Phase Stability of an Amorphous Phase Against Electron Irradiation Induced Crystallization in Fe-Based Metallic Glasses

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Electron irradiation induced nano-crystallization of melt-spun amorphous phase in Fe-Zr-B ternary alloys was investigated focusing on the difference in phase stability of amorphous phase during thermal annealing and electron irradiation. Nano-composite structure composed of nano-crystalline α -Fe precipitates with b.c.c.-structure, metallic compounds and a residual amorphous matrix was formed under 2.0 MeV electron irradiation at 298 K, while such nano-structure was hardly realized by thermal annealing. The phase stability of an amorphous phase against electron irradiation was discussed based on the relationship between thermal properties and critical onset total dose of electron irradiation induced crystallization at 298 K. [doi:10.2320/matertrans.MF200612]

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1. Introduction

Electron irradiation is known to be an effective method for solid-state amorphization (SSA) of crystalline phase due to mechanical atomic displacement induced crystal-to-glass (C-G) transition. Mori *et al.* reported that an amorphous state was realized in 37 among 70 crystalline alloys by electron irradiation.¹⁾ Okamoto *et al.* investigated the difference in phase transition behavior between irradiation induced SSA and thermal melting, and suggested the Generalized Lindemann Melting (GLM) criterion. They concluded that SSA can be considered as a kinetically constrained melting behavior.²⁾

Table 1 shows the experimental results of electron irradiation induced SSA in Fe-based materials reported to date, together with the data of amorphous phase formation by liquid quenching method (LQ).^{1,3-8)} One can notice that electron irradiation can achieve amorphous phase formation in some Fe-based compounds such as FeAl₃, Fe₁₇Nd₂, Fe₂Ti, Fe₂₃Nd₂B₃ and Fe₁₄Nd₂B in which the amorphous phase can not be obtained by LQ. Thus, electron irradiation is an effective method to induce SSA in Fe-based metallic compounds.

In contrast, little attention has been paid to the electron irradiation induced glass-to-crystal (G-C) transition in crystallization behavior although it is effective in obtaining a well-controlled nano-crystalline structure. Various characteristics in electron irradiation induced crystallization are revealed as follows;⁹⁻¹³⁾ (1) nano-crystallization in alloys which nano-structure cannot be easily realized by thermal annealing, (2) metastable phase formation, (3) unique phase selection, and (4) no coarsening of nano-crystals under electron irradiation. Furthermore, the formation of crystallographically orientated nano-crystals under focused ion beam (FIB) irradiation was reported.¹⁴⁾

Table 2 shows the crystallization and phase selection

during electron irradiation in Fe-based metallic glasses reported to date.^{3,11-13,15-24)} The irradiation induces not only SSA but also crystallization in many Fe-based alloys in spite of high glass forming ability (GFA). The parameters for predicting electron irradiation induced crystallization is not clear to date, while systematic research works for SSA gave various parameters for predicting electron irradiation induced amorphization.^{1,2)}

In the present study, the difference in crystallization behavior during electron irradiation and thermal annealing was investigated in Fe-Zr-B alloys. Then, the relationship between the onset total dose of electron irradiation induced crystallization and thermal parameters for revealing the phase stability of an amorphous phase against electron irradiation was discussed focusing on electron irradiation induced crystallization in Fe-based metallic glasses.

2. Experimental Procedure

Ternary Fe_{91-x}Zr₉B_x ($x = 3, 5, 10, 15, 20, 25$ and 30 at%) alloys were used in the present study. Master ingots of Fe-Zr-B alloys were prepared by arc melting pure Fe, Zr and ferroboron materials in a purified Ar atmosphere. Rapidly quenched ribbon with a cross section of about $2.0 \text{ mm} \times 0.02 \text{ mm}$ was produced from the ingots at a rotation speed of 42 ms^{-1} by a single roller melt-spinning method in an Ar atmosphere. Thermal properties and crystallization behavior of the ribbon were examined by differential scanning calorimeter (DSC) and differential thermal analysis (DTA) in an Ar atmosphere. Thermally crystallized specimens were prepared by two different processes; (1) specimens quenched at the temperature just after offset of primary crystallization or just before thermal melting during DTA measurement at a constant heating rate of 0.33 K s^{-1} , and (2) isothermal annealing in an evacuated silica capsule with Ti and Ta as O₂ getter. Structure of the ribbon was examined by X-ray diffractometry using Cu-K α radiation, transmission electron microscopy (TEM) using JEM-3010 operating at 300 kV and

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Table 1 Electron-irradiation induced crystal-to-glass (C-G) transition of solid-state amorphization (SSA) in various Fe-based metallic materials reported to date.

Compounds	Experimental Data (Amorphization)		Crystal Data						Ref. (E-IR)
	LQ	E-IR	Crystal System	Strukturbericht Symbol	Volume (Unit cell) [nm ³]	Number of atoms (Unit cell)	Solubility	Transition Temperature [K]	
FeAl ₃	No	Yes	monoclinic		1.488	102	2	1433	1
Fe ₂ Al ₅	No	No	orthorhombic		0.2065	16	3	1442	1
FeAl ₂	No	No	triclinic		0.2636	18	1	1426	1
FeAl	No	No	cubic	B2	0.02427	2	> 10	1583	1
Fe ₂ B	No	No	tetragonal	C16	0.111	12	0	1662	1
Fe ₃ B	Yes	Yes	tetragonal	D0 _c	0.3219	32	0	non-equilibrium	1
Fe ₁₇ Nd ₂	No	Yes							3
FeTi	No	No	cubic	B2	0.02643	2	3	1590	1
Fe ₂ Ti	No	Yes	hexagonal	C14	0.1546	12	5	1700	1
FeZr ₃	Yes	Yes	orthorhombic	E1a	0.3194	16	2	1213	4, 5
FeZr ₂	Yes	Yes	tetragonal		0.3953		1	1247	5
Fe ₄ Nd _{1.1} B ₄	No	No	tetragonal		1.78				3
Fe ₂₃ Nd ₂ B ₃	No	Yes	cubic		2.86				3
Fe ₁₄ Nd ₂ B	No	Yes	tetragonal		0.946	68			6, 7
α -Mn type (Fe ₈₁ Zr ₉ B ₁₀)	Yes	Yes	cubic		0.6922			non-equilibrium	8

LQ: Liquid quenching

E-IR: Electron irradiation

high resolution transmission electron microscopy (HREM) using a JEM-2010 operating at 200 kV. Thin foils for TEM and HREM observations were prepared by twin jet polishing in a solution of 10% perchloric and 90% acetic acid at room temperature. Some foils were electron irradiated using HU-2000 and H-3000 ultra-high voltage electron microscope (UHVEM) operating at 2.0 MV in Osaka University. The irradiation was performed in the range between 103 K and 298 K. The applied dose rate was $7.5 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ for HU-2000 and in the range between 5.0×10^{24} and $8.7 \times 10^{24} \text{ m}^{-2} \text{ s}^{-1}$ for H-3000. Changes in the bright field (BF) images and selected area diffraction (SAD) patterns were observed *in situ* by UHVEM at 2.0 MV. Effect of additional electron irradiation during *in situ* TEM observation was negligible because of the low dose rate. Structure of the irradiated ribbon was also examined by conventional TEM and HREM. The intensity profile of the SAD pattern was analyzed using a PICTRO STAT DIGITAL 400 image analyzer.

3. Results

3.1 Thermal properties and thermal crystallization behavior in melt-spun amorphous specimen

The constituent phases in melt-spun Fe-Zr-B specimens were investigated by XRD, TEM and HREM observation. An amorphous single phase without any crystallinity was formed in Fe_{91-x}Zr₉B_x ($x = 3, 5, 10, 15$ and 20) specimens, while composite structure composed of an amorphous and crystalline precipitates was formed in alloys containing more than 20 at%B.^{11,13)} Figure 1 shows the DTA curves of melt-spun specimens at a heating rate of 0.33 K s^{-1} . Sharp exothermic

peaks at the temperatures before the arrow A and endothermic peaks at the temperatures just after the arrow B are observed. The formers and lateres are corresponding to the primary thermal crystallization and thermal melting, respectively.

Although the number of the observed exothermic and endothermic peaks changes depending on the boron concentration, the position and shape of the first exothermic peak corresponding to the primary crystallization are analyzed. With increasing boron concentration, the onset temperature of crystallization (T_x) becomes higher and the crystallization enthalpy (ΔH_{cry}) increases. At and above 10 at%B, anomalous endothermic reaction corresponding to glass-to-supercooled liquid (G-L) transition starts at T_g . Thus, the boron concentration is a dominant factor of thermal crystallization in melt-spun Fe-Zr-B amorphous alloys.

The glass transition behavior of melt-spun amorphous phase was evaluated in detail by DSC analysis at a heating rate of 0.67 K s^{-1} as shown in Fig. 2(a). The glass transition starts at T_g and the supercooled liquid is maintained over the wide temperature range ($\Delta T_x = T_x - T_g$) before thermal crystallization in Fe_{91-x}Zr₉B_x ($x = 10, 15, 20, 25$ and 30) specimens, while it is rarely observed in Fe_{91-x}Zr₉B_x ($x = 3$ and 5) specimens. Both T_g and T_x increase with increasing boron concentration. Since the degree of increase in T_g and T_x is different, ΔT_x does not show the monotonical boron concentration dependence: the ΔT_x increases from 29 K at 10 at%B to 71 K at 20 at%B reaching saturation at 20 at%B. It should be noticed that the supercooled liquid region defined by ΔT_x reaches as large as about 70 K. The extremely high thermal stability with large ΔT_x enables to obtain bulk-

Table 2 Electron-irradiation induced glass-to-crystal (G-C) transition of crystallization in various Fe-based metallic materials reported to date.

Alloys [at%]	Experimental data			Glass data Glass transition (DSC, 0.67 Ks ⁻¹)	Phase selection in crystallization		Ref.
	E-IR	Conditions A.V. [MV]	Temp. [K]		Thermal annealing	Election irradiation	
Fe ₈₃ B ₁₇	Yes			No	—	—	15
Fe ₈₀ B ₂₀	No		20	No	—	—	16
Fe ₇₅ B ₂₅	No	2.5	21		—	—	17
	No	2.0	298~473	No	—	—	18
	Yes	2.0	523~573		—	—	18
Fe ₈₄ P ₁₆	No	0.4	heating	No	—	—	19
Fe ₇₈ Mo ₂ B ₂₈	No		20	No	—	—	16
Fe _{82.2} Nd _{7.1} B _{10.7}	Yes	2.0	298	No	Nd ₂ Fe ₂₃ B ₃	B.c.c.-SS, MC(Fe-Nd-B)	3
	Yes	2.0	103			B.c.c.-SS	3
Fe _{77.5} Nd ₄ B _{18.5}	Yes	2.0	298	Yes	Fe ₃ B, Nd ₂ Fe ₂₃ B ₃	B.c.c.-SS, MC(Fe-Nd-B)	20
	No	2.0	103			—	20
Fe ₇₁ Nd ₉ B ₂₀	Yes	2.0	298	No	Fe ₃ B, Nd ₂ Fe ₂₃ B ₃	B.c.c.-SS, MC(Fe-Nd-B)	3
	Yes	2.0	103			B.c.c.-SS	3
Fe ₈₀ P ₁₃ C ₇	No	0.4	heating	No	—	—	19, 21
Fe ₇₈ P ₁₅ C ₇	No	0.4	heating	No	—	—	19
Fe ₇₈ Si ₁₀ B ₁₂	Yes	0.4	heating	No	MS-I	MS-I	19
Fe _{88.0} Zr _{9.0} B _{3.0}	Yes	2.0	110, 298	No	α -Fe	B.c.c.-SS, MC(Fe-Zr)	11, 12, 13
	Yes	2.0	103			B.c.c.-SS	11, 12
Fe _{86.0} Zr _{9.0} B _{5.0}	Yes	2.0	298	No	α -Fe, α -Mn	B.c.c.-SS, MC(Fe-Zr)	Present study
Fe _{81.0} Zr _{9.0} B _{10.0}	Yes	2.0	298	Yes	α -Fe, α -Mn	B.c.c.-SS, MC(Fe-Zr)	8
	Yes	2.0	103			B.c.c.-SS	8
Fe _{76.0} Zr _{9.0} B _{15.0}	Yes	2.0	298	Yes	α -Fe, γ -Fe, unknown	B.c.c.-SS, MC(Fe-Zr)	Present study
Fe _{71.0} Zr _{9.0} B _{20.0}	Yes	2.0	298	Yes	α -Fe, Fe ₂ Zr, Fe ₃ Zr, Fe ₂ B, Fe ₃ B	B.c.c.-SS, MC(Fe-Zr, Fe-B)	13, 22
	Yes	2.0	103			B.c.c.-SS	22
Fe ₅₀ Cu ₂₀ Zr ₁₀ B ₂₀ (+)	No	2.0	298	Yes	—	—	23
	No	2.0	20				23
Fe-Cr-Ni-W	Yes	1.2, 1.5	710~830	No	α -Fe, χ -phase	B.c.c.-SS	24
	Yes	1.2, 1.5	875			Fe ₂ O ₃	24

(+) Not amorphous single phase but amorphous + f.c.c.-Cu phases

A.V.: Acceleration voltage

Temp.: Temperature

MS-I: Metastable solid solution-I

B.c.c.-SS: Solid solution with b.c.c. structure (α -Fe phase with solute elements)

MC: Metallic Compound

shaped amorphous alloys by the conventional casting method. Therefore, they are often called Bulk Metallic Glass (BMG) type amorphous alloys. The T_g and T_x are sensitive to the heating rate; a typical example is shown in Fig. 2(b) of the kinetic map in melt-spun Fe₇₁Zr₉B₂₀ alloy. Both T_x and T_g decrease with decreasing heating rate. The degree of decrease in T_x is larger than that in T_g , resulting in the intersection between two extrapolation of the least-squares fit lines at the critical heating rate. According to previous papers,^{2,25)} the intersection temperature (T_c) corresponds to the ideal glass transition temperature (T_k). This ideal glass transition temperature, namely, Kauzmann temperature is thermodynamically defined as the temperature at which the entropy of liquid equals that of crystal. In the present study, T_g and T_x determined by DSC at 0.67 Ks⁻¹ are used as the thermal parameters of melt-spun amorphous phase.

The structural change during thermal annealing was examined using specimens quenched from two stages indicated by arrows A and B in Fig. 1. The XRD patterns of the quenched specimens are shown in Fig. 3. The constituent crystalline phases in the specimens quenched at A are sensitive to boron concentration as shown in Fig. 3(a). Only peaks corresponding to α -Fe are observed in Fe₈₈Zr₉B₃ specimen. In Fe₈₆Zr₉B₅ and Fe₈₁Zr₉B₁₀ alloys, α -Mn type crystalline phase is observed together with α -Fe. The number of constituent crystalline phases increases with increasing boron concentration. A large number of crystalline phases containing intermetallics were formed in alloys containing more than 20 at%B. The increase in boron concentration leads the formation of crystals with the more complex structure. Figure 3(b) shows XRD patterns of the specimens quenched at B. These specimens can be considered to be

Fig. 1 DTA curves of melt-spun $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20, 25, 30$) alloys at a heating rate of 0.33 K s^{-1} .

reflected to the thermal equilibrium state. α -Fe and several metallic compounds are formed in Fe-Zr-B alloys with wide boron concentration. Fe_2B and B_2Zr are formed in Fe-Zr-B alloys with high boron concentration, while Fe_2Zr and Fe_3Zr can be seen in Fe-Zr-B alloys with low boron concentration. The constituent crystalline phases in the specimens quenched at A are different from these at B as shown in Fig. 3(a) and (b), respectively. This indicates that thermal equilibrium crystalline phases are not formed during primary thermal crystallization of melt-spun specimens.

Crystalline structure obtained by primary thermal crystallization is examined by isothermal annealing of the melt-spun specimens. The TEM microstructure and corresponding SAD patterns of three specimens containing 3, 10 or 20 at.% B are shown in Fig. 4; α -Fe former type $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ (a), α -Mn type crystalline phase former type $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ (b), and multi-crystalline phases former type $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ (c). The annealing temperatures of 828 K and 848 K for $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ and $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ alloys, respectively are lower than T_g by about 20 K. The annealing temperature is considered to be low enough to suppress the significant coarsening of primary crystalline precipitates in $\text{Fe}_{88}\text{Zr}_9\text{B}_3$,^{11,13} $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ ⁸) and $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ ^{13,22}) alloys. In $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ alloy annealed at 873 K for 600 s (a), nano-crystalline structure is observed in BF image. The SAD patterns show Debye-rings corresponding to α -Fe crystalline phase with b.c.c. structure. There are many research works about the nano-crystalline structure obtained by primary thermal crystallization in Fe-Zr-B alloys with low boron concentration such as $\text{Fe}_{88}\text{Zr}_9\text{B}_3$, $\text{Fe}_{90}\text{Zr}_7\text{B}_3$ and $\text{Fe}_{91}\text{Zr}_7\text{B}_2$,^{11-13,26-32}) a nano-composite structure composed of α -Fe nanocrystalline precipitates embedded in the residual amorphous phase whose quantity is too small to detect it by

Fig. 2 DSC curves of melt-spun $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20, 25, 30$) alloys at a heating rate of 0.67 K s^{-1} (a) and kinetic map of $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ alloy.

conventional XRD and TEM techniques. Such nano-crystalline structure was formed in the present study in $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ alloy. In contrast, not 10 nm-order nano-crystal but 100 nm-order sub-micrometer crystalline precipitates can be seen in α -Mn type crystalline phase former type $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ alloy annealed at 828 K for $3.6 \times 10^5 \text{ s}$ (b). The SAD patterns shows discontinuous Debye-rings corresponding to sub-micrometer order α -Mn type poly-crystalline structure. In $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ alloy annealed at 848 K for $3 \times 10^4 \text{ s}$ (c), crystalline precipitates with grain size of about 100~500 nm are embedded in the amorphous phase and each precipitate dispersed inhomogeneously. The thermal stability, crystallization behavior, phase selection and crystalline structure are very sensitive to boron concentration. The nano-crystalline structure which is very effective to prepare a superior soft magnetic materials was obtained only in α -Fe former type $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ in Fe-Zr-B alloys.

3.2 Electron irradiation induced crystallization behavior in Fe-Zr-B melt-spun amorphous phase

Figure 5 shows TEM microstructures and corresponding SAD patterns of $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15$ and 20) alloys after 2.0 MeV electron irradiation of melt-spun amorphous single phase at 298 K. The total dose of the specimens is

Fig. 3 XRD patterns of thermally annealed specimens quenched from the temperature indicated by arrows A and B in Fig. 1 during DTA measurement. (a) specimens quenched at the temperature A, (b) specimens quenched at the temperature B.

about in the range between $5 \times 10^{26} \text{ m}^{-2}$ and $5.0 \times 10^{27} \text{ m}^{-2}$; (a) $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ alloy at $4.8 \times 10^{26} \text{ m}^{-2}$, (b) $\text{Fe}_{86}\text{Zr}_9\text{B}_5$ alloy irradiated at $5.4 \times 10^{26} \text{ m}^{-2}$, (c) $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ alloy at the total dose of $1.5 \times 10^{27} \text{ m}^{-2}$, (d) $\text{Fe}_{76}\text{Zr}_9\text{B}_{15}$ alloy at $5.4 \times 10^{27} \text{ m}^{-2}$, and (e) $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ alloy at $3.5 \times 10^{27} \text{ m}^{-2}$. In all specimens, dark and bright granular contrast can be seen in BF image. SAD patterns show Debye rings and/or spotty diffraction peaks together with broad halo rings. This indicates that melt-spun amorphous phase in Fe-Zr-B alloys is not stable under electron irradiation and electron irradiation induced crystallization occurs. Nano-crystalline structure is formed regardless of the boron concentration, while such nano-crystalline structure is rarely formed during primary thermal crystallization in Fe-Zr-B alloys with high boron concentration. The number of diffraction peaks corresponding to crystalline phases decreases with increasing B concentration, indicating decrease in quantity of the crystalline precipitates.

The intensity profiles of SAD patterns of electron irradiated specimens were analyzed to examine crystallization behavior as shown in Fig. 6. The SAD patterns were obtained from the selected area (SA) aperture size of about $1 \mu\text{m}$ in UHVEM H-3000. Diffraction peaks corresponding to α -Fe crystalline phase with b.c.c. structure can be seen in all

Fig. 4 TEM microstructures and corresponding SAD patterns of $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 10, 20$) alloys after isothermal annealing of melt-spun amorphous phase in vacuum. The annealing conditions correspond to the just after first crystallization of melt-spun amorphous phase. (a) $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ alloy annealed at 873 K for 600 s, (b) $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ alloy annealed at 828 K for $3.6 \times 10^5 \text{ s}$, (c) $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ alloy annealed at 848 K for $3 \times 10^4 \text{ s}$.

specimens. There are some diffraction peaks corresponding not to α -Fe phase. Although identification of all constituent phases is difficult due to the limited number of peaks, $\text{C15-Fe}_2\text{Zr}$ with cubic structure may be formed under electron irradiation from the peak position indicated by the solid line A. However, binary Fe-Zr, Fe-B and Zr-B intermetallic compounds precipitated during thermal annealing are not detected. There is a great difference in phase selection between thermal crystallization and electron irradiation induced crystallization. These results clearly show that electron irradiation is very effective to obtain nano-crystalline α -Fe phase and a unique nano-crystalline structure in Fe-Zr-B alloys. One can notice that the peak positions of b.c.c.-

Fig. 5 TEM microstructures and corresponding SAD patterns of $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$) alloys after 2.0 MeV electron irradiation of melt-spun amorphous phase at 298 K. (a) $\text{Fe}_{88}\text{Zr}_9\text{B}_3$ alloy irradiated at the total dose of $4.8 \times 10^{26} \text{ m}^{-2}$, (b) $\text{Fe}_{86}\text{Zr}_9\text{B}_5$ alloy irradiated at the total dose of $5.4 \times 10^{26} \text{ m}^{-2}$, (c) $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ alloy irradiated at the total dose of $1.5 \times 10^{27} \text{ m}^{-2}$, (d) $\text{Fe}_{76}\text{Zr}_9\text{B}_{15}$ alloy irradiated at the total dose of $5.4 \times 10^{27} \text{ m}^{-2}$, (e) $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ alloy irradiated at the total dose of $3.5 \times 10^{27} \text{ m}^{-2}$.

Fig. 6 Electron diffraction intensity profiles of nano-crystalline $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$) alloys obtained by 2.0 MeV electron irradiation induced crystallization of melt-spun amorphous phase at 298 K, together with the data of X-ray diffraction intensity of various intermetallics and precipitates in Fe-Zr-B crystalline alloys.

solid solution obtained by electron irradiation induced crystallization are not perfectly corresponding to those of pure α -Fe phase. The difference in peak positions is due to the solution of Zr and B atoms in α -Fe phase. Not pure α -Fe phase but super-saturated b.c.c.-solid solution was formed under electron irradiation.

3.3 Phase stability of an amorphous phase against electron irradiation in Fe-Zr-B and Fe-Nd-B metallic glasses

Phase stability of an amorphous phase against electron irradiation can be evaluated by the onset total dose at which electron irradiation induced crystallization begins.^{33,34} In the present study, the onset total dose was defined as the critical total dose at which Debye rings and/or diffraction spots corresponding to crystalline phases appeared in the SAD pattern during electron irradiation. This is the same as that in Zr-Cu based metallic glasses reported in previous papers.^{33,34} Figure 7(a) shows change in constituent phases in melt-spun $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$) amorphous phase by electron irradiation total dose under 2.0 MeV electron irradiation at 298 K; cross mark ($\times$), open circle ($\circ$) and closed circle ($\bullet$) represent amorphous phase, the onset total dose for crystallization and the nano-composite structure composed of nano-crystalline precipitates and residual

Fig. 7 Critical onset total dose of electron irradiation induced crystallization of melt-spun amorphous phase in $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$) alloys. (a) Change in constituent phases in melt spun $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$) alloys by irradiation total dose under 2.0 MeV electron irradiation at 298 K, (b) Temperature dependence of critical onset total dose of electron irradiation induced crystallization of melt-spun amorphous phase in $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$) alloys.

amorphous matrix, respectively. There is an incubation total dose in electron irradiation induced crystallization of an amorphous phase. The onset total dose is sensitive to the boron concentration, and it monotonically increases with increasing boron concentration. The onset total dose at 298 K is summarized in Fig. 7(b), together with the data at 203 and 103 K. The irradiation temperature gives a great effect on the onset total dose. The lower the irradiation temperature is, the higher the onset total dose is. It should be noticed that the onset total dose increases with increasing boron concentration regardless of the irradiation temperatures. There is a positive correlation between the onset total dose and boron concentration. These tendencies indicate that phase stability of an amorphous phase against electron irradiation increases with increasing boron concentration in Fe-Zr-B alloys.

The phase stability of an amorphous phase against thermal crystallization and electron irradiation induced crystallization increases with increasing boron concentration. Many parameters have been used to predict the glass forming ability (GFA) and thermal stability in metallic materials. It is

of interest to discuss the relationship between thermal parameters and electron irradiation induced crystallization behavior. In the present study, the onset total dose of electron irradiation induced crystallization at room temperature of 298 K (TD_{298}) was plotted as a function of the thermal parameters. The results are shown in Fig. 8, together with the experimental data of Fe-Nd-B alloy systems.^{3,6,20} The following 12 parameters are used referred from the other papers.³⁵⁻⁴³⁾

- (1) Onset temperature of thermal crystallization (T_x). T_x was evaluated by conventional DSC measurements at a heating rate of 0.67 Ks^{-1} .
- (2) Peak temperature of primary thermal crystallization (T_p). T_p was also determined by conventional DSC measurements at a heating rate of 0.67 Ks^{-1} .
- (3) The onset temperature of melting (T_m). T_m was determined by conventional DTA measurements at a heating rate of 0.33 Ks^{-1} .
- (4) Liquidus temperature (T_l). In the present study, T_l is considered as the offset temperature of thermal melting and is evaluated by conventional DTA measurements at a heating rate of 0.33 Ks^{-1} .
- (5) ΔT^* parameter proposed by Donald and Davies for predicting GFA.³⁴⁾ The parameter is given as follows:

$$\Delta T^* = \frac{T_m^{\text{mix}} - T_m}{T_m^{\text{mix}}} \quad (1)$$

$$T_m^{\text{mix}} = \sum_i^n n_i T_m^i$$

where n_i and T_m^i are the mole fraction and melting temperature, respectively. It was reported that Fe- and Ni-based metallic glasses had values of $\Delta T^* \geq 0.2$.

- (6) Glass-to-supercooled liquid transition temperature (T_g). T_g was evaluated by conventional DSC measurements at a heating rate of 0.67 Ks^{-1} .
- (7) The parameter defined by the temperature interval between T_x and T_g (ΔT_x). This parameter is regarded as the empirical indicator of GFA. In general, the larger the ΔT_x value, the higher the GFA³⁷⁾ becomes. ΔT_x is defined as follows:

$$\Delta T_x = T_x - T_g \quad (2)$$

- (8) Reduced glass transition temperature (T_{rg}). T_{rg} is the ratio between T_g and T_m (T_g/T_m).^{38,39)} The higher the ratio T_g/T_m , the higher the viscosity at the nose of the TTT and CCT curves becomes, and hence the smaller the critical cooling rate (R_c).
- (9) The ratio between T_g and T_l (T_g/T_l) is also recognized as T_{rg} . It is reported that T_g/T_l seems to be favorable for predicting GFA rather than T_g/T_m based on the research work about the collation among T_g/T_m , T_g/T_l and GFA.⁴⁰⁾
- (10) γ parameter proposed by Z. P. Lu and C. T. Liu. This parameter is reported to have a much better interrelation with GFA than T_{rg} (T_g/T_l)⁴¹⁾ and defined as follows:

$$\gamma = \frac{T_x}{T_g + T_l} \quad (3)$$

Fig. 8 Relationship between thermal properties of melt-spun amorphous phase and critical onset total dose of 2.0 MeV electron irradiation induced crystallization at 298 K in $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15, 20$), $\text{Fe}_{77.5}\text{Nd}_{4.5}\text{B}_{18.5}$ and $\text{Fe}_{81}\text{Nd}_9\text{B}_{20}$ alloys. (a) T_x : crystallization temperature, (b) T_p : peak temperature of first thermal crystallization, (c) T_m : melting temperature, (d) T_l : liquidus temperature, (e) ΔT^* : delta-T-star parameter, (f) T_g : glass transition temperature of amorphous-to-supercooled liquid temperature, (g) ΔT : temperature interval of supercooled liquid region defined by $T_x - T_g$, (h) $T_{rg} = T_g/T_m$, reduced glass transition temperature calculated by T_g and T_m , (i) $T_{rg} = T_g/T_l$, reduced glass transition temperature calculated by T_g and T_l , (j) γ , gamma parameter defined by $T_x/(T_g + T_l)$, (k) K_{gl} : K_{gl} parameter (l) S: a stability parameter.

- (11) K_{gl} proposed by Hruby is used as a measure of the glass forming tendency of materials and this parameter is given by the following equation.⁴²⁾

$$K_{gl} = \frac{T_x - T_g}{T_g - T_m} \quad (4)$$

K_{gl} parameter is based on the concept that the thermal stability of a glass on subsequent reheating is directly proportional to the case of its formation.

- (12) A stability parameter S proposed by Saad and Poulain is defined as follows.⁴³⁾

$$S = \frac{(T_p - T_x)(T_x - T_g)}{T_g} \quad (5)$$

This parameter has taken into account the temperature difference between T_p and T_x , as well as the position of glass transition and crystallization exotherm.

Among above described 12 parameters, ΔT_x , T_{rg} , γ , K_{gl} and S parameters can not be independently evaluated without T_g , resulting that only 4 experimental data of TD_{298} can be used for revealing the general tendency about phase stability of an amorphous phase against electron irradiation in Fe-based alloys. In contrast, 8 experimental data of TD_{298} in Fe-based alloy of $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15$ and 20), $\text{Fe}_{77.5}\text{Nd}_{4.5}\text{B}_{18.5}$, $\text{Fe}_{81}\text{Nd}_9\text{B}_{20}$ and $\text{Fe}_{82.2}\text{Nd}_{7.1}\text{B}_{10.7}$ alloys can be used when we adopt T_x , T_p , T_m , T_l and ΔT^* parameters. In Fig. 8, TD_{298} in Fe-Zr-B alloys are jointed by the solid lines because of systematic change in boron concentration. Among T_x , T_p , T_m , T_l and ΔT^* parameters in Figs. 8(a)(b)(c)(d)(e), changes in T_x and T_p seem to have a positive correlation with that in TD_{298} rather than other parameters. The TD_{298} monotonically increases with increase in T_x and T_p shown in Fig. 8(a) and (b), respectively. Although TD_{298} increases with increasing in ΔT^* , the TD_{298} can not be evaluated simultaneously in both alloy systems because of difference in ΔT^* between Fe-Zr-B and Fe-Nd-B alloys. In the case of T_g , ΔT_x , T_{rg} , γ , K_{gl} and S parameters in Fig. 8(f)(g)(h)(i)(j)(k)(l), it may be difficult to reveal the relationship between these parameters and TD_{298} because of few experimental data. The ΔT_x , γ and K_{gl} parameters seem to be better parameters for evaluating TD_{298} among T_g , ΔT_x , T_{rg} , γ , K_{gl} and S.

4. Discussion

In the present study, crystallization of melt-spun amorphous phase under electron irradiation was observed in $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15$ and 20) alloys. The origin of electron irradiation induced crystallization of an amorphous phase in Fe-Zr-B alloys was discussed in the previous papers about α -Fe former type $\text{Fe}_{88}\text{Zr}_9\text{B}_3$,^{11,13)} α -Mn type former type $\text{Fe}_{81}\text{Zr}_9\text{B}_{10}$ ⁸⁾ and multi-crystalline phases former type $\text{Fe}_{71}\text{Zr}_9\text{B}_{20}$ ^{13,22)} alloys based on two factors; (1) promotion of atomic diffusion assisted by atomic displacements due to electron knock-on effect enough for phase transition, and (2) phase stability of crystalline phase for maintaining the original structure against electron irradiation. α -Fe crystalline phase with b.c.c.-structure is formed through electron irradiation induced crystallization in $\text{Fe}_{91-x}\text{Zr}_9\text{B}_x$ ($x = 3, 5, 10, 15$ and 20) alloys. This indicates that α -Fe crystalline phase shows high phase stability against electron irradiation and precipitates under electron irradiation. Once this phase is formed under electron irradiation by promotion of atomic diffusion based on electron irradiation induced mixing effect, this phase can maintain the original structure and does not transform to an amorphous phase through SSA, resulting in forming α -Fe nano-crystalline precipitates under electron

irradiation. The satisfaction of the above two factors explains why electron irradiation induced crystallization occurs in Fe-Zr-B alloys, while the irradiation can induce solid state amorphization in many Fe-based compounds. The origin of electron irradiation induced crystallization of melt-spun amorphous phase was also discussed from the viewpoint of thermodynamics; (1) temperature-Gibbs free energy diagram and concept of energizing,^{44,45)} and (2) change in potential energy of an amorphous phase and crystalline phases by electron irradiation.^{44–46)} Electron irradiation induced crystallization in Fe₈₁Zr₉B₁₀ alloys can be explained by these thermodynamical models,⁸⁾ and these models can be applied for other Fe_{91-x}Zr₉B_x ($x = 3, 5, 15$ and 20) alloys.

In Fe-based Fe-Zr-B and Fe-Nd-B alloys, phase stability of an amorphous phase against electron irradiation gives a positive correlation with T_x , T_p , ΔT_x , γ and K_{gl} among T_x , T_p , T_m , T_l , ΔT^* , T_g , ΔT_x , T_{rg} , γ , K_{gl} and S thermal parameters. The systematic experimental data of electron irradiation induced crystallization behavior was established not only in metal-metalloid type Fe-based alloys but also in metal-metal type Zr-based alloys.^{33,47,48)} In this section, we try to reveal the general tendency of phase stability of an amorphous phase against electron irradiation in various type metallic materials. Figure 9 shows TD_{298} as a function of thermal parameters of T_x , T_p , ΔT_x , γ and K_{gl} . The experimental data of TD_{298} in metal-metal type Zr-based alloys of Zr_{66.7}-Cu_{33.3},^{33,34)} Zr_{66.7}Ni_{33.3},⁴⁹⁾ Zr_{66.7}Pd_{33.3},⁵⁰⁾ Zr₈₀Pt₂₀, Zr₆₅Al_{7.5}-Cu_{27.5},^{33,34)} and Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5},^{33,34,51)} are added to Fig. 8. The TD_{298} of Zr₆₀Al₁₅Ni₂₅ is not added because of the anomalous high phase stability of the amorphous phase in Zr-based alloys.⁴⁹⁾ The TD_{298} increases with increasing T_x in Zr-based alloys as well as Fe-based alloys as shown in Fig. 9(a). The degree of increase in TD_{298} in Fe-based alloys with T_x is much larger than that of Zr-based alloys. The T_x in Zr-based alloys is much lower than that of Fe-based alloys, resulting that the region of Zr-based alloys group surrounded by dashed-line circle does not overlap with that of Fe-based alloys group represented by solid-line circle in Fig. 9(a). The same tendency can be seen in T_p vs. TD_{298} graph (b). In the case of ΔT_x , γ and K_{gl} , the experimental data of Zr-based alloys are limited in 4 alloys because other two alloys show no glass transition during conventional DSC measurement. The TD_{298} of Fe-Zr-B alloys is higher than that of Zr-based alloys at same ΔT_x , γ or K_{gl} . The degree of increase in TD_{298} with ΔT_x in Fe-Zr-B alloys is much larger than that in Zr-based alloy. This tendency can be also seen in γ vs. TD_{298} and K_{gl} vs. TD_{298} graphs (d)(e). In other words, TD_{298} in Fe-Zr-B alloys is more sensitive to the thermal parameters of ΔT_x , γ and K_{gl} rather than Zr-based alloys. The difference in the parameter dependence on TD_{298} between Fe-based alloys and Zr-based alloys may be due to the difference in constituent elements. Although the parameters to completely predict the phase stability of an amorphous phase against electron irradiation is not revealed in the present study, the following tendencies are revealed;

- (1) Increase in T_x , T_p , ΔT_x , γ and K_{gl} leads to the increase in phase stability of an amorphous phase against electron irradiation. Increase in thermal stability of an amorphous phase is favorable for stabilizing the phase against electron irradiation.

Fig. 9 Relationship between thermal properties of melt-spun amorphous phase and critical onset total dose of 2.0 MeV electron irradiation induced crystallization at 298 K in Fe-based Fe_{91-x}Zr₉B_x ($x = 3, 5, 10, 15, 20$), Fe_{91-x}Zr₉B_x ($x = 3, 5, 10, 15, 20$) and Zr-based Zr_{66.7}Cu_{33.3}, Zr_{66.7}Ni_{33.3}, Zr_{66.7}Pd_{33.3}, Zr₈₀Pt₂₀, Zr₆₅Al_{7.5}Cu_{27.5} and Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} metallic glasses. The cross mark (×), open circle (○) and closed circle (●) represent Zr-based alloys, Fe-Zr-B alloys and Fe-Nd-B alloys, respectively. (a) T_x : crystallization temperature, (b) T_p : peak temperature of first thermal crystallization, (c) ΔT_x : temperature interval of supercooled liquid region defined by $T_x - T_g$, (d) γ , gamma parameter defined by $T_x/(T_g + T_l)$, (e) K_{gl} : K_{gl} parameter.

- (2) There is a difference in the degree of increase in the phase stability of an amorphous phase against electron irradiation with increasing T_x , T_p , ΔT_x , γ and K_{gl} between Fe-based alloys and Zr-based alloys.

Takeuchi suggested chemical mixing enthalpy (ΔH_{chem}) and mismatch entropy normalized by Boltzmann constant (S_σ/k_b) for predicting GFA.^{52–54)} The TD_{298} shows the clear positive correlation with ΔH_{chem} normalized by the largest negative value (ΔH_{chem})_{L.N.} and (S_σ/k_b) normalized by the maximum value (S_σ/k_b)_{max} in Fe-Zr-B alloys and Fe-Nd-B alloys.^{55,56)} Not only present parameters of T_x , T_p , T_l , T_m , T_g , ΔT_x , T_{rg} , γ , K_{gl} and S based on temperature parameters but the parameters based on thermodynamic data-base such as (ΔH_{chem}) and (S_σ/k_b) are very important for predicting the phase stability of an amorphous phase against electron irradiation induced crystallization.

5. Conclusion

Electron-irradiation induced nano-crystallization behavior

of melt-spun amorphous phase in Fe-Zr-B ternary alloys was investigated focusing on the nano-crystallization and phase stability of the amorphous phase against electron irradiation. The results were summarized and the following conclusions were reached:

- (1) Melt-spun amorphous phase in $\text{Fe}_{91-x}\text{Zr}_9\text{B}_{20}$ ($x = 3, 5, 10, 15, 20$) alloys was not stable under 2.0 MeV electron irradiation at 298 K. Electron irradiation induced crystallization occurred and nano-crystals precipitated from the amorphous phase. Nano-composite structure composed of α -Fe phase (b.c.c.-solid solution), metallic compounds and a residual amorphous matrix was formed through electron irradiation induced nano-crystallization, while such nano-crystalline structure was hardly realized by thermal annealing.
- (2) The phase stability of melt-spun amorphous phase against electron irradiation in Fe-Zr-B ternary alloys increases with increasing thermal stability of this phase, resulting that the critical onset total dose of electron irradiation induced crystallization shows the positive correlation with thermal stability parameters of T_x , T_p , ΔT_x , γ and K_{gl} . The critical total dose of Fe-based metallic glasses is higher than that of Zr-based metallic glasses at same ΔT_x , γ and K_{gl} parameters.

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