Local Atomic Structures of Amorphous $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ Alloys Studied by Electron Diffraction

Akihiko Hirata¹, Yoshihiko Hirotsu¹ and Eiichiro Matsubara²

¹*Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan*

²*Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan*

Effect of Nb addition on the stabilization of amorphous $\text{Fe}_{80}\text{B}_{20}$ alloy was studied by electron diffraction structure analysis with the help of computer simulation. Atomic structure models with dense-random-packing 5000 atoms were constructed to reproduce interference functions obtained experimentally for the amorphous $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ alloys. In the structure models so obtained, prism-type local atomic arrangements dominated around B atoms in both the alloys, while deformed-bcc and icosahedral-like clusters were frequently found around Fe atoms. The icosahedral-like clusters and short Fe-Fe bondings were more frequently found in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. The difference of glass forming abilities of these alloys is discussed in relation to the local structural differences.

(Received July 20, 2005; Accepted September 12, 2005; Published December 15, 2005)

Keywords: nanoscale phase separation, glass forming ability, energy filtered electron diffraction, reverse Monte Carlo simulation

1. Introduction

In the last decade, numerous bulk metallic glasses (BMGs) have been found in the Mg-, La-, Pd-, Zr-, Fe-based alloy systems.¹⁾ Extremely high glass forming ability is necessary to synthesize BMGs, where cooling rates are as low as 10^2 K/s or less. In order to develop new BMGs, it is important to know physical origins of the high glass forming ability in metallic glasses. Effects of atomic size, chemical bonding, and valence electron have been discussed to elucidate the origins.¹⁻³⁾ From the structural point of view, it is significant to compare a difference in local atomic arrangements between amorphous structures having low and high glass forming abilities.

Amorphous alloys are usually formed in the vicinity of a eutectic composition. This fact implies that the liquid phase in amorphous alloys tends to separate into the related solid phases on cooling, when the atomic diffusivity is not prohibited. Even if the amorphous structure is obtained, the structural fluctuation is, more or less, considered to occur at an atomistic level, since atomic diffusion as small as one atomic distance cannot be prohibited by the cooling from the melt. Our group has actually found local structural fluctuation (we call it nanoscale phase separation) in the several amorphous alloy systems by means of transmission electron microscopy.⁴⁾ For instance, the fcc-Pd and Pd-Si compound-like clusters were found in the a-Pd-Si alloy.⁵⁾ The configuration-types and their fractions of atomic clusters found in the nanoscale phase separated state are considered to affect the glass forming ability. The cluster sizes and their observation frequency are dependent on the cooling rate.

Recently, in Fe-B-based alloy systems, many metallic glasses with high glass forming ability have been produced by addition of the third elements to the binary Fe-B alloys. Among these systems, the amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ (M is the transition metal) alloys are found to have a large supercooled liquid region.⁶⁾ As for $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$, the temperature span of supercooled liquid region is about 54 K. In contrast, a supercooled liquid region cannot be detected on normal heating in the binary $\text{Fe}_{80}\text{B}_{20}$.⁷⁾ In this paper, we describe our

recent investigation of the effect of Nb substitution to Fe on the local atomic arrangement of amorphous $\text{Fe}_{80}\text{B}_{20}$ alloy studied by diffraction intensity analysis with the help of computer simulation. As the diffraction technique, we used electron diffraction in this study, by taking advantage of its high scattering amplitude against light element like B and its scattering information up to high scattering angles as high as those in the synchrotron X-ray diffraction. On the basis of the results, the structural differences between these two alloys are discussed based on the concept of nanoscale phase separation.

2. Experimental Procedure

The $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ metallic glasses were made by single-roll rapid quenching technique. TEM specimens were prepared by using low-angle and low-voltage Ar beam thinning (Gatan PIPS and LINDA IV3/L). Selected area diffraction patterns (SAED) were taken by 200 kV TEM (LEO-922D) equipped with an in-column-type energy filter. We took the electron diffraction patterns eliminating inelastic part of intensities. Energy window width for selecting zero-loss intensities was adjusted to be about 20 eV. The camera-length was corrected by taking a diffraction pattern for fine gold particles. The diffraction patterns were taken up to a high scattering angle with a scattering vector $Q = 200 \text{ nm}^{-1}$ ($Q = 4\pi \sin \theta / \lambda$; θ : scattering angle; λ : electron wave length). The electron intensities were recorded on imaging plates (IPs) and read using an IP reader (DITABIS-MICRON).

From each recorded intensity profile, reduced interference function can be obtained by⁸⁾

$$Q_i(Q) = \frac{[I_{\text{obs}}(Q) - BG(Q)]Q\langle f^2 \rangle}{BG(Q)\langle f \rangle^2} \quad (1)$$

where $I_{\text{obs}}(Q)$ is the observed intensity of the elastic scattering and f the atomic scattering factor. $BG(Q)$ is the background intensity, which smoothly links the middle points of the intensity maxima and minima in the intensity profile.

In order to obtain plausible structural models, we combined a static relaxation and a reverse Monte-Carlo (RMC) simulation.⁹⁾ We firstly prepared initial structures with randomly distributed 5000 atoms in the cubic cells. To determine dimensions of the structural models, we measured the physical densities of the as-formed $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ specimens by Archimedean technique, and they were 7.31 and 7.68 g/cm³, respectively. Dimensions of the cells were then determined as (3.76 nm)³ for $\text{Fe}_{80}\text{B}_{20}$ and (3.79 nm)³ for $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ with 5000 atoms based on the measured densities. Note that we also used the measured densities as input parameters in the later RMC calculation. The structures were subsequently relaxed by using Lennard-Jones atomic potentials to satisfy plausible atomic distances for Fe–Fe, Fe–Nb, Fe–B, Nb–Nb, Nb–B, and B–B found in their crystalline phases. So that the interference functions from the structure models reproduce the experimental ones, we finally performed the RMC simulation for these initial structure models by fitting the calculated interference function to the experimental one using weighting factors depend on Q values. The simulation was carried out using RMCA program.¹⁰⁾ For final simulated atomic configurations, we performed the Voronoi polyhedral analysis to examine characteristics of the local atomic environments. In order to remove the short edges, Voronoi polyhedra were created by merging vertices closer than a distance of 0.01 nm.¹¹⁾

3. Results

Figure 1 shows experimental interference functions obtained from $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$, together with the calculated profiles from the RMC-simulated final structure models. Although Nb atoms are included in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$, there is no marked difference between both of these profiles in appearance. In the profile of $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$, however, each peak is slightly broadened in comparison with that in $\text{Fe}_{80}\text{B}_{20}$. The agreements between the experimental and simulated profiles are very well in both the alloys.

Total and partial PDFs obtained from the final structural models of $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ are shown in Figs. 2(a) and (b), respectively. The total PDF for each alloy is almost the same in shape. Peak tops of Fe–B, Fe–Fe peaks for $\text{Fe}_{80}\text{B}_{20}$ and those of Fe–B, Fe–Fe, and Fe–Nb for $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ are found at 0.210, 0.258, 0.210, 0.252, and 0.270 nm, respectively. It should be noted that the average bond length of Fe–Fe pair is shortened by the Nb substitution.

In order to clarify characteristics of the structure models, we performed the Voronoi polyhedral analyses for the models of $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. Figures 3(a) and (b) correspond to numbers of Voronoi polyhedra around B and Fe atoms in their final structural models, respectively. We show coordination numbers in parenthesis, together with Voronoi indices. The total numbers of atoms in the structure models are 4000 Fe and 1000 B for $\text{Fe}_{80}\text{B}_{20}$ and 3500 Fe, 500 Nb and 1000 B for $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. Around B atoms, polyhedra represented as “0 4 4 0 0 0” and “0 3 6 0 0 0” almost dominate and these polyhedra are found from 54% of B atoms in $\text{Fe}_{80}\text{B}_{20}$ and 43% of B atoms in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. The polyhedra of “0 4 4 0 0 0” and “0 3 6 0 0 0” can be regarded

Fig. 1 Interference functions of (a) $\text{Fe}_{80}\text{B}_{20}$ and (b) $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ obtained experimentally together with calculated profiles using the final structure models.

as the Archimedean antiprism and the trigonal prism with three capping atoms, respectively. The prism-related local structures are inherently formed around B atoms in both of the alloys. Around Fe atoms, on the other hand, characteristics of polyhedra in these two alloys are slightly different with each other, although the indices of “0 3 6 4 0 0” and “0 1 10 2 0 0” indicating deformed-bcc and icosahedral-like clusters with a common coordination number of 13 are frequently found commonly in both the alloys. Polyhedra with indices of “0 2 8 2 0 0” and “0 2 8 1 0 0” with smaller coordination numbers (11–12), which belong to icosahedral-like clusters, are enriched in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ in comparison with those in $\text{Fe}_{80}\text{B}_{20}$. The perfect icosahedral clusters with “0 0 12 0 0 0” index also present with a higher frequency in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. In $\text{Fe}_{80}\text{B}_{20}$, on the other hand, there are many polyhedra with “0 2 8 4 0 0”, “0 3 6 5 0 0” and “0 4 4 6 0 0”

Fig. 2 Total and partial pair distribution functions of (a) Fe₈₀B₂₀ and (b) Fe₇₀Nb₁₀B₂₀ derived from the final structure models.

with a high coordination number of 14, which are regarded as deformed-bcc clusters. The frequency of finding these polyhedra is larger than that in the Fe₇₀Nb₁₀B₂₀ structure.

4. Discussion

On the basis of high-resolution electron microscopy (HREM) and nanobeam electron diffraction, amorphous alloy structures have been understood to have a structure with nanoscale-phase-separation in which some crystal-like cluster regions with structures similar to those in the crystallization stage are formed locally with sizes of 1–2 nm.^{5,12)} In the amorphous Fe₈₀B₂₀ and Fe₇₀Nb₁₀B₂₀ alloys, our group already found nanoscale phase separation with bcc-Fe and compound-like local ordered regions by using nanobeam electron diffraction technique together with HREM.^{13,14)} We

Fig. 3 Fractions of Voronoi polyhedra with central (a) B atoms and (b) Fe atoms.

now discuss a difference of the glass forming abilities between the two alloys based on the local atomic arrangements derived from the final structure models.

The crystalline phases and their basic structural units already found in the ternary Fe–Nb–B system¹⁵⁾ are represented in Fig. 4. The compositions of Fe₈₀B₂₀ and Fe₇₀Nb₁₀B₂₀ are also shown in the diagram. Among these phases, bcc-Fe, Fe₂B, and Fe₂Nb are stable, whereas the Fe₃B, α -Mn, and (Fe,Nb)₂₃B₆ phases are metastable.¹⁴⁾ The iron-boride (Fe₂B, Fe₃B, (Fe,Nb)₂₃B₆) structures are basically constructed by the network of Archimedean antiprism (Voronoi index is “0 4 4 0 0”). In both of the present alloys, the basic structural unit of iron-boride crystal structures was found to be enriched in the amorphous structures, since the antiprism clusters “0 4 4 0 0” and the trigonal prism “0 3 6 0 0 0” dominate in both structure models. Thus, the atomic arrangements around B atoms are almost the same in these two alloys. Around Fe atoms, on the other hand, icosahedral (-like) atomic clusters with coordination number of 11–12 were rather enriched in Fe₇₀Nb₁₀B₂₀ compared with Fe₈₀B₂₀. It should be noted that the α -Mn and Fe₂Nb phases appear in the Fe–Nb–B system and the crystal structures of these phases are characterized by topologically closed packed ones

Fig. 4 Diagram of crystal structures found in Fe–Nb–B ternary system.

and their common main structural unit is the icosahedral cluster.^{16,17)} The frequent existence of icosahedral (-like) clusters in the as-formed $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ alloy indicates that a more closely packed structure is realized in the amorphous structure of $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ than in $\text{Fe}_{80}\text{B}_{20}$. Actually, the Nb substitution leads a shrinking of the average Fe–Fe bond length [see Fig. 2(b)]. In the binary $\text{Fe}_{80}\text{B}_{20}$ model, on the other hand, the bcc-like clusters with a coordination number of 14 are relatively enriched in numbers in comparison with those in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. This fact means that in the amorphous $\text{Fe}_{80}\text{B}_{20}$ alloy local atomic arrangements with loosely packed atoms forming deformed-bcc clusters are found more frequently than in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. We can conclude that a more closely packed atomic structure realized in the ternary $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ glass increases the glass forming ability.

5. Conclusion

We constructed structure models of $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ to reproduce the interference functions obtained by electron diffraction experimentally. In both of the models, prism-type clusters dominated around B atoms, which are basic structure units found in some Fe-boride compounds. Around Fe atoms, the icosahedral (-like) clusters found in Fe–Nb compounds are rather enriched in the ternary $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ alloy. On the other hand, atomic arrangements of deformed bcc clusters with a large coordination number are more frequently observed around Fe atoms in $\text{Fe}_{80}\text{B}_{20}$

than in $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$. Since the icosahedral (-like) clusters are regarded as topologically closed packed structure, the higher glass forming ability of $\text{Fe}_{70}\text{Nb}_{10}\text{B}_{20}$ is ascribed to the high atomic packing density around Fe atoms.

Acknowledgement

This work is partly supported by the Grant in Aid of Ministry of Education, Culture, Sports, Science and Technology, Priority Area on “Materials Science of Bulk Metallic Glasses” and by Special Coordination Funds for Promoting Science and Technology on “Nanohetero Metallic Materials” from the Science and Technology Agency of Japan. We thank Prof. V. Bengus for supplying the samples. One of us (A.H.) also acknowledges Drs. T. Ohkubo and M. Naito for developing computer programs, and Drs. I.-T. Bae and T. Hanada for their technical helps.

REFERENCES

- 1) A. Inoue: *Acta Mater.* **48** (2000) 279–306.
- 2) Z. P. Lu, C. T. Liu and Y. D. Dong: *J. Non-Cryst. Solids* **341** (2004) 93–100.
- 3) W. Chen, Y. Wang, J. Qiang and C. Dong: *Acta Mater.* **51** (2003) 1899–1907.
- 4) Y. Hirotsu, T. Ohkubo and M. Matsushita: *Novel Nanocrystalline Alloys and Magnetic Nanomaterials*, ed. by B. Cantor, Chapter 2, (Institute of Physics Publishing, Bristol and Philadelphia, 2004) 16–41.
- 5) T. Ohkubo and Y. Hirotsu: *Phys. Rev. B* **67** (2003) 094201-1–094201-9.
- 6) E. Matsubara, S. Sato, M. Imafuku, T. Nakamura, H. Koshiba, A. Inoue and Y. Waseda: *Mater. Sci. Eng.* **312** (2001) 136–144.
- 7) I. Tellería and J. M. Barandiarán: *Thermochimica Acta* **280/281** (1996) 279–287.
- 8) S. R. Elliott: *Physics of Amorphous Materials*, Section 3, (Longman Science and Technology, Essex, 1990).
- 9) R. L. McGreevy: *J. Phys.: Condens. Matter* **13** (2001) R877–R913.
- 10) available at <http://www.studsvik.uu.se/>
- 11) G. Bushnell-Wye and J. L. Finney: *J. Phys (Paris)* **46** (1985) C3-311–C3-321.
- 12) Y. Hirotsu, T. Hanada, T. Ohkubo, A. Makino, Y. Yoshizawa and T. G. Nieh: *Intermetallics* **12** (2004) 1081–1088.
- 13) T. Hanada, Y. Hirotsu and T. Ohkubo: *Mater. Trans.* **45** (2004) 1194–1198.
- 14) Y. Hirotsu, A. Hirata, T. Hanada and H. Mori: *Arch. Mater. Sci.* **26** (2005) 25–29.
- 15) M. Imafuku, S. Sato, H. Koshiba, E. Matsubara and A. Inoue: *Scr. Mater.* **44** (2001) 2369–2372.
- 16) F. C. Frank and J. S. Kasper: *Acta Cryst.* **12** (1959) 483–499.
- 17) J. Hafner: *Phys. Rev. B* **15** (1977) 617–630.