal stability is strongly dependent upon the element M. A temperature span of the supercooled liquid region ($\Delta T_c$) in an amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ alloy is systematically change by selecting a transition metal M in Group VI to VIII of the periodic table. The $\Delta T_c$ is the maximum value of 89 K in an amorphous $\text{Fe}_{70}\text{Hf}_{10}\text{B}_{20}$ alloy and zero in an amorphous $\text{Fe}_{70}\text{Cr}_{10}\text{B}_{20}$ alloy. In the previous study in amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ ($\text{M} = \text{Cr}, \text{Nb}$ and Zr) alloys, their local structures have been determined.$^8$ A resemblance among their local atomic structures has been found in spite of the difference in their thermal stability. In order to verify the previous result and discuss their structural features in a systematic manner for understanding the origin of their thermal stability in the amorphous state, local atomic structures in amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ alloys for $\text{M} = \text{Hf}$ and $\text{W}$ as well as $\text{M} = \text{Zr}$, Nb and Cr have been analyzed by both the anomalous X-ray scattering (AXS) and EXAFS methods.

2. Experimental

Ingots of $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ ($\text{M} = \text{Hf}, \text{Zr}, \text{Nb}, \text{W}$ and $\text{Cr}$) alloys were prepared by arc-melting mixtures of pure metals and boron crystal in nominal compositions. Amorphous ribbons 0.03 mm thick and 3 mm wide were prepared by the melt spinning technique in argon atmosphere. Grass transition and crystallization temperatures, determined by the differential scanning calorimetry at a heating rate of 0.67 K/s, are 871 K and 960 K in the amorphous $\text{Fe}_{70}\text{Hf}_{10}\text{B}_{20}$ alloy, 860 K and 947 K in the amorphous $\text{Fe}_{70}\text{Zr}_{10}\text{B}_{20}$ alloy, 833 K and 886 K in the amorphous $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ alloy and 819 K and 860 K in the amorphous $\text{Fe}_{70}\text{W}_{10}\text{B}_{20}$ alloy. The crystallization temperature was observed at 772 K and no glass transition exists in the amorphous $\text{Fe}_{70}\text{Cr}_{10}\text{B}_{20}$ alloy. For X-ray measurements, some pieces of the ribbons of about 20 mm long were prepared and closely arranged on an aluminum frame with a window of 15 mm by 10 mm. At low scattering angles, scattering intensities were measured with a symmetrical transmission geometry and at high angles a symmetrical reflection geometry was applied.

AXS and EXAFS were measured at BL-7C in the Photon Factory of Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Energy differential intensity profiles for M elements were obtained from the AXS intensities at 50 and 300 eV below the Hf $L_{III}$, Zr K, Nb K and W $L_{III}$ ab-

---

*Graduate Student, Tohoku University.
sorption edges in the amorphous Fe\textsubscript{70}Hf\textsubscript{10}B\textsubscript{20}, Fe\textsubscript{70}Zr\textsubscript{10}B\textsubscript{20}, Fe\textsubscript{50}Nb\textsubscript{10}B\textsubscript{20} and Fe\textsubscript{70}W\textsubscript{10}B\textsubscript{20} alloys, respectively. The environmental radial distribution functions (RDFs) around M were evaluated by their Fourier transformation. The EXAFS spectra were measured at the Fe K, Zr K, Nb K, Cr K, Hf L\textsubscript{III} and W L\textsubscript{III} absorption edges.

The total interference function is calculated from the intensity profile in absolute units by the following equation: \[ Q_i(Q) = \frac{I_{00}(Q) - \langle f^2 \rangle}{\langle f \rangle^2} \quad (1) \]

\[ \langle f \rangle = \sum_{j=1}^{N} x_j f_j \text{ and } \langle f^2 \rangle = \sum_{j=1}^{N} x_j f_j^2, \quad (2) \]

where \( x_j \) and \( f_j \) are the atomic fraction and X-ray atomic scattering factor of the element \( j \) and \( N \) is the total number of constituent elements. The total Warren-type RDF\textsuperscript{11} is given by the Fourier transformation of the total interference function

\[ Q \Delta i_A(Q, E_1, E_2) = \frac{(I_{00}(Q, E_1) - \langle f^2(Q, E_1) \rangle) - (I_{00}(Q, E_2) - \langle f^2(Q, E_2) \rangle)}{W(Q, E_1, E_2)} \quad (5) \]

and

\[ W(Q, E_1, E_2) = \sum_{j=1}^{N} x_j \Re[f_j(Q, E_1) + f_j(Q, E_2)]. \quad (6) \]

where \( \Re \) indicates the real part of the term in parentheses. The Fourier transformation of the energy differential interference function gives the environmental RDF around A.

\[ 2\pi^2 \rho_A(r) = 2\pi^2 \rho_0 + \frac{1}{x_A} \frac{f_A}{f_A'(E_2)} \times \int_0^{Q_{\text{max}}} Q \Delta i_A(Q) \sin(Qr) dQ \quad (7) \]

and

\[ \rho_A(r) = \sum_{j=1}^{N} \Re[f_j(Q, E_1) + f_j(Q, E_2)] \rho_A(j) \quad (8) \]

where \( \rho_A \) and \( \rho_A(j) \) are the environmental number density function around A and the partial number density function of A-j pairs, respectively.

Narten and Levy\textsuperscript{12} proposed an expression of the total interference function by the following equation.

\[ Q_i(Q) = \sum_{j=1}^{N} \sum_{k=1}^{N} x_j f_j f_k N_{jk} \exp(-b_{jk}Q^2) \sin Qr_{jk} \]

\[ + \sum_{j=1}^{N} \sum_{k=1}^{N} 4\pi \rho_0 x_j x_k f_j f_k \frac{f_k}{f_j} \times \exp(-b_{jk}Q^2) \frac{Q R_{jm} \cos Q R_{jm} - \sin Q R_{jm}}{Q^2}. \quad (9) \]

where \( N_{jk}, r_{jk} \) and \( b_{jk} \) are the coordination number, atomic distance and mean square variation of j-k pairs, and \( R_{jm} \) and \( B_{jm} \) are the size and variation of the boundary region in eq. (1).

\[ 2\pi^2 \rho(r) = 2\pi^2 \rho_0 + \int_0^{Q_{\text{max}}} Q i(Q) \sin(Qr) dQ \quad (3) \]

and

\[ \rho(r) = \sum_{j=1}^{N} \sum_{k=1}^{N} c_j f_j f_k \left( \frac{f_j}{f_k} \right)^2 \rho_{jk}(r). \quad (4) \]

where \( \rho, \rho_{jk} \) and \( \rho_0 \) are the total number density function, the partial number density function of j-k pairs and the average number density.

The energy differential interference function for the element A is evaluated from the difference between two intensities in absolute units observed at two incident energies of \( E_1 \) and \( E_2 \) below the absorption edge of A.

3. Results and Discussion

Fourier transforms of \( k^3 \chi(k) \) by EXAFS measurements at Fe K absorption edge are shown in Fig. 1. The Fourier transformation was done over a \( k \)-range from 35 to 140 nm\textsuperscript{-1} and the phase shift was not corrected for all amorphous alloys. They show the similar profiles in all samples. This indicates that the atomic structure around Fe is identical. Fourier transforms of M that are shown in Fig. 2 also resemble each other except for a small shift among the profiles. This shift is ex-
Fig. 1  Fourier transforms of EXAFS at Fe K absorption edge in amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb, W and Cr) alloys.

Fig. 2  Fourier transforms of EXAFS at Cr K, W L$_{III}$, Nb K, Zr K and Hf L$_{III}$ absorption edges in amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb, W and Cr) alloys.

Fig. 3  The total (solid) and environmental RDFs (broken) in the amorphous Fe$_{70}$M$_{10}$B$_{20}$ alloys. (a) Fe$_{70}$Hf$_{10}$B$_{20}$, (b) Fe$_{70}$Zr$_{10}$B$_{20}$, (c) Fe$_{70}$Nb$_{10}$B$_{20}$, (d) Fe$_{70}$W$_{10}$B$_{20}$ and (e) Fe$_{70}$Cr$_{10}$B$_{20}$. The positions of Fe–B, Fe–Fe and M–Fe pairs are labeled ‘1’, ‘2’ and ‘3’.

(e). On the other hand, those of Fe–Fe pairs in the total RDFs labeled ‘2’ are located at the same position. This result is consistent with that in the EXAFS measurements in Figs. 1 and 2. Coordination numbers and atomic distances determined from the RDFs are summarized in Table 1. Total coordination numbers of Fe and M around B are 5.7, 5.6, 5.7, 5.7 and 5.2 for M = Hf, Zr, Nb, W and Cr, respectively. They are close to 6 for B–Fe pairs in the Fe$_3$B crystal. This suggests that a local structural unit in these amorphous alloys is like a triangular prism consisting of a B atom at the center surrounded by 6 Fe atoms at the vertices in the crystal. Fractions of the M elements calculated from the coordination numbers of Fe and M around B are 0.14, 0.13, 0.14 and 0.14 in the amorphous Fe$_{70}$Hf$_{10}$B$_{20}$, Fe$_{70}$Zr$_{10}$B$_{20}$, Fe$_{70}$Nb$_{10}$B$_{20}$ and Fe$_{70}$W$_{10}$B$_{20}$ alloys, respectively, and close to 0.13 that is calculated from the concentration of M. This indicates that the M elements randomly replace the positions of Fe at the vertices.

According to the results of the EXAFS and AXS measurements, the basic atomic structure resembles in all amorphous samples although the $\Delta T_f$ values largely change. Only difference of atomic structures that have been found in the amorphous state is a shape of the triangular prism as the local structural units due to a size difference between Fe and M. Namely, the amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) alloys with the non-zero $\Delta T_f$ values form a random network structure consisting of the triangular prisms of an irregular shape. On the other hand, the thermally unstable and conventional-type amorphous Fe$_{70}$Cr$_{10}$B$_{20}$ alloy is a random network structure of regular-shaped prisms like that in the Fe$_3$B crystal. Consequently, the thermal stability of the amorphous Fe$_{70}$M$_{10}$B$_{20}$ alloy appears to be closely related with a shape of the local structural unit. It is interesting to note a quite good linear relation between the $\Delta T_f$ values and the size differences between Fe and M in Fig. 4 in connection with the

explained by a size difference of the element M because this peak is attributed to M–Fe pairs. Namely, atomic radii of Hf, Zr, Nb, W and Cr are 0.167, 0.160, 0.146, 0.141 and 0.130 nm, respectively.

The total and environmental RDFs around M are compared in Fig. 3. The solid and broken curves correspond to the total and environmental RDFs, respectively. The positions of the first peaks of M–Fe pairs in the environmental RDFs labeled ‘3’ are gradually moved to a lower r-value in Fig. 3(a) through
Structural Study of Amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = CR, W, NB, ZR and HF) Alloys by X-ray Diffraction

Table 1 Coordination numbers and atomic distances of the amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb, W and Cr) alloys and crystalline Fe$_2$B. Their experimental errors are ±0.002 nm and ±0.2.

<table>
<thead>
<tr>
<th>Paris</th>
<th>M = Hf</th>
<th>r/nn</th>
<th>N</th>
<th>M = Zr</th>
<th>r/nn</th>
<th>N</th>
<th>M = Nb</th>
<th>r/nn</th>
<th>N</th>
<th>M = W</th>
<th>r/nn</th>
<th>N</th>
<th>M = Cr</th>
<th>r/nn</th>
<th>N</th>
<th>Fe$_2$B crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-Fe</td>
<td>0.214</td>
<td>4.9</td>
<td></td>
<td>0.212</td>
<td>4.9</td>
<td></td>
<td>0.214</td>
<td>4.9</td>
<td></td>
<td>0.214</td>
<td>4.9</td>
<td></td>
<td>0.242</td>
<td>5.2</td>
<td></td>
<td>0.207</td>
</tr>
<tr>
<td>B-M</td>
<td>0.250</td>
<td>0.8</td>
<td></td>
<td>0.260</td>
<td>0.7</td>
<td></td>
<td>0.250</td>
<td>0.8</td>
<td></td>
<td>0.238</td>
<td>0.8</td>
<td></td>
<td>0.249</td>
<td>8.4</td>
<td></td>
<td>0.258</td>
</tr>
<tr>
<td>Fe-Fe$_1$</td>
<td>0.254</td>
<td>7.7</td>
<td></td>
<td>0.254</td>
<td>8.2</td>
<td></td>
<td>0.253</td>
<td>8.1</td>
<td></td>
<td>0.249</td>
<td>8.4</td>
<td></td>
<td>0.253</td>
<td>8.9</td>
<td></td>
<td>0.258</td>
</tr>
<tr>
<td>Fe-M$_1$</td>
<td>0.290</td>
<td>1.3</td>
<td></td>
<td>0.293</td>
<td>0.8</td>
<td></td>
<td>0.282</td>
<td>1.1</td>
<td></td>
<td>0.272</td>
<td>1.2</td>
<td></td>
<td>0.276</td>
<td>2.7</td>
<td></td>
<td>0.281</td>
</tr>
<tr>
<td>Fe-Fe$_2$</td>
<td>0.272</td>
<td>2.7</td>
<td></td>
<td>0.284</td>
<td>2.5</td>
<td></td>
<td>0.272</td>
<td>2.4</td>
<td></td>
<td>0.280</td>
<td>2.2</td>
<td></td>
<td>0.276</td>
<td>2.7</td>
<td></td>
<td>0.281</td>
</tr>
<tr>
<td>Fe-M$_2$</td>
<td>0.330</td>
<td>0.5</td>
<td></td>
<td>0.323</td>
<td>0.7</td>
<td></td>
<td>0.316</td>
<td>0.6</td>
<td></td>
<td>0.298</td>
<td>0.3</td>
<td></td>
<td>0.276</td>
<td>2.7</td>
<td></td>
<td>0.281</td>
</tr>
</tbody>
</table>

Fig. 4 A relation between a size difference between Fe and M, $\Delta r$ and a temperature span of supercooled liquid region, $\Delta T_{x}$, in various amorphous Fe$_{70}$M$_{10}$B$_{20}$ alloys. The M elements are indicated in the figure.

above arguments.

In the Fe$_2$B crystal, the triangular prisms are connected in two different ways. Namely, one third of Fe atoms are connected by sharing Fe at the vertex of the prism and the others by sharing the edge. The coordination numbers of the first and second neighbors around Fe with the two types of connections in the Fe$_2$B crystal are summarized in Table 2. Since the M elements appear to occupy the vertices in a random manner, the average coordination numbers of the first and second neighbors around Fe and M atoms in Table 2 were evaluated from the coordination numbers of Fe–Fe and M–Fe pairs. The coordination numbers in the amorphous Fe$_{70}$Cr$_{10}$B$_{20}$ alloy are close to the average values in the Fe$_2$B crystal. The values in the other amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) alloys are, however, different to those in the crystal. Accordingly, both edge- and vertex-sharing are present in the amorphous Fe$_{70}$Cr$_{10}$B$_{20}$ alloy that has a random network structure of a regular-shaped prism. On the other hand, the way of connections of slightly the irregular shape prisms in Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) alloys is different from that in the Fe$_2$B crystal.

The profiles of the differential scanning calorimetry (DSC) in the amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb W and Cr) alloys are compared in Fig. 5. It is noted that there are two exothermic peaks in the amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) alloys and only a single peak in the amorphous Fe$_{70}$Cr$_{10}$B$_{20}$ alloy. Observations of the crystallization process in these amorphous alloys with and without the glass transition suggest that rearrangements of the irregular shape prisms during crystallization in the amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) alloys appear to be more difficult than those of the regular shape prisms in the amorphous Fe$_{70}$Cr$_{10}$B$_{20}$ alloy. This would retard the crystallization and stabilize the amorphous phase.

This is also verified from the fact that the metastable crystalline phase in the Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) systems has a complicated crystal structure with a large unit cell containing more than 100 atoms. In order to understand the further details about a relation between the thermal stability and the local atomic structure in the amorphous state, the local environments around M in the metastable crystalline phase must be solved by using the AXS method.

4. Summary

The local atomic structure in the amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb, W and Cr) alloys were determined by the ordinary X-ray diffraction, AXS and EXAFS methods. The local structural unit in all samples is the triangular prism consisting of a B at the center and 6 Fe at the vertices. The M elements randomly replace some of these Fe atoms. Thus, their basic atomic structures resemble each other through their $\Delta T_{x}$ values region varies from 0 to about 90 K. The only difference in the atomic structures in the amorphous state is a shape of the prism. The amorphous Fe$_{70}$M$_{10}$B$_{20}$ (M = Hf, Zr, Nb and W) alloys with the non-zero $\Delta T_{x}$ consist of a random network structure of the irregular shaped local unit structures. On the other hand, the amorphous Fe$_{70}$Cr$_{10}$B$_{20}$ alloy with no
glass transition, is a random network structure of the regularly shaped units.

Acknowledgements

The AXS and EXAFS measurements with synchrotron radiation at the Photon Factory of Institute of the Materials Science (IMSS) were carried out under the Proposal No. 99G186 and 2000G239. This work was supported by Special Cooperation Funds for Promoting Science and Technology on “Nanohetero Metallic Materials” from the Science and Technology Agency.

REFERENCES