Formation of nanocrystalline structure during electron irradiation induced crystallization in amorphous Fe–Zr–B alloys

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Abstract

Effect of electron irradiation on the crystallization and phase stability of Fe\textsubscript{90}Zr\textsubscript{10}B\textsubscript{3} and Fe\textsubscript{90}Zr\textsubscript{0}B\textsubscript{20} amorphous alloys was examined. Electron irradiation at an accelerated voltage of 2000 kV was performed at room temperature. The Fe\textsubscript{90}Zr\textsubscript{10}B\textsubscript{3} alloy showed a wide supercooled liquid region and the $\Delta T_c$ value was 71 K, while no glass transition was observed in Fe\textsubscript{90}Zr\textsubscript{10}B\textsubscript{3} alloy. The amorphous phase in Fe–Zr–B alloys was not stable under irradiation and crystallization from the amorphous phase was accelerated by the irradiation. Nanocrystalline structure composed of $\alpha$-Fe and cubic-Fe\textsubscript{3}Zr was formed in Fe\textsubscript{90}Zr\textsubscript{10}B\textsubscript{3} alloy by irradiation induced crystallization, while no nanoscale precipitates of intermetallic compounds were formed during annealing. In Fe\textsubscript{90}Zr\textsubscript{0}B\textsubscript{20} alloy, the formation of nanocrystalline precipitates was also confirmed by irradiation induced crystallization, although the formation of nanocrystalline structure had not been realized in high B concentration Fe–Zr–B alloys by annealing. These new results show that electron irradiation is effective in producing a new nanocrystalline structure. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Great interest has recently been focused on control of the nanocrystalline structure which often induces superior mechanical and physical properties. In nanocrystalline alloys, good mechanical properties [1,2], soft magnetism [3,4], hard magnetism [5,6], high magnetostriction in low applied field [7], and high catalytic properties [8] have been reported. Many techniques have been developed to produce nanocrystalline alloys: mechanical alloying [9], reactive milling [10], chemical reduction [11], chemical leaching [12] and evaporation method [13,14]. The nanocrystalline alloys were produced by crystallization of an amorphous phase [15–33]. Control of the crystallization of the amorphous phase is known to be one of the most effective techniques for obtaining nanocrystalline materials. However, the nanocrystalline structure was realized during annealing in a limited number of Mg- [15,16], Al- [17–20], Fe- [3,4,21–26] and Zr-based [27–33] amorphous alloys. Since the first success in obtaining the amorphous phase in the Au–Si system [34], a great number of amorphous alloys have been developed.

The crystallization process of the amorphous phase is known to be controlled not only by thermal annealing but also by external factors such as electron and neutron irradiation and magnetic applied field [35,36]. In the previous paper examining the effects of electron irradiation on the phase transformation and stability of amorphous and crystalline phases in melt-spun Fe\textsubscript{90}Zr\textsubscript{10}B\textsubscript{3} alloys, the irradiation accelerated the crystallization of the amorphous phase and a nanocrystalline structure composed of cubic-Fe\textsubscript{3}Zr and $\alpha$-Fe surrounded by the amorphous was formed [36]. This paper presents the effect of electron irradiation on crystallization behavior and phase stability of Fe–Zr–B amorphous alloys and the possibility of achieving nanocrystalline structure.

2. Experimental procedure

Master ingots of ternary Fe\textsubscript{91−x}Zr\textsubscript{x}B\textsubscript{3} ($x = 3.0, 5.0, 10.0, 15.0, 20.0, 25.0,$ and $30.0$ at.%) alloys were prepared by arc melting in a purified Ar atmosphere. Rapidly quenched ribbons with a cross-section of about $2.0 \text{ mm} \times 0.02 \text{ mm}$
were produced from the ingot at a rotation speed of 42 m/s by a single roller melt-spinning method in an Ar atmosphere. The thermal stability and the crystallization process of the specimens as melt-spun were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s in Ar atmosphere. Some specimens were annealed at various temperatures. Specimens for transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HREM) observation were thinned by twin jet polishing in a solution of 10% perchloric and 90% acetic acid at room temperature (298 K). The specimens as melt-spun were irradiated by an ultra high voltage electron microscope (UHVEM) of H-3000 and H-2000 operating at 2000 kV. The applied dose rate was in the range of 7.5 \times 10^{15} \text{ to } 1.7 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}, with the maximum dose density of irradiation being 3.4 \times 10^{27} \text{ m}^{-2}. The irradiation was performed at room temperature (298 K). Change in the microstructure during electron irradiation was observed by bright field (BF) images and selected area diffraction (SAD) patterns in UHVEM. Structures of melt-spun, annealed and electron irradiated ribbons were examined by X-ray diffractometry using Cu Kα radiation and electron diffraction (ED) patterns.

3. Results

3.1. Thermal analysis of Fe–Zr–B alloys as melt-spun

Fig. 1 shows the X-ray diffraction patterns of melt-spun Fe_{91−x}Zr_{x}B_{3} alloys. A typical broad peak corresponding to the amorphous state at around 2θ = 44° is observed for each B concentration, and the peak broadens with B concentration. In the alloys with x = 25 and 30, sharp diffraction peaks corresponding to a crystalline phase appear but the crystalline structure is not determined. In the present study, Fe_{71}Zr_{29}B_{3} alloy as melt-spun has the highest B concentration among Fe–Zr–B alloys showing the amorphous single phase.

Fig. 2(a) shows DSC curves of melt-spun Fe_{91−x}Zr_{x}B_{3} alloys. The exothermic peaks with high intensity due to crystallization can be seen in all these curves. The shape

![Fig. 1. X-ray diffraction patterns of Fe_{91−x}Zr_{x}B_{3} (x = 3–30) alloys as melt-spun.]

![Fig. 2. DSC curves of Fe_{91−x}Zr_{x}B_{3} (x = 3–30) alloys as melt-spun.]

of the exothermic peak becomes sharper and the intensity becomes stronger with increasing B concentration. The crystallization process is very sensitive to B concentration: as the concentration rises, the crystallization behavior changes from multi-stage to single-stage and the simultaneous precipitation of more than two kinds of constituent phases occurs. Fig. 2(b) shows the details of DSC curves just before the crystallization. An endothermic reaction due to the glass transition appears above 10 at.% B alloys. The glass transition occurs and the supercooled liquid state is observed below the onset temperature of crystallization. The temperature range of the supercooled liquid state becomes broader with increasing B concentration. The glass transition temperature ($T_g$) increases monotonously from about 840 to 920 K with increasing B concentration from 10 to 30 at.%. The onset temperature of crystallization ($T_x$) shows a similar compositional dependence to that for $T_p$, but the increase in $T_x$ is larger than for $T_p$. Fe$_{71}$Zr$_{5}$B$_{30}$ alloy shows the largest $\Delta T_x$. The transition from amorphous state to supercooled liquid state in Fe$_{71}$Zr$_{5}$B$_{30}$ alloy starts at 864 K and the supercooled liquid state is maintained over a wide temperature range of $\Delta T_x = 71$ K, then crystallization occurs at 935 K. The $T_x$ and $\Delta T_x$ values of Fe$_{71}$Zr$_{5}$B$_{30}$ amorphous alloy are one of the largest values among Fe-based amorphous alloys. This suggests that Fe$_{71}$Zr$_{5}$B$_{30}$ amorphous alloy has high thermal stability. In this study, two typical but different types of amorphous alloys were chosen to examine the effect of electron irradiation on the crystallization process and phase stability of the amorphous phase: Fe$_{88}$Zr$_{6}$B$_{3}$ alloy with no supercooled liquid state [37] and Fe$_{71}$Zr$_{5}$B$_{30}$ alloy with high thermal stability of the amorphous state.

3.2. Microstructure after first crystallization

Fig. 3 shows the X-ray diffraction patterns of Fe$_{88}$Zr$_{6}$B$_{3}$ alloy annealed at 873 K for 600 s and Fe$_{71}$Zr$_{5}$B$_{30}$ alloy annealed at 923 K for 3600 s whose annealing conditions achieve the structures just after the first crystallization [36–38]. The XRD patterns of Fe$_{88}$Zr$_{6}$B$_{3}$ alloy shows only $\alpha$-Fe phase with bcc structure, while many sharp peaks due to crystalline phases are seen for Fe$_{71}$Zr$_{5}$B$_{30}$ alloy. The XRD patterns of Fe$_{71}$Zr$_{5}$B$_{30}$ alloy corresponded to $\alpha$-Fe, Fe$_2$Zr, Fe$_3$Zr, orthorhombic-Fe$_2$B and Fe$_3$B phases. This indicates that not only the crystallization process but also the crystalline constituent phases precipitated from the amorphous phase are very sensitive to B concentration in Fe–Zr–B amorphous alloys.

TEM images and selected-area diffraction patterns of Fe$_{88}$Zr$_{6}$B$_{3}$ alloy annealed at 873 K for 600 s and Fe$_{71}$Zr$_{5}$B$_{30}$ alloy annealed at 923 K for 3600 s are shown in Fig. 4. In Fe$_{88}$Zr$_{6}$B$_{3}$ alloy, the structure consists of a mostly single $\alpha$-Fe phase with a homogeneous nanoscale grain size of about 20 nm and no obvious intermetallic compound is observed. In contrast, course crystalline phases more than 100 nm in size and inhomogeneous grain distribution are observed in Fe$_{71}$Zr$_{5}$B$_{30}$ alloy. The nanocrystalline structure through the first crystallization of the amorphous phase cannot be seen in Fe$_{71}$Zr$_{5}$B$_{30}$ alloy which has high thermal stability and a wide supercooled liquid region during annealing.

3.3. Microstructure after electron irradiation induced crystallization

Fig. 5 shows TEM microstructures and diffraction patterns of irradiated Fe$_{88}$Zr$_{6}$B$_{3}$ alloy at the radiation dose density of $2.0 \times 10^{27}$ m$^{-2}$ for (a) and (b) and Fe$_{71}$Zr$_{5}$B$_{30}$ alloy at the radiation dose density radiation dose of $3.4 \times 10^{27}$ m$^{-2}$ for (c) and (d). From BF images and SAD patterns, electron irradiated specimens show nanocrystalline structure in Fe$_{88}$Zr$_{6}$B$_{3}$ alloy and duplex structure composed of nanocrystalline phases surrounded by the amorphous phase in Fe$_{71}$Zr$_{5}$B$_{30}$ alloy. This indicates that the amorphous phase of Fe–Zr–B alloys is unstable under electron irradiation and crystallization of the amorphous phase is accelerated by electron irradiation even at room temperature lower than $T_x$. The SAD pattern of Fe$_{88}$Zr$_{6}$B$_{3}$ alloy shows no halo rings corresponding to the amorphous phase; only distinct Debye rings corresponding to $\alpha$-Fe and cubic-Fe$_2$Zr phase are observed. According to previous results on the crystallization in low B concentration Fe–Zr–B amorphous alloys by annealing [22,37,44–46], cubic-Fe$_2$Zr precipitates of nanoscale grain size were not observed. Electron irradiation stimulates the unusual crystallization which differs from
Fig. 4. TEM microstructures and diffraction patterns of Fe₅₀Zr₅B₇ alloy annealed at 873 K for 600 s (a, b) and Fe₇₅Zr₀B₂₀ alloy annealed at 923 K for 3600 s (c, d).

Fig. 5. TEM microstructures and diffraction patterns of irradiated Fe₅₀Zr₅B₇ alloy at the radiation dose density of 2.0 × 10¹⁷ m⁻² (a, b) and Fe₇₅Zr₀B₂₀ alloy at the radiation dose density of 3.4 × 10¹⁷ m⁻² (c, d). Electron irradiation performed at 298 K and the accelerated voltage is 2000 kV.
that in Fe\textsubscript{85}Zr\textsubscript{B} amorphous alloy by annealing. On the contrary, dark granular contrast of about 10 nm in size appears in the featureless contrast matrix in Fe\textsubscript{72}Zr\textsubscript{B} alloy. The SAD pattern shows not only halo rings but also some Debye rings and spotty diffraction patterns. Some Debye rings correspond to (110), (200) and (211) diffraction of α-Fe, although the (110) diffraction overlaps on the halo ring for the amorphous phase. The diffraction spots and Debye rings corresponding to cubic-Fe\textsubscript{2}Zr and Fe\textsubscript{2}B are also observed. The precipitation of Fe\textsubscript{2}Zr and orthorhombic-Fe\textsubscript{2}B which crystallized from the amorphous phase during annealing is not confirmed from the Debye rings. The quantity of these crystalline phases might be too small to confirm their existence only from the data of SAD pattern. From the viewpoint of the simultaneous precipitation of more than two kinds of constituent crystalline phases, there is no significant difference between electron irradiation induced crystallization and thermal crystallization in Fe\textsubscript{72}Zr\textsubscript{B} alloy. The total dose for Fe\textsubscript{72}Zr\textsubscript{B} alloy shown in Fig. 5(c) and (d) is about 1.5 times larger than that for Fe\textsubscript{85}Zr\textsubscript{B} alloy shown in Fig. 5(a) and (b). Broad halo rings corresponding to the amorphous phase can be seen in Fe\textsubscript{72}Zr\textsubscript{B} alloy, while only Debye rings appear in Fe\textsubscript{85}Zr\textsubscript{B} alloy. The rate of electron irradiation induced crystallization is lowered in Fe\textsubscript{72}Zr\textsubscript{B} than in Fe\textsubscript{85}Zr\textsubscript{B}.

To examine the details of the crystallization process induced by electron irradiation, the structural change in Fe\textsubscript{85}Zr\textsubscript{B} alloy irradiated at various dose densities was observed in situ. Fig. 6 shows changes in BF images and SAD patterns of melt-spun Fe\textsubscript{85}Zr\textsubscript{B} alloy irradiated at various dose densities. As melt-spun, the BF image shows featureless contrast and only halo rings corresponding to the amorphous phase are seen in the SAD pattern. The amorphous state is confirmed by a typical maze-like contrast in the HREM image. No significantly developed MRO domains or small clusters with a crystalline structure are observed. The crystalline precipitates nanoscale in size appear during electron irradiation in Fig. 6(c). The broad halo rings become shaper and some discontinuous diffraction spots appear. The quantity of the crystalline phase increases with increasing irradiation dose. After irradiation at the dose of 4.5 × 10\textsuperscript{29} m\textsuperscript{−2}, the featureless contrast corresponding to the amorphous phase changes to island-like contrast in the BF image. Two fairly sharp Debye rings are seen together with strong halo rings corresponding to the amorphous phase. The two rings are identified as (200) and (422) diffractions for the cubic-Fe\textsubscript{2}Zr phase, but no Debye rings for the α-Fe phase are visible. After irradiation at the dose of 1.4 × 10\textsuperscript{30} m\textsuperscript{−2} in Fig. 6(e) and (f), the nanocrystalline structure is seen to be similar to that in Fig. 5(a). Debye rings for the cubic-Fe\textsubscript{2}Zr with more high intensity are observed, and several distinct diffraction rings for α-Fe. The crystallization of an amorphous phase during electron irradiation is different from that during thermal annealing and its process is as follows:

\[
\text{Amorphous} \rightarrow \text{Cubic-Fe}_2\text{Zr} + \text{Amorphous} \rightarrow \text{Cubic-Fe}_2\text{Zr} + \alpha-\text{Fe}
\]

Although the crystallization process was divided into two stages and distinct time interval between precipitation of a primary crystalline phase and subsequent crystallization was observed during annealing [37], there was not a distinct time interval during electron irradiation.

Fig. 7 shows HREM images of electron irradiated Fe\textsubscript{85}Zr\textsubscript{B} and Fe\textsubscript{72}Zr\textsubscript{B} alloys at the radiation dose of 1.4 × 10\textsuperscript{27} and 3.4 × 10\textsuperscript{27} m\textsuperscript{−2}, respectively. Crystalline lattice images with nanoscale grain size of about 10 nm are observed in both alloys. Fig. 7(b) shows a typical example of nanoscale precipitates with lattice fringes spaced 0.24 and 0.27 nm apart. This nanocrystalline precipitate was identified as cubic-Fe\textsubscript{2}Zr intermetallic compound from the fringe spacing and geometry of cross-fringe image. In the figure, A and B represent α-Fe and cubic-Fe\textsubscript{2}Zr phases, respectively. The formation of nanocrystalline structures composed of α-Fe and cubic-Fe\textsubscript{2}Zr was confirmed from the HREM image in Fe\textsubscript{85}Zr\textsubscript{B} alloy. In Fe\textsubscript{72}Zr\textsubscript{B} alloy, not only cubic-Fe\textsubscript{2}Zr but also the nanocrystalline phases such as α-Fe and Fe\textsubscript{2}B are also distributed in the amorphous matrix. Nanocrystals about 10 nm in size were uniformly embedded in the amorphous phase. These results clearly show that electron irradiation is very effective to obtain the nanocrystalline structure in Fe–Zr–B amorphous alloys.

4. Discussion

4.1. The phase stability of amorphous phase under electron irradiation

Atoms in material are known to be dynamically replaced by an electron knock-on effect under electron irradiation; each atom is forced to diffuse at room temperature. In crystalline alloys, fracture of the crystalline structure and the decrease in the degree of order often occur through the replacement of atoms. If a crystalline phase could not maintain the original crystal structure with the replacement of constituent atoms by the electron knock-on effect, it would transform other crystalline or amorphous phases with a metastable structure. The electron knock-on effect occurs not only in the amorphous phase but also in crystalline phases. In this section, the stability of crystalline phases against electron irradiation is considered. We reported that α-Fe, Fe\textsubscript{2}Zr and Fe\textsubscript{2}B phases are stable under electron irradiation at the accelerated voltage of 2000 kV [36]. In the Fe–B binary system, the amorphous phase was formed only in the composition range of 10–28 at.% B by rapid quenching from liquid [39,40], and the amorphous phase of Fe\textsubscript{2}B was not confirmed under electron irradiation [41]. These reports indicate that α-Fe, cubic-Fe\textsubscript{2}Zr and Fe\textsubscript{2}B crystalline
phases are stable against electron irradiation. When constituent atoms are dynamically replaced by an electron knock-on effect and encounter other atoms, nanocrystalline phase of $\alpha$-Fe and cubic-$\text{Fe}_2\text{Zr}$ are formed in Fe$_{88}$Zr$_8$B$_{14}$ alloy to decrease Gibbs free energy at the localized region in the amorphous matrix. $\alpha$-Fe, cubic-$\text{Fe}_2\text{Zr}$ and $\text{Fe}_2\text{B}$ phases may be formed in Fe$_{71}$Zr$_9$B$_{20}$ alloy by a similar mechanism. Dynamic displacement of atoms by electron knock-on effect and the high stability of crystalline phases against electron irradiation cause easy crystallization in Fe–Zr–B amorphous alloys under electron irradiation.

Fig. 6. Change in TEM microstructures and diffraction patterns of Fe$_{88}$Zr$_8$B$_{14}$ alloys as melt-spun and irradiated for various dose. Electron irradiation performed at 298 K and the accelerated voltage is 2000 kV. (a, b) As melt-spun, (c, d) radiation dose density of $4.5 \times 10^{36}$ m$^{-2}$, (e, f) radiation dose density of $1.4 \times 10^{37}$ m$^{-2}$. 
4.2. Crystallization process of Fe$_{68}$Zr$_3$B$_3$ amorphous alloy under electron irradiation

Diffusion of atoms by thermal annealing is controlled by the thermal activation process. Diffusion constant for Zr atoms in the Fe$_{68}$Zr$_3$ amorphous phase was reported to be much smaller than that of Fe [42]. Since the atomic radius of Zr is about 25% larger than that of Fe, Zr atoms in Fe–Zr–B alloys may diffuse more slowly than Fe atoms during annealing. Therefore, α-Fe precipitates are formed in the first crystallization process in Fe$_{68}$Zr$_3$B$_3$ amorphous alloy by the fast diffusion of Fe atoms by annealing. In contrast, Fe and Zr atoms are dynamically replaced by an electron knock-on effect under electron irradiation; both atoms are forced to diffuse at room temperature during the irradiation. Thus, the controlling factors for the motion of atoms may be different between the electron irradiation and thermal annealing. This difference may be one of the causes of the preferential crystallization of cubic-Fe$_2$Zr and the lack of a distinct time interval between cubic-Fe$_2$Zr and α-Fe crystallization during electron irradiation in Fe$_{68}$Zr$_3$B$_3$ amorphous alloy.

4.3. The relationship between thermal stability of amorphous phase and electron irradiation induced crystallization

The degree of a dense randomly packed (DRP) atomic structure is known to be closely related to the atomic diffusivity in amorphous phase. The increase in B concentration in Fe–Zr–B alloys increases the degree of the DRP atomic structure from topological and chemical points of view resulting in an increase in thermal stability of the amorphous phase. As the degree of DRP atomic structure increases, the atomic configuration becomes more closely packed and the atomic interaction among constituent atoms increases within a short range. Therefore, an increase in B concentration in Fe–Zr–B alloys may decrease not only atomic diffusion during annealing but also the replacement rate of atoms by the electron knock-on effect during electron irradiation. The relation between the thermal stability of amorphous phase and the electron irradiation induced crystallization is discussed in this section.

The thermal stability of an amorphous phase is known to be related to the nucleation and growth rates of a crystalline
phase. High thermal stability is induced by the low atomic diffusivity in the growth of crystalline phases, and suppression of the nucleation of a crystalline phase resulting from increase in the solid–liquid interface energy. The first crystallization of $\alpha$-Fe occurs from the amorphous phase which forms a nanocrystalline structure during annealing in $\text{Fe}_8\text{Zr}_5\text{B}_3$ alloy. $\alpha$-Fe, $\text{Fe}_2\text{Zr}$, $\text{Fe}_5\text{Zr}$, $\text{Fe}_2\text{B}$ and orthorhombic-$\text{Fe}_2\text{B}$ simultaneously precipitate from the amorphous phase in $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ alloy. Since the composition of these crystalline phases is different from that of the amorphous phase, atomic redistribution based on atomic diffusivity are necessary for the progress of the crystallization in $\text{Fe}_8\text{Zr}_5\text{B}_3$ and $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ alloys; namely, the crystallization is controlled by atomic diffusion. Retardation of the crystallization reaction is due to the decrease of atomic diffusion with increasing B concentration in Fe–Zr–B amorphous alloys, resulting in an increase in thermal stability. In electron irradiation induced crystallization of $\text{Fe}_8\text{Zr}_5\text{B}_3$ and $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ amorphous alloys, the crystalline phases whose compositions are different from those of the amorphous phase also precipitate from the amorphous phase. Atomic diffusion is also necessary for the precipitation of these crystalline phases. As described in Section 4.1, the promotion of atomic diffusion by electron knock-on effect causes the acceleration of crystallization under electron irradiation. The rate of electron irradiation induced crystallization from $\text{Fe}_8\text{Zr}_5\text{B}_3$ amorphous alloy is higher than that from $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ amorphous alloy. This is due to the decrease in atomic diffusion under electron irradiation by electron knock-on effect with increasing B concentration in Fe–Zr–B amorphous alloys.

4.4. Formation of nanocrystalline structures during thermal annealing and electron irradiation

A nanocrystalline structure is known to form from the amorphous phase during annealing when the following four factors are satisfied [43]: (1) the multistage crystallization mode to the precipitation of a primary crystalline phase, (2) the ease of homogeneous nucleation of the primary phase, (3) the difficulty of subsequent crystal growth reaction, and (4) the high thermal stability of the residual amorphous phase. The crystallization process in low B concentration Fe–Zr–B amorphous alloys such as $\text{Fe}_8\text{Zr}_5\text{B}_3$ was examined and it is concluded that the nanocrystalline structure is obtained because of the rejection of Zr and B atoms in the amorphous matrix from primary crystalline $\alpha$-Fe precipitates and homogeneous nucleation of $\alpha$-Fe precipitates [22,37,44–46]. The enrichment of Zr and B atoms in the amorphous phase suppresses the growth of nanocrystalline $\alpha$-Fe precipitates and increases the thermal stability of the residual amorphous phase. After first crystallization, $\alpha$-Fe precipitates with nanoscale grain size ranging between about 10 and 20 nm are embedded in the residual amorphous phase in low B concentration Fe–Zr–B alloys. In the second crystallization process, Fe–Zr intermetallic compounds crystallize from the residual amorphous phase with the high thermal stability. $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ amorphous alloy, in contrast, shows the single-stage crystallization process through the simultaneous precipitation of more than two kinds of constituent crystalline phases. Formation of the residual amorphous phase in $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ alloy is not observed during annealing [38]. The nanocrystalline structure is not formed by the crystallization from the amorphous phase during annealing because the above four factors are poorly satisfied. This tendency is found in other Fe-based amorphous alloys with a wide supercooled liquid region before crystallization, such as Fe–(Al, Ga)–(P, C, B, Si), (Fe, Co, Ni)–(Zr, Nb, Ta)–B and Fe–Co–(Zr, Nb)–(Mo, W)–B [47–51] alloys.

Although the electron knock-on effect also assists atomic diffusion and accelerates the crystallization of the amorphous phase, the activation process of constituent elements is different from that in thermal annealing. This may induce a high nucleation rate of crystalline phases. Interstitials and vacancies are continuously produced by electron irradiation in crystalline precipitates under electron irradiation. Grain refinement of crystalline precipitations may occur through the rearrangement of a large quantity of defects produced by the irradiation; grain refinements of $\alpha$-Fe, $\text{Fe}_2\text{Zr}$ and $\text{Fe}_5\text{Zr}$ phases was observed in low B concentration $\text{Fe}_8\text{Zr}_5\text{B}_3$ crystalline alloy with the grain size of about 50 nm under electron irradiation [35]. This phenomenon is also effective in producing nanocrystalline structure under electron irradiation in both $\text{Fe}_8\text{Zr}_5\text{B}_3$ and $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ amorphous alloys with a wide supercooled liquid region.

5. Conclusion

The effect of electron irradiation on the crystallization process, the phase stability of the amorphous phase and the microstructure control was examined in Fe–Zr–B amorphous alloys. The results were summarized and the following conclusions reached:

1. The amorphous Fe$_{91-x}$Zr$_x$B$_{20}$ single phase is obtained in the B concentration range of $x = 3–20$ at.%. The increase in B concentration in Fe–Zr–B alloys increases the stability of the amorphous phase. The amorphous phase with a supercooled liquid region is formed at more than 10 at.% B. $T_a$ and $T_s$ monotonously increased with increasing B concentration. $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ amorphous alloy shows a wide supercooled liquid region of $\Delta T_s = 71$ K.

2. The amorphous phase was not stable under electron irradiation. Crystallization from this phase was accelerated by electron irradiation in $\text{Fe}_8\text{Zr}_5\text{B}_3$ and $\text{Fe}_7\text{Zr}_3\text{B}_{20}$ amorphous alloys. The rate of crystallization by electron irradiation decreased with increasing B concentration.

3. The crystallization process induced by electron irradiation was different from that by thermal annealing in $\text{Fe}_8\text{Zr}_5\text{B}_3$ alloy; a nanocrystalline structure composed
of cubic-Fe₃Zr and α-Fe phases was formed in the crystallization process under electron irradiation. In electron irradiated Fe₂ZrB₀ alloy, nanoscale crystalline precipitates of α-Fe, cubic-Fe₃Zr and Fe₂B were formed. Electron irradiation for the amorphous phase is effective for obtaining new nanocrystalline structures in Fe–Zr–B alloys.

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