Electron Irradiation Induced Phase Transformation in Fe-Nd-B Alloys

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The effect of electron irradiation on the phase transformation in binary Fe-Nd and ternary Fe-Nd-B alloys was investigated. Electron irradiation induced nano-crystallization of amorphous-to-crystal (A-C) transition was observed in several Fe-Nd-B metallic glasses. In Nd₂Fe₁₄B compound, solid-state amorphization (SSA) of crystal-to-amorphous (C-A) transition occurred under electron irradiation. With further irradiation, the amorphous phase obtained by SSA transformed to the nano-crystalline phase through irradiation induced crystallization, resulting in crystal-to-amorphous-to-crystal (C-A-C) transition. A-C, C-A and C-A-C transition were also observed in some ternary Fe-Nd-B and binary Fe-Nd alloys. The electron irradiation technique is effective for the formation and control of nano-crystalline structure through A-C transition of amorphous phase and/or C-A-C transition of metallic compounds. [doi:10.2320/matertrans.MJ200702]

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1. Introduction

Solid-state amorphization caused by electron irradiation has been discovered in many metallic compounds.¹⁻⁵⁾ If constituent atoms in a crystalline lattice were frequently replaced by electron knock-on effect under high energy electron irradiation, the crystalline lattice structure would be destroyed by the accumulation of lattice defects in some metallic crystalline compounds, resulting in solid-state amorphization. Electron irradiation is of great interest because of *in situ* observation of the phase transformation and simplicity in experimental conditions such as there being no change in chemical composition, no oxidation, negligible contamination and temperature increase.¹⁾ In recent years, solid-state crystallization by electron irradiation has been found in various types of metallic amorphous alloys and metallic glasses; binary Zr-based alloys,⁶⁻⁹⁾ ternary Zr-based alloys⁶⁻⁸⁾ containing quasi-crystal former type,⁹⁾ Zr₆₅Al_{7.5}-Ni₁₀Cu₁₅ alloy with the largest ΔT_x value,^{6,10,11)} ternary Fe-Zr-B alloys^{12,13)} and Fe-Nd-B alloy.^{14,15)} In the above alloys, a nano-crystalline structure was realized through electron irradiation induced nano-crystallization. More recently, crystal-to-amorphous-to-crystal (C-A-C) type transition of metallic compounds was found in a binary Zr-based alloy^{16,17)} and ternary Fe-based alloys,^{4,5)} in which a unique nano-crystalline structure was formed. Thus, electron irradiation on amorphous and crystalline phases in metallic glass former alloy systems is very effective to obtain nano-crystalline structures.

In Fe-Nd-B alloys, many systematic studies on annealing conditions and/or the solidification process for the formation and control of nano-crystalline structure by annealing condition and/or solidification process have been made to improve the hard magnetic properties.¹⁸⁻²¹⁾ Superior hard magnetic properties appear in Fe-Nd-B alloys with a nano-crystalline structure composed of nano-crystalline soft-magnetic crystalline phases and hard magnetic nano-crystalline phases. Not only grain size but also phase selection in crystallization is very important for hard magnetic properties.

However, there are many difficulties in preparing an optimum nano-crystalline structure by thermal annealing and rapid solidification techniques. As one possible method, formation of the nano-crystalline structure by electron irradiation was reported; nano-crystallization of melt-spun amorphous phase in Fe₇₇Nd_{4.5}B_{18.5} alloy,^{14,15)} nano-crystalline structure formation in a Nd₂Fe₁₄B metallic compound through C-A-C transition⁴⁾ and modification of nano-crystalline structure through amorphization and crystallization in Fe₈₆Nd₉B₅ alloy.²²⁾ Such novel experimental works imply the possibility of optimum nano-crystalline structure formation in Fe-Nd-B alloy by electron irradiation.

In the present study, the effect of electron irradiation on various ternary Fe-Nd-B alloys and a binary Fe-Nd alloy was examined and the dominant factors for formation and control of a nanocrystalline structure through electron irradiation induced A-C, C-A and C-A-C transitions were discussed.

2. Experimental Procedure

Master ingots of binary Fe-Nd and ternary Fe-Nd-B alloys were prepared by arc melting under a highly purified Ar atmosphere using raw materials of 99.9% Fe, 99.9% Nd and Fe-18.9 mass%B mother alloy. Their chemical compositions are given in Table 1. Rapidly quenched ribbon was produced from the ingots by a single roller melt-spinning method at a roll surface velocity of 42 ms⁻¹ in an Ar atmosphere. The copper-drum with 200 mm in diameter was used for preparing melt-spun ribbon. The melt was ejected from a silica-nozzle at an applied pressure of 0.04 MPa. The thickness of

Table 1 Alloy compositions used in present study.

Alloy	Fe (at%)	Nd (at%)	B (at%)
No. 1	89.5	10.5	0
No. 2	86	9	5
No. 3	82.4	11.8	5.8
No. 4	82.2	7.1	10.7
No. 5	77	4.5	18.5
No. 6	71	9	20
No. 7	44	12	44

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the melt-spun ribbon was about 40 μm . 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. The chemical composition of unirradiated and irradiated areas in the specimen was examined by the energy-dispersive X-ray analysis (EDX) technique in TEM. Thin foils for TEM and HREM observation were ion-thinned by Ar⁺ with the accelerating voltage of 5 kV and an angle of incidence beam of 11 degrees. Electron irradiation on the melt-spun ribbon was performed by an ultra-high voltage electron microscope (UHVEM) of H-3000 operated at 2.0 MV in Osaka University. The applied dose rate was chosen to be between 3.7×10^{24} and 1.0×10^{25} electrons per square meter per second ($\text{em}^{-2} \text{s}^{-1}$). 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 Electron irradiation on ternary Fe-Nd-B alloys

Effect of electron irradiation on phase transformation behavior in melt-spun specimens was investigated for ternary Fe-Nd-B alloy systems ($\text{Fe}_{86}\text{Nd}_9\text{B}_5$, $\text{Fe}_{82.4}\text{Nd}_{11.8}\text{B}_{5.8}$, $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$, $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$, $\text{Fe}_{71}\text{Nd}_9\text{B}_{20}$ and $\text{Fe}_{44}\text{Nd}_{12}\text{B}_{44}$). An amorphous state was realized by melt-spun in $\text{Fe}_{82.2}\text{Nd}_{47.1}\text{B}_{10.7}$ (No. 4), $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ (No. 5) and $\text{Fe}_{71}\text{Nd}_9\text{B}_{20}$ (No. 6) alloys, although $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$ (No. 4) alloy contained α -Fe and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ crystalline phases. Other binary and ternary alloys in Table 1, namely, $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1), $\text{Fe}_{86}\text{Nd}_9\text{B}_5$ (No. 2) and $\text{Fe}_{82.4}\text{Nd}_{11.8}\text{B}_{5.8}$ (No. 3) were composed of crystalline phases without amorphous phase. Effects of electron irradiation on crystalline phases were examined in $\text{Fe}_{82.4}\text{Nd}_{11.8}\text{B}_{5.8}$ (No. 3) and $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$ (No. 4) alloys. The tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound in $\text{Fe}_{82.4}\text{Nd}_{11.8}\text{B}_{5.8}$ (No. 3) alloy was transformed to amorphous under electron irradiation at 298 K with a dose rate of $1.0 \times 10^{25} \text{em}^{-2} \text{s}^{-1}$.⁴⁾ Another example of electron irradiation induced amorphization is indicated in Fig. 1. α -Fe and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ phases exist in melt-spun $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$ (No. 4) alloy which has the metastable $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ composition quenched from 905 K. After electron irradiation at 298 K with a total dose of $5.4 \times 10^{26} \text{em}^{-2}$, diffraction spots corresponding to α -Fe are observed accompanied by halo rings, but the $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ compound disappears. The $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ compound cannot retain their original structure under 2.0 MV electron irradiation, and electron irradiation induced C-A transition occurs while the α -Fe phase is fairly stable under this irradiation condition. Similar electron irradiation induced C-A transition was reported in various binary alloys.¹⁻³⁾

Electron irradiation induced nano-crystallization of melt-spun amorphous phase occurred in $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ (No. 5) and $\text{Fe}_{71}\text{Nd}_9\text{B}_{20}$ (No. 6) alloys. In $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ (No. 5), nano-crystalline precipitates of α -Fe, Fe-Nd and Fe-Nd-B compounds were confirmed after electron irradiation at 298 K with a dose rate of $1.0 \times 10^{25} \text{em}^{-2} \text{s}^{-1}$ for $1.8 \times 10^3 \text{s}$.¹⁴⁾

Fig. 1 Change in BFIs and SADPs of polycrystalline specimen composed of α -Fe and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ crystalline compound in $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$ (No. 4) during electron irradiation. (a) and (c) as melt-spun; (b) and (d) electron irradiated at 298 K at $5.4 \times 10^{26} \text{em}^{-2}$.

Fig. 2 Change in BFIs and SADPs of $\text{Fe}_{71}\text{Nd}_9\text{B}_{20}$ (No. 6) specimen during electron irradiation. (a)(c) as melt-spun, (b)(d) electron irradiated at 298 K at $8.3 \times 10^{27} \text{em}^{-2}$.

Figure 2 shows changes in EM image and SADPs of $\text{Fe}_{71}\text{Nd}_9\text{B}_{20}$ (No. 6) alloy during the electron irradiation. The BFI of melt-spun specimen (a) shows a featureless contrast corresponding to amorphous phase. Only broad halo rings without any crystalline diffraction spots can be seen in SADP (c). After irradiation, nano-crystalline precipitates with granular contrast (b), new Debye rings corresponding to α -Fe and some intermetallic compounds (d) appear. Electron irradiation realizes not only amorphization but also crystallization of an amorphous phase.

A unique phase transformation during electron irradiation of C-A-C transition was found for $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound in $\text{Fe}_{82.4}\text{Nd}_{11.8}\text{B}_{5.8}$ (No. 3) alloy which has the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ composition.⁴⁾ Under electron irradiation, Nd_2 -

Fig. 3 Crystal-to-amorphous-to-crystal transition in polycrystalline specimen composed of α -Fe and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ crystalline compound in $\text{Fe}_{82.2}\text{-Nd}_{7.1}\text{B}_{10.7}$ (No. 4) during electron irradiation. (a)(d) before electron irradiation, (b)(e) electron irradiated at 298 K at $5.4 \times 10^{26} \text{ em}^{-2}$, (c)(f) electron irradiated at 298 K at $2.4 \times 10^{28} \text{ em}^{-2}$.

Fe_{14}B compound could not maintain the crystalline structure and amorphization occurred. With further electron irradiation, very fine granular contrast corresponding to nano-crystalline precipitates of α -Fe appeared.⁴⁾ The C-A-C transition occurred under electron irradiation in $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound. Another example of the C-A-C transition under electron irradiation in $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$ (No. 4) alloy is shown in Fig. 3. A crystalline structure composed of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ grains about 100 nm order and α -Fe in nano size is seen in the annealed specimen (a,d). During electron irradiation $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ cannot maintain its original crystal structure and amorphization takes place while α -Fe exists even under electron irradiation (b,e). With further irradiation, crystallization of α -Fe from the amorphous phase occurs resulting in the formation of nano-crystalline structure (c,f). Electron irradiation is an effective method to obtain nano-crystalline structure in ternary Fe-Nd-B alloys.

3.2 Electron irradiation for binary Fe-Nd alloys

The irradiation experiments of binary Fe-B, Fe-Nd and Nd-B alloys are very effective for investigating the dominant factors of electron irradiation induced C-A, A-C and C-A-C transition in ternary Fe-Nd-B alloys. In the present study, electron irradiation was also performed in binary Fe-Nd alloys. Although an amorphous phase was reported to be obtained by rapid solidification in these alloys,²³⁾ crystalline phases in $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1) alloy which has the stoichiometric $\text{Fe}_{17}\text{Nd}_2$ composition were used in the present study. Figure 4 shows the electron irradiation results of the binary Fe-Nd crystalline phase of melt-spun alloy No. 1. The BFI and SADP of polycrystalline $\text{Fe}_{17}\text{Nd}_2$ and α -Fe are seen in (a) and (c) before irradiation. After irradiation at 104 K with the total dose of $4.2 \times 10^{26} \text{ em}^{-2}$, some areas in the irradiation region shown in the BFI (b) were changed from grains with bright and dark contrast to a featureless contrast corresponding to an amorphous phase. In the SAD pattern (d), many electron diffraction spots are annihilated and broad halo rings corresponding to an amorphous phase newly appear. Only electron diffraction spots corresponding to α -Fe remain under electron irradiation. The $\text{Fe}_{17}\text{Nd}_2$ crystalline structure is destroyed by electron knock-on effect and an amorphous phase is formed through electron irradiation induced C-A

Fig. 4 Change in BFIs and SADPs of polycrystalline specimen composed of α -Fe and $\text{Fe}_{17}\text{Nd}_2$ crystalline compound in $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1) during electron irradiation. (a)(c) as melt-spun, (b)(d) electron irradiated at 104 K at $4.2 \times 10^{26} \text{ em}^{-2}$.

transition. Electron irradiation induced amorphization is observed only in $\text{Fe}_{17}\text{Nd}_2$ compound, while no amorphization of α -Fe occurs. In Figs. 4(a) and (b), the crystalline grains marked by arrows indicate the same crystalline phase of α -Fe.

The electron irradiation induced C-A transition in $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1) alloy was examined by HREM and the results are shown in Fig. 5. A typical salt and pepper contrast corresponding to an amorphous phase can be seen in Fig. 5(a). In contrast, the α -Fe crystalline phase maintains its original structure as shown in Fig. 5(b). From the lattice image, nano-crystalline α -Fe is confirmed.

Further electron irradiation was performed in the specimen irradiated at 104 K with the total dose of $4.2 \times 10^{26} \text{ em}^{-2}$. Figure 6 shows BFI and SADP of the specimen irradiated at 104 K with the total dose of $1.9 \times 10^{28} \text{ em}^{-2}$. Fine granular contrast appears in the central region of the irradiated area (a) and new Debye rings can be seen in the SADP (b). This indicates that electron irradiation induced A-C transition occurs in binary alloy No. 1, resulting in the C-A-C transition of $\text{Fe}_{17}\text{Nd}_2$ compound.

Electron irradiation induced C-A transition of SSA and C-A-C transition occurs not only in ternary Fe-Nd-B alloys⁴⁾ but also in binary Fe-Nd alloy. Electron irradiation induced amorphization was reported in binary Fe-B alloys,¹⁾ while electron irradiation induced crystallization was observed in Fe-B alloys. However, crystallization and amorphization in Nd-B alloys have not yet been investigated. The electron irradiation induced phase transition in binary Fe-Nd, Fe-B and Nd-B alloys is not completely known. The present experimental result in binary Fe-Nd alloy offers useful information for achieving an optimum hard magnetic nano-composite structure in Fe-Nd-B alloy system.

The various types of phase transformation of C-A, A-C and unique C-A-C transition were observed under electron irradiation. Table 2 summarizes the phase transformations induced by electron irradiation in binary Fe-Nd and ternary

Fig. 5 HREM image of polycrystalline specimen composed of α -Fe and $\text{Fe}_{17}\text{Nd}_2$ crystalline compound in $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1) irradiated at 104 K at $4.2 \times 10^{26} \text{ em}^{-2}$. (a) amorphous region obtained by solid-state amorphization in $\text{Fe}_{17}\text{Nd}_2$ crystalline compound, (b) crystalline region in the α -Fe phase.

Fig. 6 BFI and SADP of polycrystalline specimen composed of α -Fe and $\text{Fe}_{17}\text{Nd}_2$ crystalline compound in $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1) electron-irradiated at 104 K at $1.9 \times 10^{28} \text{ em}^{-2}$.

Fe-Nd-B alloys. Electron irradiation induced C-A transition was observed in both these alloys.

4. Discussion

The mechanism of electron irradiation induced amorphization was investigated in detail.^{1,24)} The crystalline phases cannot maintain their original structure under electron irradiation when replacement of atoms by electron knock-on effect occurs more frequently than thermal recovery of the original positions at atomic sub-lattice sites. The electron irradiation induced crystallization and C-A-C transition is discussed.

Under electron irradiation, atomic diffusion in materials is enhanced by the electron knock-on effect. If a nanocrystalline structure were formed and the crystalline phase could retain its original structure under electron irradiation, the crystalline phase would remain in the amorphous matrix and crystallization would occur. Electron irradiation induced crystallization was not observed in some ternary Fe-Nd-B alloys. In $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ (No. 5) alloy, such crystallization occurred at 298 K, while it was not observed at 108 K. In general, the introduction of mechanical atomic displacement

Table 2 Electron irradiation induced phase transformation in binary Fe-Nd alloy and Fe-Nd-B alloys investigated up to date.

Alloy	Conditions		Melt-spun	Before Irradiation	Phase Transitions			Phase selection (Electron irradiation)	Reference
	Acceleration Voltage [MV]	Temperature [K]			C-A (Amorphization)	A-C (Crystallization)	C-A-C (Additional irradiation after C-A)		
No. 1	2.0	298	α -Fe, $\text{Fe}_{17}\text{Nd}_2$	α -Fe, $\text{Fe}_{17}\text{Nd}_2$	Yes	—	Yes	α -Fe, MC	Present study
	2.0	104			Yes	—	Yes	α -Fe, MC	
No. 2	2.0	298	α -Fe, $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$, Fe3B	α -Fe, $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$, Fe3B	Yes	—	Yes	α -Fe, MC	22)
	2.0	112			Yes	—	Yes	α -Fe, MC	
No. 3	2.0	298	$\text{Nd}_2\text{Fe}_{14}\text{B}$	$\text{Nd}_2\text{Fe}_{14}\text{B}$	Yes	—	Yes	α -Fe, MC	4)
	2.0	103			Yes	—	Yes	α -Fe	
No. 4	2.0	298	Amorphous, α -Fe, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$	α -Fe, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ *	Yes	—	Yes	α -Fe, MC	Present study
	2.0	104			Yes	—	Yes	α -Fe	
No. 5	2.0	298	Amorphous	Amorphous	—	Yes	—	α -Fe, MC	14,15)
	2.0	108			—	No	—	—	
No. 6	2.0	298	Amorphous	Amorphous	—	Yes	—	α -Fe, MC	Present study
	2.0	103			—	Yes	—	α -Fe	
No. 7	2.0	298	Amorphous, $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$	Amorphous	—	No	—	—	Present study
	2.0	104			—	No	—	—	

*Quenched at 905 K

MC: Metallic Compound (Fe-Nd and/or Fe-Nd-B compound)

in metallic materials shows no significant temperature dependence because the elastic collision between high energy electrons and constituent atoms is independent of temperature. In contrast, thermal recovery effect decreases with decreasing temperature. The quantity of lattice defects in irradiated crystalline phase increases with decreasing the irradiation temperature, resulting that the phase stability of crystalline phase against electron irradiation decreases with decreasing the temperature. The electron irradiation induced crystallization behavior in $\text{Fe}_{77}\text{Nd}_{4.5}\text{B}_{18.5}$ (No. 5) alloy depends on the thermal recovery process of crystalline phase against electron irradiation. Table 2 reveals that the melt-spun amorphous phase in $\text{Fe}_{44}\text{Nd}_{11}\text{B}_{44}$ (No. 7) alloy shows extremely high phase stability against electron irradiation. The origin of the high phase stability of this alloy is not yet clear.

Some alloys in which C-A transition was observed under electron irradiation, namely, binary $\text{Fe}_{17}\text{Nd}_2$ compound in $\text{Fe}_{89.5}\text{Nd}_{10.5}$ (No. 1) alloy, and ternary $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{-Fe}_{23}\text{B}_3$ compounds in $\text{Fe}_{86}\text{Nd}_9\text{B}_5$ (No. 2) alloy showed C-A-C transition with further irradiation. One may assume that C-A-C transition is caused by a chemical composition change, contamination and oxidation during electron irradiation. The chemical composition of the specimen does not change because impurity atoms are not introduced in the specimen due to high vacuum in UHVEM.^{1,24} TEM-EDX analysis results also imply that C-A-C transition is not due to the above-described effects.⁴ Furthermore, the calculated temperature rise is about 10 K under electron irradiation.⁴ The origin of C-A-C transition is not due to temperature increase during irradiation. As shown in Fig. 7(a), Gibbs free energy of an amorphous phase exists in the range between the unrelaxed amorphous phase and the perfectly relaxed amorphous phase of an ideal glass.^{24,25} In the present study, the crystalline phase obtained by C-A-C transition is different from that before electron irradiation.

In metallic materials, the energy of an amorphous phase is higher than that of metastable and thermal equilibrium crystalline phases without electron irradiation, and the energy of thermal equilibrium crystalline phase is the lowest among them. If the atomic diffusion were sufficiently frequent to change the original structure of an amorphous phase by thermal annealing, the amorphous phase would transform to a crystalline phase because free energy of the system is reduced by thermal crystallization. The electron irradiation induced phase transformation behavior can be considered based on change in free energy of these phases under electron irradiation.²⁵⁻²⁷

When lattice defects are introduced in a metastable crystal of rapid quenched specimen by electron irradiation, the Gibbs free energy of the defective metastable crystal increases to the energy indicated by the hatched area in Fig. 7(b). The energy of the defective metastable crystal increases with increasing dose rate and becomes higher than that of amorphous because the increase in the energy of the defective metastable crystal is more accelerated than that of amorphous phase. The C-A transition occurs during electron irradiation and then the amorphous phase thermodynamically transforms to nano-crystal with different structure, namely C-A-C transition occurs as shown in Fig. 7(b).

Fig. 7 Schematic free energy diagrams of perfect crystal, defective crystal, perfectly relaxed amorphous phase of ideal glass, un-relaxed amorphous phase and liquid, together with the phase transformation pass of C-A-C transition. The symbol the white head arrow, open circle ($\circ$), closed circle ($\bullet$), closed square ($\blacksquare$) and hatched area correspond to phase transformation pass, metastable crystalline phase obtained by rapid solidification, amorphous phase, nano-crystalline phase obtained by electron irradiation and overlapped zone. (a) Gibbs free energy as a function of temperature, (b) Change in the free energy of amorphous and crystalline phases together with phase transformation pass of C-A-C transition.

The C-A-C transition can be explained by kinetics as well as thermodynamics. The kinetics of electron irradiation induced amorphization and crystallization is discussed based on the relation between total-dose and irradiation temperature.¹⁶ The main kinetic feature focusing on the balance between production of lattice defects by electron irradiation and thermal recovery of them was described in other papers.^{3,28-31} At higher temperatures than a critical temperature (T_c), the irradiation induced defects are thermally recovered and the transition from the metastable crystal to a thermally equilibrium phase occurs instead of electron irradiation induced amorphization. At temperatures below T_c an initial transition from the metastable crystal to amorphous phase occurs as shown in Fig. 7(b). The critical total dose for the phase transition increases with increasing

irradiation temperature because lattice defects induced by electron knock-on effect are relaxed by atomic diffusion. The further irradiation induces the phase transformation from amorphous to stable crystal. In this case the phase transformation near T_c occurs at smaller total dose than at low temperatures.

5. Conclusion

The effect of electron irradiation on phase transformation behavior in binary Fe-Nd and ternary Fe-Nd-B was investigated, focusing on the occurrence of A-C, C-A and C-A-C transition under electron irradiation. The results were summarized and the following conclusions were reached:

- (1) A-C transition of crystallization of melt-spun amorphous phase was achieved in Fe₇₇Nd_{4.5}B_{18.5} (No. 5) and Fe₇₁-Nd₉B₂₀ (No. 6), while that Fe₄₄Nd₁₂B₄₄ (No. 7) alloys was not observed.
- (2) C-A transition of solid-state amorphization of crystalline phases was observed in Fe_{89.5}Nd_{10.5} (No. 1), Fe₈₆Nd₉B₅ (No. 2), Fe_{82.4}Nd_{11.8}B_{5.8} (No. 3) and Fe_{82.2}Nd_{7.1}B_{10.7} (No. 4) alloys under 2.0 MV electron irradiation.
- (3) C-A-C transition was observed in all alloys which showed C-A transition under electron irradiation. Electron irradiation induced C-A-C transition of the crystalline phase as well as A-C transition of the melt-spun amorphous phase are very effective for formation and control of a nano-crystalline structure in Fe-Nd-B alloy system.

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