Electron Irradiation Induced Nano-Crystallization in Fe₇₇Nd_{4.5}B_{18.5} Metallic Glass

Akihiro Nino,*¹ Takeshi Nagase and Yukichi Umakoshi*²

Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Phase transformation behavior in Fe₇₇Nd_{4.5}B_{18.5} metallic glass during electron irradiation and thermal annealing was investigated. Crystallization from glassy phase during thermal annealing occurred in multi-stages forming α -Fe and several intermetallic compounds. Electron irradiation induced crystallization occurred at 298 K and nanostructure composed of α -Fe, Nd₂Fe₁₄B and Fe₁₇B₂ precipitates embedded in amorphous matrix was formed. The electron irradiation induced crystallization behavior was discussed by atomic displacement due to electron knock-on effect and atomic diffusion via free volume in amorphous phase.

(Received April 7, 2005; Accepted June 14, 2005; Published August 15, 2005)

Keywords: metallic glass, crystallization, electron irradiation, thermal annealing, nanostructure, iron neodymium boron alloy

1. Introduction

Nanocrystalline materials are known to exhibit excellent mechanical and functional properties which cannot be realized in conventional crystalline and amorphous materials.^{1,2} Fe–Nd–B alloys with a nanostructure are of significant interest as a superior hard magnetic material.^{3,4} Nanocrystalline structure is obtained by several thermal processes such as rapid solidification and thermal crystallization of an amorphous phase.^{5,6} A large number of studies have been carried out focusing on the effects of alloy composition, cooling rate of liquid and annealing condition of an amorphous phase on the nanostructure in Fe–Nd–B based alloys.^{7–11}

Recently, it was found that nanocrystallization of an amorphous phase can be achieved in several metallic glass by electron irradiation and a unique nano-crystalline structure is obtained.^{12–15} Electron irradiation stimulates atomic displacement in an amorphous phase by electron knock-on effect. The activation process of the atomic movement differs significantly from the thermal activation process. Thus, electron irradiation to amorphous alloys and metallic glass is effective in producing a new nanocrystalline structure.

The aim of this work was to examine the electron irradiation induced crystallization and to control nanostructures in Fe₇₇Nd_{4.5}B_{18.5} metallic glass focusing on the difference in crystallization behavior between thermal annealing and electron irradiation.

2. Experimental Procedure

A master ingot of Fe₇₇Nd_{4.5}B_{18.5} (at.%) alloy was prepared by arc melting under highly purified Ar atmosphere using raw materials of 99.9% Fe, 99.9% Nd and Fe-18.9mass%B mother alloy. Rapidly quenched ribbon was produced from the ingot by a single roller melt-spinning method at a roll surface velocity of 10, 21, 31 and 42 ms⁻¹ in an Ar atmosphere. The thermal stability and crystallization behavior were examined in the atmosphere by differential scanning

calorimetry (DSC) and differential thermal analysis (DTA) at heating rates of 0.67 and 0.33 Ks⁻¹, respectively. The structure of the ribbon was examined by X-ray diffractometry (XRD) using Cu-K α radiation, transmission electron microscopy (TEM) using a JEM-3010 microscope operated at 300 kV and high resolution transmission electron microscopy (HREM) using a JEM-2010 microscope operated at 200 kV. Thin foils for TEM and HREM observations were prepared by an ion milling method. Electron irradiation on the melt-spun ribbon was performed at 298 K by an ultra-high voltage electron microscope (UHVEM) of H-3000 operated at 2 MV and at applied dose rates between 4.0×10^{24} and 1.0×10^{25} m⁻²s⁻¹. Change in the microstructure during electron irradiation was observed in situ by bright field images (BFIs) and selected area diffraction patterns (SADPs) in the UHVEM.

3. Results

3.1 Thermal crystallization of melt-spun Fe₇₇Nd_{4.5}B_{18.5} alloy

The microstructure of rapidly quenched ribbon was investigated by XRD, TEM and HREM. XRD patterns showed a typical broad peak corresponding to the amorphous state at around $2\theta = 43$ degrees. TEM observation showed a featureless contrast in BFIs and only halo rings in SADPs corresponding to the amorphous phase but accompanied by no crystalline phases. An amorphous single phase was obtained at all tested roll surface velocities. Figure 1 shows a typical example of an HREM image of melt-spun ribbon. Maze-like patterns corresponding to an amorphous phase are seen and no nano-crystalline precipitates were confirmed.

Figure 2(a) shows a DSC curve of the melt-spun ribbon. The glass transition and the crystallization temperature are indicated by T_g and T_x in the figure. The T_g , T_x and the supercooled liquid region ($\Delta T_x = T_x - T_g$) were 786, 837 and 51 K, respectively. The wide supercooled liquid region suggests high thermal stability of the amorphous phase against thermal crystallization. The exothermic peaks of A, B and C correspond to precipitation of crystalline phases. The crystallization behavior was characterized by DTA measure-

*¹Graduate Student, Osaka University

*²Corresponding author, E-mail: umakoshi@mat.eng.osaka-u.ac.jp

Fig. 1 HREM image of Fe₇₇Nd_{4.5}B_{18.5} metallic glass prepared by single roller melt-spinning method at a roll surface velocity of 42 ms⁻¹.

ment as shown in Fig. 2(b). The DTA curve exhibits several exothermic peaks corresponding to thermal crystallization. The thermal crystallization of the amorphous ribbon occurs in multi-stages. Specimens were quenched from the temperatures indicated by arrows to examine the crystallization behavior corresponding to each exothermic peak.

Table 1 shows constituent phases determined by XRD analysis for each specimen quenched from the indicated temperatures in Fig. 2. Many binary and ternary intermetallic compounds together with α -Fe were detected. From the results of the DTA curve and XRD analysis, the thermal crystallization process is summarized as follows:

- (1) Fe₃B and Nd₂Fe₂₃B₃ phases are simultaneously formed from a glassy phase after primary crystallization of Fe₃B.
- (2) The thermal crystallization occurs in multi-stages and several metastable phases containing Nd₂Fe₂₃B₃, Fe₃B and Nd_{1.1}Fe₄B₄ are formed.
- (3) The thermal equilibrium phases are composed of α -Fe, Fe₂B and Nd₂Fe₁₄B.

Fig. 2 DSC (a) and DTA (b) curves of melt-spun amorphous ribbon of Fe₇₇Nd_{4.5}B_{18.5} metallic glass.

Figure 3 shows TEM microstructure of specimens 3, 5 and 6 quenched from 930, 1135 and 1340 K, respectively. The microstructure of the specimen quenched from 930 K shows bright and dark granular contrast with a size of about 20 nm. The main precipitates are composed of Fe₃B and Nd₂Fe₂₃B₃ phase. The grain size of the Nd₂Fe₁₄B precipitates rapidly increases with increase in annealing temperature as shown in Figs. 3(b) and (c).

Table 1 Crystalline phases in Fe₇₇Nd_{4.5}B_{18.5} specimens quenched from various temperatures indicated in Fig. 2.

Quenched position	(Quenched temperature)	α -Fe	Nd ₂ Fe ₁₄ B	Nd ₂ Fe ₂₃ B ₃	Fe ₃ B	Fe ₂ B	Nd _{1.1} Fe ₄ B ₄
1	(850 K)				⊙		
2	(890 K)			○	⊙		
3	(930 K)			⊙	⊙		
4	(1005 K)		⊙	⊙	⊙		○
5	(1135 K)	⊙	⊙	○	○		○
6	(1340 K)	⊙	⊙		○	⊙	○

⊙ Main phase

Fig. 3 Changes in TEM microstructures and the corresponding SADPs of $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ metallic glass quenched from various temperatures during DTA analysis. (a) 930 K, (b) 1135 K and (c) 1340 K.

Fig. 4 Change in TEM microstructures of $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ metallic glass during electron irradiation. (a) and (d) as melt-spun; (b) and (e) electron irradiated at $1.8 \times 10^{28} \text{ m}^{-2}$; (c) and (f) electron irradiated at $3.6 \times 10^{28} \text{ m}^{-2}$.

3.2 Electron irradiation induced phase transformation in $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ metallic glass

Change in microstructures of $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ metallic glass during electron irradiation was examined by in situ TEM observation. Figure 4 shows BFIs and the corresponding SADPs of melt spun specimens electron irradiated at 298 K with a dose rate of $1.0 \times 10^{28} \text{ m}^{-2} \text{ s}^{-1}$. A melt-spun specimen shows a featureless contrast in BFI (a) and broad halo rings in SADP (d). After irradiation for $1.8 \times 10^3 \text{ s}$ (b), fine granular contrast appears in the central region of electron irradiation as shown in Fig. 4(b). In the SADP (e), new Debye rings corresponding to nanocrystalline precipitates appear accompanied by halo rings. An amorphous phase is not stable under electron irradiation and therefore crystallization is induced although the amorphous phase shows high thermal stability. With further electron irradiation, the intensity of Debye rings increases accompanied by weakening of the halo rings. The quantity of the nanocrystalline precipitates increased with total dose but Debye ring radius did not change during electron irradiation. No significant coarsening of grain size in the irradiation specimen was confirmed with increase in the dose density from $1.8 \times 10^{28} \text{ m}^{-2}$ to $3.6 \times 10^{28} \text{ m}^{-2}$. As a result of electron irradiation, a nanocrystalline structure with average grain size of 8 nm was obtained. Such a ultra-fine nanocrystalline structure has not before been realized by thermal crystallization of Fe–Nd–B metallic glass.^{6,16,17)}

In order to identify constituent phases in electron irradiated specimens, electron intensities in the diffraction patterns

were analyzed using a PICTRO STAT DIGITAL 400 image analyzer. Figure 5 shows change in intensity profiles of the electron irradiated specimens. Precipitation of $\alpha\text{-Fe}$ phase was identified in the specimen electron irradiated at total doses of $1.8 \times 10^{28} \text{ m}^{-2}$ and $3.6 \times 10^{28} \text{ m}^{-2}$ by the diffraction profile. The quantity of $\alpha\text{-Fe}$ increased with increase in total dose. Some other diffraction peaks not corresponding to $\alpha\text{-Fe}$ are also seen. Although those peaks seem to be due to $\text{Nd}_2\text{Fe}_{14}\text{B}$ or $\text{Fe}_{17}\text{Nd}_2$ phase, the identification is difficult because of the small difference in their peak positions. To identify the constituent phases in detail, HREM observation was performed.

Figure 6 shows an HREM image of the specimen electron irradiated with a total dose of $3.6 \times 10^{28} \text{ m}^{-2}$. A nanocrystalline structure with an average grain size under 10 nm was formed as shown in Fig. 6(a). The nanoscale grains are randomly oriented. Electron irradiation induced crystallization may progress in consequence of nucleation and growth processes. The HREM image also shows a maze-like contrast corresponding to residual amorphous phase between nanocrystalline precipitates. Figures 6(b) and (c) show typical examples of nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Fe}_{17}\text{Nd}_2$ crystalline phases, respectively. From the spacing and geometry of cross-fringe image, nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Fe}_{17}\text{Nd}_2$ precipitates were identified in Figs. 6(b) and (c), respectively. Namely, the periodic fringe contrast with a spacing of 0.30 nm in Fig. 6(b) corresponds to (221) of the $\text{Nd}_2\text{Fe}_{14}\text{B}$. In

Fig. 5 Change in electron diffraction intensity profiles of $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ metallic glass as melt-spun and electron irradiated at various total doses. (a) as melt-spun, (b) electron irradiation at $1.8 \times 10^{28} \text{ m}^{-2}$, (c) electron irradiation at $3.6 \times 10^{28} \text{ m}^{-2}$.

Fig. 6 HREM images of $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ metallic glass electron irradiated at the total dose of $3.6 \times 10^{28} \text{ m}^{-2}$. (b) and (c) are high magnification images of (a).

Fig. 6(c) the periodic fringe contrasts with the spacing of 0.25 and 0.15 nm correspond to (300) and (226) in $\text{Fe}_{17}\text{Nd}_2$, respectively. This result suggests that phase selection in electron irradiation induced crystallization is greatly different from that in thermal crystallization; $\text{Fe}_{17}\text{Nd}_2$ is formed under electron irradiation while it cannot be confirmed during thermal crystallization in this alloy composition.^{3,16)}

4. Discussion

Electron irradiation is known to induce atomic displacement in amorphous and crystalline phases by an electron knock-on effect. In general, the numerous atomic displacements destroy the original structure of a crystalline phase and result in amorphization of the crystalline phase in many alloys. In contrast, atomic diffusion is promoted by free volume induced by electron irradiation and crystallization occurs in amorphous phase.

Simultaneous precipitation of several constituent phases containing $\text{Fe}_{17}\text{Nd}_2$ which was never observed during thermal annealing occurred during electron irradiation. Figure 7 shows relationship between composition ratio of

Fig. 7 Relationship between volume of unit cell and composition ratio of Fe/(Fe + Nd + B) for crystalline phases formed in Fe₇₇Nd_{4.5}B_{18.5} alloys. Solid circles represent crystalline phases formed during thermal annealing in present Fe₇₇Nd_{4.5}B_{18.5} metallic glass and open squares shows crystalline phases precipitated in Fe₇₇Nd_{4.5}B_{18.5} under electron irradiation.

Fe to (Fe + Nd + B) of constituent phases appearing in Fe–Nd–B ternary alloys and relative volume of unit cell normalized by α -Fe. In the figure crystalline phases obtained in present Fe₇₇Nd_{4.5}B_{18.5} metallic glass by thermal annealing and electron irradiation are indicated by solid circles and open squares, respectively. The composition ratio of the present metallic glass is indicated by the dotted line. Stability of crystalline phase may decrease with increasing unit volume under electron irradiation because thermal recovery by atomic diffusion becomes difficult. With larger deviation of the composition ratio of a crystalline phase from the dotted line, more frequent redistribution of solute atoms is required to form the crystalline phase resulting in greater difficulty of crystallization from the viewpoint of kinetics in phase transformation. In fact, crystalline phases whose compositions show no large deviation from the dotted line preferentially appear during thermal annealing and electron irradiation. However, phase selection for electron irradiation induced crystallization is influenced by not only the phase stability but also kinetics of crystallization under electron irradiation. In electron irradiation induced crystallization, crystalline phases which have higher Fe composition than the dotted line were selected. This may be due to the difference in electron knock-on effect among Fe, Nd and B atoms. Since the atomic radius of Nd is the biggest among these three elements, dynamic displacement of Nd by elastic collision of electrons occurs more frequently than that of Fe and B atoms

by electron knock-on effect, while the light atomic weight of B induces a high tendency for the long-distance atomic displacement. Therefore, Fe-rich crystalline phases may show higher stability against Nd-rich and B-rich phases under electron irradiation. In the present study the Fe₁₇Nd₂ phase which had not appeared by thermal annealing was observed. The Fe-rich and chemical composition near the amorphous phase may have contributed to formation of Fe₁₇Nd₂ under electron irradiation.

5. Conclusions

The thermal crystallization and electron irradiation induced crystallization behavior in Fe₇₇Nd_{4.5}B_{18.5} metallic glass were investigated focusing on the difference between thermal process and non-thermal process of electron irradiation. The results were summarized and the following conclusions were reached.

- (1) Fe₇₇Nd_{4.5}B_{18.5} metallic glass shows high thermal stability of amorphous phase because of high T_x of 837 K and a wide ΔT_x of 51 K. Nanocrystallines of Fe₃B, Nd₂Fe₁₄B and α -Fe precipitated from the amorphous phase during thermal annealing but they were rapidly coarsened. The thermal crystallization occurs in multi-stages forming α -Fe and several intermetallic phases of Fe₃B, Nd₂Fe₁₄B and Nd_{1.1}Fe₄B₄, Nd₂Fe₂₃B₃ and Fe₂B.
- (2) Nanostructures of α -Fe, Nd₂Fe₁₄B and Fe₁₇Nd₂ were formed from the amorphous phase during electron irradiation. The crystallization occurs due to atomic displacement of constituent elements by electron knock-on effect and promotion of atomic diffusion *via* free volume.
- (3) Fe₁₇Nd₂ phase appeared during electron irradiation. The phase selection during the irradiation induced crystallization is controlled by the frequency and ease of atomic displacement depending on atomic radius and atomic weight of the constituent elements, respectively. The phase stability of Fe-rich crystalline phases may be higher than that of Nd-rich and B-rich phases under electron irradiation.

Acknowledgements

A part of the present experiments was carried out using a facility in the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University. The authors are grateful to Prof. H. Mori and Dr. T. Sakata of the Research Center for operating the H-3000 UHVEM. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area A, "Materials Science of Metallic Glasses" from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Part of the work was also supported by the same Ministry's "Priority Assistance of the Formation of Worldwide Renowned Centers of Research–The 21st Century COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design)".

REFERENCES

- 1) A. Inoue, A. Takeuchi, A. Makino and T. Masumoto: *Mater. Trans., JIM* **36** (1995) 962–971.
- 2) D. H. Ping, K. Hono, H. Kanekiyo and S. Hirose: *Acta Mater.* **47** (1999) 4641–4651.
- 3) Y. Q. Wu, D. H. Ping, B. S. Murty, H. Kanekiyo, S. Hirose and K. Hono: *Scr. Mater.* **45** (2001) 355–362.
- 4) K. Hono: *Prog. Mater. Sci.* **47** (2002) 621–729.
- 5) G. H. Tu, Z. Altounian, D. H. Ryan and J. O. Ström-Olsen: *J. Appl. Phys.* **63** (1988) 3330–3332.
- 6) S. Hirose, Y. Shigemoto, T. Miyoshi and H. Kanekiyo: *Scr. Mater.* **48** (2003) 839–844.
- 7) D. H. Ping, K. Hono and S. Hirose: *J. Appl. Phys.* **83** (1998) 7769–7775.
- 8) S. Hirose, H. Kanekiyo and M. Uehara: *J. Appl. Phys.* **73** (1993) 6488–6490.
- 9) N. Sano, T. Tomida, S. Hirose, M. Uehara and H. Kanekiyo: *Mater. Sci. Eng. A* **250** (1998) 146–151.
- 10) K. Suzuki, J. M. Cadogan, M. Uehara, S. Hirose and H. Kanekiyo: *J. Appl. Phys.* **85** (1999) 5914–5916.
- 11) K. Suzuki, J. M. Cadogan, M. Uehara, S. Hirose and H. Kanekiyo: *Scr. Mater.* **42** (2000) 487–492.
- 12) T. Nagase and Y. Umakoshi: *J. Appl. Phys.* **93** (2002) 912–918.
- 13) T. Nagase and Y. Umakoshi: *Mater. Sci. Eng. A* **343** (2003) 13–21.
- 14) T. Nagase, Y. Umakoshi and N. Sumida: *Sci. Technol. Adv. Mater.* **3** (2002) 119–128.
- 15) T. Nagase, Y. Umakoshi and N. Sumida: *Mater. Sci. Eng. A* **323** (2002) 218–225.
- 16) Q. F. Xiao, T. Zhao, Z. D. Zhang, E. Brück, K. H. J. Buschow and F. R. de Boer: *J. Magn. Magn. Mater.* **223** (2001) 215–220.
- 17) L. Shandong, D. Yaodong, B. X. Gu, T. Zongjun and D. Youwei: *J. Alloys. Compd.* **339** (2002) 202–206.