High Saturation Magnetization and Soft Magnetic Properties of bcc Fe–Zr–B and Fe–Zr–B–M (M = Transition Metal) Alloys with Nanoscale Grain Size

K. Suzuki*, A. Makino**, N. Kataoka*, A. Inoue* and T. Masumoto*

A mostly single bcc phase with nanoscale grain sizes of 10 to 20 nm was found to form by annealing amorphous Fe–Zr–B, Fe–Zr–B–Cu and Fe–Zr–B–Cu–M (M = Hf, Nb or Ta) alloys for 3.6 ks in the range of 750 to 900 K. The composition range of the bcc phase extends from 5 to 7% Zr and 1 to 8% B for the Fe–Zr–B system and 5 to 8% Zr and 1 to 16% B for the Fe–Zr–B–1% Cu system. The bcc alloys exhibit high permeability (\(\mu_r\)) above 10000 at 1 kHz combined with high saturation magnetization (\(B_s\)) above 1.5 T and the highest values reach 14000 and 1.70 T for Fe_{99}Zr_{97}B_{3} and 20000 and 1.55 T for Fe_{97}Zr_{7}B_{3}Cu_{1}. The addition of 1 at% Cu causes an enhancement of \(\mu_r\) through the decrease of the bcc grain size from 20 to 10 nm, in addition to an extension of the formation range of the bcc phase. It should be noted that the highest \(B_s\) value is almost comparable to that for Fe–6.5 mass% Si and considerably higher than those of other practical soft magnetic materials while the \(\mu_r\) values are much higher than that for the Fe–Si alloy. Accordingly, the combined characteristics of high \(B_s\) and \(\mu_r\) values for the bcc Fe–Zr–B base alloys allow us to expect a subsequent development as a novel soft magnetic material.

(Received October 11, 1990)

Keywords: high magnetization, permeability, soft magnetism, iron-zirconium-boron system, bcc alloy, nanoscale grain structure, amorphous phase, crystallization

I. Introduction

Soft magnetic amorphous materials are divided into Fe-based alloys with high saturation magnetization (\(B_s\)) and Co-based alloys with high permeability (\(\mu_r\)). The \(B_s\) value in Fe-based amorphous alloys is usually dependent on Fe content and hence the development of soft magnetic alloys exhibiting high \(B_s\) has been performed in Fe-rich composition ranges. The formation of an amorphous phase in Fe-based alloys by liquid quenching is usually in the range of 70 to 84 at% \(^{1(1)}\) for Fe-metalloid system such as Fe–P–C, Fe–Si–B and Fe–P–B alloys and 88 to 91 at% \(^{2(2)}\) for Fe–Zr and \(^{3(3)}\) for Fe–Hf alloys, being located at a more Fe-rich side for the Fe-transition metal system. In addition, it has been reported \(^{4(4)}\) that the addition of a small amount of B to Fe–Zr and Fe–Hf alloys results in an extension of the glass formation range and an improvement of soft magnetic properties. However, the Fe-rich Fe–Zr and Fe–Hf amorphous alloys exhibit an Invar effect \(^{5(5)}\)–\(^{8(8)}\) which gives rise to the degradation of Curie temperature (\(T_c\)) and the decrease of magnetization value at room temperature and hence the \(B_s\) values of the Fe–Zr and Fe–Hf amorphous alloys are much lower than that of Fe–Si–B amorphous alloys with lower Fe concentrations. If a metastable bcc solution is formed in the Fe–Zr–B and Fe–Hf–B systems, the solid solution is expected to exhibit a high \(B_s\). Furthermore, when the magnetostriction of the bcc solid solution is smaller than that (\(1.0 \times 10^{-4}\) to \(2.7 \times 10^{-5}\)) \(^{9(9)}\) of the amorphous phase, there is a possibility that the bcc alloys exhibit good soft magnetic properties.

It is known \(^{10(10)}\) that a metastable bcc phase with ultrafine grain structure is obtained by annealing of Fe–Si–B amorphous alloys at temperatures well below crystallization temperature (\(T_c\)). It has subsequently been reported \(^{11(11)}\) that the mixed structure consisting of fine bcc particles embedded in the amorphous matrix produced by partial crystallization of Fe–Si–B amorphous alloys exhibits improved soft magnetic properties as compared with those of the amorphous single phase with the same alloy composition. It has recently been reported \(^{12(12)}\) that the crystallization of Fe–Si–B amorphous alloys containing 3% Nb and 1% Cu gives rise to a bcc structure with an ultrafine grain size of about 10 nm and the bcc alloys exhibit soft magnetic properties of 1.24 T for \(B_s\) and 100000 at 1 kHz for \(\mu_r\). In addition to the melt-spun Fe–Si–B–Nb–Cu alloys, it has been reported \(^{13(13)}\) that Fe–Zr and Fe–Hf thin films prepared by vapour deposition consist of a bcc supersaturated solution with ultrafine grain sizes of 10 to 20 nm and exhibit a high permeability of 1800 at 1 MHz as well as a small magnetostriction of \(1 \times 10^{-4}\).

On the basis of the above-described knowledge of soft magnetic materials consisting of amorphous or

---

* Institute for Materials Research, Tohoku University, Sendai 980, Japan.
† On leave from Research and Development, Alps Electric Co. Ltd., Nagaoka 940, Japan.
nanocrystalline structures, the present authors have recently carried out a systematic study on the development of new soft magnetic materials in Fe–Zr–B and Fe–Hf–B systems because of an expectation of obtaining B, higher than 1.5 T. As a result, it has been reported in a previous short paper\(^{(10)}\) that the crystallization of Fe–Zr–B and Fe–Hf–B amorphous alloys causes a super-saturated bcc phase with an ultrafine grain size less than 20 nm and the bcc alloys exhibit novel soft magnetic characteristics of 1.5 to 1.7 T for B, and 10000 to 18000 at 1 kHz for \(\mu_r\). The addition of small amounts of metallic elements to Fe–Zr–B and Fe–Hf–B alloys is expected to cause further improved soft magnetic properties. The purpose of this paper is to present the microstructures and magnetic properties of Fe–Zr–B and Fe–Zr–B–M (M=transition metal) alloys and to clarify the compositional effect on them.

II. Experimental Procedure

Alloy ingots in Fe–Zr–B ternary, Fe–Zr–B–Cu quaternary and Fe–Zr–B–Cu–M (M=Ti, Hf, V, Nb, Ta, Cr, Mo or W) and Fe–Zr–B–Nb–X (X=Ni, Pd, Pt or Au) pentad systems were produced by arc melting mixtures of pure Fe, Zr, Cu, M and X metals and pure B crystal in an argon atmosphere. The subsricts are assumed to be those of the unalloyed pure elements since the difference between nominal and chemically analyzed compositions was less than 0.8 mass% for Zr and 0.1 mass% for B. Rapidly solidified ribbons with a cross section of about 0.02 × 1 mm were produced in an argon atmosphere by a single-roller melt spinning method in which the copper roller with a diameter of about 200 mm is rotated at a constant circumferential speed of 42 m/s. The ejection pressure of the molten alloy was also controlled in the range of 90 to 110 kPa in order to obtain a ribbon sample with the constant cross section. The as-quenched samples were subjected to heating for 3.6 ks at various temperatures ranging from 573 to 973 K inside a vaccum-sealed quartz tube, followed by water quenching. As-quenched and annealed structures were examined by X-ray diffractometry using Cu \(K_\alpha\) radiation and transmission electron microscopy (TEM). The decomposition behavior upon continuous heating at a rate of 0.17 K/s was also examined by differential scanning calorimetry (DSC), differential thermal analysis (DTA) and X-ray diffractometry. Magnetization under an applied field of 800 kA/m (\(B_{sat}\)) was measured in the temperature range of room temperature to 1073 K at a heating rate of 0.083 K/s with a vibrating sample magnetometer. Coercive force (\(H_c\)) under 800 A/m and effective permeability in the frequency range of 1 to 10\(^4\) kHz under 0.8 A/m were evaluated with a DC B–H loop tracer and a vector impedance analyzer, respectively. In addition, magnetostriction was measured in an applied field up to 8 kA/m (100 Oe) by an optical cantilever method.

III. Results

1. Microstructure of the crystallized alloys

Figure 1 shows the DTA curve of an amorphous Fe\(_{89}\)Zr\(_{10}\)B\(_2\) alloy. An exothermic peak with high intensity is seen in the range of 769 to 800 K, indicating that the crystallization takes place in the temperature range. In addition, another exothermic peak with low intensity is seen in the high temperature range of 1014 to 1040 K. In order to clarify the structural change corresponding to the two exothermic peaks, X-ray diffractometry analysis was made for the samples heated up to 965, 1050 and 1100 K at a heating rate of 0.17 K/s which is the same as that for the DTA measurement. Figure 2 shows the X-ray diffraction patterns of the Fe\(_{89}\)Zr\(_{10}\)B\(_2\) samples in the as-quenched and heated states. The as-quenched sample consists only of a halo peak revealing the formation of an amorphous phase. The sample heated up to 965 K corresponding to the temperature just below the onset temperature of the second exothermic peak shows diffraction peaks consisting only of a bcc structure with a lattice parameter of 0.2871 nm and no broad peaks due to an amorphous structure are seen. The sample heated up to 1050 K just above the second exothermic peak is composed of a mixed structure of \(\alpha\)-Fe, hexagonal(C36) or cubic(C15) Fe\(_7\)Zr and cubic Fe\(_7\)Zr\(_2\)\(^{(15)}\) and the further increase of heating temperature to 1100 K causes a progress of the replacement of Fe\(_7\)Zr by Fe\(_7\)Zr. No appreciable peaks of Fe\(_7\)B and Fe\(_7\)B are observed in the entire heating temperature range and there is no appreciable solubility of B into \(\alpha\)-Fe in an equilibrium state\(^{(15)}\). Accordingly, the small amount of B seems to have been dissolved into the Fe\(_7\)Zr and Fe\(_7\)Zr phases. Thus, the low- and high-temperature exothermic peaks are due to the structural changes from amorphous to bcc phases and from bcc to \(\alpha\)-Fe + cubic Fe\(_7\)Zr (B) + cubic Fe\(_7\)Zr (B) phases, respectively. In the temperature range above the high-temperature peak, the transition of Fe\(_7\)Zr (B) to Fe\(_7\)Zr (B) proceeds gradually, indicating that the equilibrium structure consists of \(\alpha\)-Fe and Fe\(_7\)Zr (B) phases. It should be

![Figure 1](image-url)  
**Fig. 1** Differential thermal analytical (DTA) curve of an amorphous Fe\(_{89}\)Zr\(_{10}\)B\(_2\) alloy.
noted that the mostly single bcc phase is obtained in the wide temperature interval of 200 K between the first and the second exothermic peaks.

The annealing temperature range leading to the mostly single bcc phase in the isochronal annealing for 3.6 ks was also examined for the Fe96Zr4B3 amorphous alloy, because of an engineering importance of the annealing treatment. Figure 3 shows the change of the X-ray diffraction pattern with annealing temperature ($T_a$). The transition of amorphous to bcc phases begins to occur at 673 K and is almost completed at 723 K and the bcc phase remains unchanged in the wide temperature range of 723 to 950 K. The further increase of $T_a$ results in a mixed structure of $\alpha$-Fe and Fe$_9$(Zr$_3$, B). The lattice parameter ($a_0$) of the bcc phase is measured to be 0.2876 nm at 723 K and 0.2870 nm at 923 K and there is a tendency for the $a_0$ to decrease with increasing $T_a$. These $a_0$ values are slightly larger than that (0.28664 nm) for pure $\alpha$-Fe, indicating that the bcc phase contains the solute elements. The $a_0$ value in nonequilibrium bcc Fe–Zr binary alloys produced by vapor deposition or mechanical alloying has been examined as a function of Zr content in the range below 10 at% Zr[11]. The previous data indicate that the $a_0$ value at 7 at% Zr is about 0.2884 nm which is considerably larger than that (0.2876 nm at 723 K) of the bcc Fe$_9$(Zr$_3$, B) alloy. Furthermore, in the series of studies on the effect of B on the microstructure and mechanical properties of Fe–B–M (M = V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni or Cu) ternary alloys, it has been shown[20] that the dissolution of B into the bcc phase results in a decrease of $a_0$ value in all the alloy systems and the decrease of the $a_0$ value per one atomic percent is approximated to be 0.0002 to 0.0003 nm. Accordingly, the smaller $a_0$ value of the present bcc Fe$_9$Zr$_3$B$_3$ alloy in comparison with that for the bcc Fe$_9$Zr$_3$ alloy seems to originate from the reduction of the $a_0$ value by the dissolution of B. It is thus concluded that the mostly single bcc phase is formed in a wide temperature range of 720 to 950 K in the simple Fe–Zr–B ternary system, being different from the previous result[12,13] for amorphous Fe–Si–B–Nb–Cu alloys that the simultaneous addition of Nb and Cu elements is essential for the formation of the bcc phase at a wide temperature interval.

2. Change in the magnetic properties upon crystallization

Figure 4 shows the changes in the magnetization at an applied field of 800 kA/m ($B_{800}$) and the effective permeability ($\mu_e$) at 1 kHz and 0.8 A/m as a function of $T_a$ for the amorphous Fe$_9$Zr$_3$B$_3$ alloy. As shown in Fig. 4(a), although the $B_{800}$ is as small as 0.2 T in the $T_a$ range below 673 K, it increases sharply to 1.2 T in the narrow range of 673 to 723 K, followed by a gradual increase to 1.70 T in the range of 723 to 923 K. From the comparison of Fig. 4(a) with Fig. 3, one can notice that the temperature range, in which the $B_{800}$ increases rapidly, agrees
Fig. 4 Changes in the magnetization in an applied field of 800 kA/m ($B_{app}$) and the permeability at 1 kHz and 0.8 A/m ($\mu_s$) as a function of annealing temperature ($T_a$) for 3.6 ks for an amorphous Fe$_x$Zr$_y$B$_z$ alloy.

with that where the amorphous phase changes into the bcc phase. Judging from the composition dependence of $T_a$ in amorphous Fe–Zr–B alloys, the $T_a$ value of the Fe$_x$Zr$_y$B$_z$ amorphous alloy seems to lie in the vicinity of room temperature. Accordingly, the rapid increase of $B_{app}$ is presumably due to the structural change of the amorphous phase with a low $T_a$ value resulting from the Invar effect to the ferromagnetic bcc phase with a much higher $T_a$ value. The continuous increase of $B_{app}$ in the $T_a$ range above 723 K suggests that an amorphous phase remains in the temperature range above 723 K. As shown in Fig. 4 (b), the $\mu_s$ value is very low in the amorphous state in the $T_a$ range below 673 K, but it begins to increase at 723 K because of the onset of precipitation of the bcc phase, followed by a rapid increase of $\mu_s$ at 773 K resulting from a structural change from amorphous to bcc phases. The highest $\mu_s$ value is 14000 at $T_a=923$ K and the further increase of $T_a$ to 973 K gives rise to a drastic decrease of $\mu_s$ to 190 because of the structural decomposition to $\alpha$-Fe + Fe$_3$(Zr, B) phases.

In order to clarify the reason for the change of the $\mu_s$ value with $T_a$, the annealed structure was examined by TEM. As exemplified for the Fe$_x$Zr$_y$B$_z$ amorphous alloy annealed for 3.6 ks at 923 K in Fig. 5, the samples exhibiting high $\mu_s$ values above 10000 consist of a bcc structure with a nanoscale grain size of 17 nm. Accordingly, it is presumed that the excellent soft magnetic characteristics for the bcc Fe$_x$Zr$_y$B$_z$ alloy are due to the reduction of apparent anisotropy through the suppression of the magnetocrystalline anisotropy caused by the refinement of grain size. In addition, the grain size of the bcc phase is much smaller than the size of the magnetic domain wall and hence the present bcc alloy can be regarded not to include structural inhomogeneity which hinders the movement of magnetic domain wall, leading to the good soft magnetic properties.

The soft magnetic properties appear to be dependent on both the grain size of the bcc phase and the solution amount of solute elements. In order to clarify the dependence, the lattice spacing of $(110)_{bcc}$ and the grain size determined from the half width of the $(110)_{bcc}$ reflection peak were plotted as a function of $T_a$ in Fig. 6. Since the bcc phase precipitates gradually during annealing for 3.6 ks and hence the magnitude of the internal stress in the bcc phase is thought to be rather low, the Sherrer’s equation$^{(21)}$ was used to evaluate the grain size of the bcc phase. The lattice spacing at $T_a=723$ K is 0.4% larger than that of pure $\alpha$-Fe and approaches that of $\alpha$-Fe with increasing $T_a$, indicating that the solution amount of the solute elements in the bcc phase decreases with increasing $T_a$. The grain size of the bcc phase is 15 to 18 nm in the $T_a$ range of 723 to 923 K, increases rapidly at $T_a$ higher than 923 K and reaches as large as 50 nm at 973 K. Accordingly, the decrease of $\mu_s$ in the $T_a$ range of 923 to 973 K shown in Fig. 2(b) is also thought to originate from the rapid grain growth of the bcc phase, in addition to the precipitation of Fe$_3$(Zr, B).
3. Compositional effect on the microstructure and magnetic properties in the bcc Fe–Zr–B alloys

Figure 7 shows the compositional dependences of $B_{200}$ and $\mu_e$ at 1 kHz for Fe–Zr–B alloys subjected to annealing for 3.6 ks at 873 K, along with the phase field in the melt-spun state. The amorphous single phase is obtained in a wide composition range of 0 to 15% Zr and 0 to 25% B, being nearly the same as the glass-formation range reported by Ohnuma et al. The amorphous alloys in the range of 0 to 11% Zr and 0 to 20% B have good ductility which is shown by a 180 degree bending without fracture. In comparison between the $\mu_e$ in the annealed state and the melt-spun structure, the $\mu_e$ value is higher than 1000 in the range of 5 to 7% Zr and 2 to 6% B, where an amorphous single phase and coexistent amorphous and bcc phases are obtained. The $\mu_e$ value decreases significantly both in the lower solute content range where coexistent bcc and compound phases are formed and in the higher solute content range where an amorphous phase with higher thermal stability is obtained. This result indicates that the achievement of the high $\mu_e$ values does not always require the formation of an amorphous single phase in an as-quenched state. The $B_{200}$ increases with increasing Fe content and reaches as high as 1.7 T in the vicinity of 90% Fe. It is thus found that the bcc Fe–Zr–B alloys ranging from 5 to 7% Zr and 2 to 6% B exhibit novel soft magnetic properties of B, ranging from 1.6 to 1.7 T and $\mu_e$ ranging from 10000 to 15000.

In addition, the effect of B content on the microstructure and soft magnetic properties in a crystallized state was examined for Fe$_{90-x}$Zr$_x$B$_y$ alloys. Figure 8 shows the bright-field electron micrographs of the Fe$_{91}$Zr$_{13}$B$_4$, Fe$_{92}$Zr$_{13}$B$_3$ and Fe$_{93}$Zr$_{13}$B$_2$ alloys annealed for 3.6 ks at 873 K. It is seen that the increase of B content causes an increase of inhomogeneity in the distribution of grain size of the bcc phase. The increase of the microstructural inhomogeneity resulted in a significant decrease in $\mu_e$ from the values higher than 10000 at 2 and 4% B to 3000 at 6% B, as shown in Fig. 7. Accordingly, the soft magnetic properties may be improved through an increase of microstructural homogeneity in the bcc phase. The formation of the bcc phase with a high degree of microstructural homogeneity was attempted for Fe–Zr–B–Cu quaternary alloys containing less than 5 at% Cu, on the basis of the previously obtained result that the addition of the Cu, Au and Ag elements which are immiscible to Fe element brings about a homogeneous precipitation of ultrafine bcc particles embedded in an amorphous matrix in the Fe–P–C and Fe–Si–B systems.

4. Improvement of soft magnetic properties by the addition of Cu

The addition of Cu up to 3 at% for Fe$_{97-x}$Zr$_x$B$_y$Cu$_z$ alloys was found to be effective for the extension of the
temperature range for formation of the bcc phase as well as the refinement of the grain size. As an example, Fig. 9 shows the DTA curves of Fe$_{97}$Zr$_{3}$B$_{6}$ and Fe$_{96}$Zr$_{3}$B$_{6}$Cu$_{1}$ amorphous alloys. Similarly to the result (Fig. 1) for the Fe$_{97}$Zr$_{3}$B$_{6}$ amorphous alloy, the low- and high-temperature exothermic peaks which seem to correspond to the precipitation of the bcc and the compound, respectively, are seen on the DTA curves of both alloys. Furthermore, the onset temperature of the first (low-temperature) exothermic peak shifts to a lower-temperature side by the addition of Cu, indicating that the addition of Cu results in an extension of the bcc phase field.

Figure 10(a) and (b) show the changes in $B_{\text{m0}}$ and $\mu_r$ at 1 kHz of the amorphous Fe$_{97-x}$Zr$_{3}$B$_{6}$Cu$_{x}$ ($x=0$ and 1%) alloys as a function of $T_s$. The $B_{\text{m0}}$ of both alloys increases rapidly from 0.7 to 1.5 T in the $T_s$ range of 723 to 773 K, because of the phase transition of an amorphous phase to coexisting bcc and amorphous phases. The $\mu_r$ value of the Fe$_{97}$Zr$_{3}$B$_{6}$ alloy without Cu element exhibits a maximum value of 8200 in the $T_s$ range below 723 K probably because of an annihilation of quenching-induced internal stress in the amorphous phase and decreases significantly to about 3000 in the crystallized state. On the other hand, the $\mu_r$ value of the Cu-containing alloy increases remarkably upon crystallization in the $T_s$ range of 723 to 773 K and reaches as high as 18000 in the crystallized state after annealing for 3.6 ks at 823 K, indicating that the permeability in the crystallized state is remarkably improved by the addition of 1 at% Cu. In order to clarify the reason for the remarkable improvement of the $\mu_r$ value for the Cu-containing alloy, the microstructure of the amorphous Fe$_{97}$Zr$_{3}$B$_{6}$ and Fe$_{96}$Zr$_{3}$B$_{6}$Cu$_{1}$ alloys annealed for 3.6 ks at 873 K was examined by TEM. As shown in Fig. 11(a) and (b), the distribution of grain size of bcc phase in the Fe–Zr–B–Cu

![Fig. 9 DTA curves of amorphous Fe$_{97}$Zr$_{3}$B$_{6}$ and Fe$_{96}$Zr$_{3}$B$_{6}$Cu$_{1}$ alloys.](image)

![Fig. 10 Changes in the $B_{\text{m0}}$ and $\mu_r$ at 1 kHz as a function of $T_s$ for 3.6 ks for amorphous Fe$_{97}$Zr$_{3}$B$_{6}$ and Fe$_{96}$Zr$_{3}$B$_{6}$Cu$_{1}$ alloys.](image)

![Fig. 11 Bright- and dark-field electron micrographs of (a) Fe$_{97}$Zr$_{3}$B$_{6}$ and (b) Fe$_{96}$Zr$_{3}$B$_{6}$Cu$_{1}$ alloys annealed for 3.6 ks at 873 K. The dark-field micrographs were taken from the (110) reflection ring of the bcc phase.](image)
high saturation magnetization and soft magnetic properties of bcc Fe-Zr-B and Fe-Zr-B-M alloys

Fig. 12 Change in the $\mu_e$ value at 1 kHz as a function of Cu content for amorphous Fe$_{27-}$Zr$_8$B$_{4}$Cu$_{5}$ alloys annealed for 3.6 ks at 873 K.

Alloy is more homogeneous and the grain size is much finer, as compared with that in the Fe-Zr-B alloy with the same B content. The structural change appears to cause an improvement of soft magnetic properties. The magnetostriction was also measured to be positive and as small as about $9 \times 10^{-7}$ for the bcc Fe$_{27}$Zr$_8$B$_{4}$Cu$_{5}$ sample prepared by annealing for 3.6 ks at 873 K, suggesting that the achievement of the high $\mu_e$ value is related to the small magnetostriction. Considering the previous data that the sputtered Fe-Zr film with fine bcc grain structure exhibits a small magnetostriction of about $1 \times 10^{-3}$, the small magnetostriction for the Cu-containing alloy with bcc structure seems to originate from the bcc Fe-Zr base phase. In addition, Fig. 12 shows the relation between $\mu_e$ at 1 kHz and Cu content for the bcc Fe$_{27-}$Zr$_8$B$_{4}$Cu$_{5}$ alloys obtained by annealing the amorphous phase for 3.6 ks at 873 K. Further increase of the $\mu_e$ value is not achieved by the addition of Cu more than 1 at%. Accordingly, the subsequent study on the compositional dependence of magnetic properties for the Cu-containing alloys was carried out in Fe$_{27-}$Zr$_8$B$_{4}$Cu$_{5}$ quaternary alloys.

Figure 13 shows the compositional dependences of $B_{500}$ and $\mu_e$ at 1 kHz of amorphous Fe$_{27-}$Zr$_8$B$_{4}$Cu$_{5}$ alloys annealed for 3.6 ks at 873 K, along with the data of the glass formation range in the quaternary system. There is no distinct difference in the glass formation range between Fe-Zr-B ternary and Fe-Zr-B-1%Cu quaternary alloys nor appreciable degradation in the bending ductility of the amorphous alloy by the addition of 1% Cu. Furthermore, the high $\mu_e$ values above 10000 were observed in the compositional range of 5 to 8% Zr and 2 to 12% B where an amorphous single phase and coexistent amorphous and bcc phases were obtained. Judging from the result that the high $\mu_e$ values above 10000 are obtained in the range of 5 to 7% Zr and 2 to 6% B for Fe-Zr-B ternary alloys, the addition of 1 at% Cu is concluded to cause a remarkable extension of the composition range in which the high $\mu_e$ values above 10000 are obtained.

In the Fe-Zr-B-1%Cu quaternary alloys, good soft magnetic properties were obtained in the high B concentration range with higher glass-forming ability. Furthermore, there is a high possibility for the high B content alloys that an amorphous phase is formed even in the replacement of Zr by the other transition elements leading to a decrease of the glass-forming ability. In the subsequent study, we examined the glass formation range in rapidly solidified Fe$_{27-}$Zr$_8$B$_{4}$Cu$_{5}$M, (M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo or W) alloys and magnetic properties of their crystallization-induced bcc phase alloys. Figure 14 shows the as-quenched phase field in the Fe-Zr-B-Cu-M pentad alloys containing 1 to 5% M. The melt-spinning condition and the resulting sample thickness are just the same as those for Fe-Zr-B ternary and Fe-Zr-B-Cu quaternary alloys which were described in section II. The glass-formation range is the widest for the Hf-
containing alloys and decreases in the order of Zr > Nb > Ti = Ta = Mo = W > V = Cr. Thus, the glass formation is easier for the IV- and V-group transition elements belonging to the fifth and sixth periodicities in the periodic table. Figure 15 shows the change in the $\mu_e$ value at 1 kHz as a function of M content for the Fe-Zr-B-Cu-M alloys obtained by annealing of the as-quenched phase for 3.6 ks at 873 or 923 K. The $\mu_e$ value is the lowest for V and Cr elements which require a larger amount of addition for formation of an amorphous phase, while the alloys containing Zr, Hf and Nb elements leading to the formation of an amorphous phase even by a smaller amount of addition exhibit higher $\mu_e$ values. Thus, the high $\mu_e$ values ranging from 11000 to 18000 are obtained in the vicinity of 3%M (Zr + M = 7%) for the Fe-Zr-B-Cu-M (M = Zr, Hf or Nb) alloys.

In addition, the replacement of Cu in the bcc Fe<sub>66</sub>Zr<sub>14</sub>Nb<sub>6</sub>B<sub>4</sub>Cu<sub>4</sub> alloy exhibiting a high $\mu_e$ of 18000 by other transition metals of Ni, Pd, Pt or Au was tried with the aim of obtaining a higher $\mu_e$ value. Table 1 summarizes the magnetic properties of $B_{BOE}$, $\mu_e$ at 1 kHz and coercivity ($H_C$) for the Fe<sub>66</sub>Zr<sub>14</sub>Nb<sub>6</sub>B<sub>4</sub>Cu<sub>4</sub>X (X = Ni, Pd, Pt or Au) alloys obtained by annealing for 3.6 ks at 873 or 923 K and the onset temperature of crystallization ($T_C$) for the as-quenched amorphous phase, along with the data of the bcc Fe-Zr-Nb-B<sub>4</sub>Cu<sub>4</sub> alloys. All Fe-Zr-Nb-B-Cu alloys exhibit $\mu_e$ values above 9300, being much higher than that (3500) for the Fe-Zr-Nb-B alloys without the Cu or X element. Although the reason for the improvement of soft magnetic properties is not clear, it may be due to an increase of the formation tendency of the bcc phase through the degradation of thermal stability in the amorphous structure by the dissolution of Cu and X elements.

Figure 16 shows the frequency dependence of $\mu_e$ for the bcc Fe<sub>66</sub>Zr<sub>14</sub>Nb<sub>6</sub>B<sub>4</sub>Cu<sub>4</sub> alloy with the highest $B$, value and the bcc Fe<sub>66</sub>Zr<sub>14</sub>Nb<sub>6</sub>B<sub>4</sub>Cu<sub>4</sub> alloy with the highest $\mu_e$ value at 1 kHz, along with that for a Co<sub>90</sub>Fe<sub>9</sub>Si<sub>12</sub>Mo<sub>2</sub> amorphous alloy exhibiting high $\mu_e$ values combined with nearly zero magnetostriiction. The $\mu_e$ values of the Fe-Zr-B and Fe-Zr-B-Cu alloys are 14000 and 20000, respectively, at 1 kHz and decreases gradually to 7000 and 10000 at 100 kHz and significantly in the higher frequency range. However, in comparison with the $\mu_e$ values for the amorphous Co-Fe-Si-B alloy, no distinct degradation in the $\mu_e$ value for the bcc Fe-Zr-B-Cu alloy is seen in the wide range of 1 to 10<sup>4</sup> kHz and the $\mu_e$ value at a high frequency of 1 MHz for the Fe-Zr-B-Cu alloy keeps a high level of 1800 which is nearly the same as that (1900) for the Co-Fe-Si-B alloy. Besides, typical magnetic properties for the Fe-Zr-B base alloys subjected to optimum annealing treatments are summarized in Table 2, where the data of some typical soft magnetic materials and Fe-Si-B-Nb-Cu alloys with nanoscale bcc structure are also shown.

Table 1: The permeability at 1 kHz and 0.8 A/m ($\mu_e$) and coercivity ($H_C$) for bcc Fe<sub>66</sub>Zr<sub>14</sub>Nb<sub>6</sub>B<sub>4</sub>Cu<sub>4</sub> (M = Ni, Pd, Pt, Au) alloys obtained by annealing the amorphous phase for 3.6 ks at 873 and 923 K. The $T_C$ value of their amorphous alloys is also shown for reference.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_C$ (K)</th>
<th>$T_m$ (K)</th>
<th>$B_r$ (T)</th>
<th>$\mu_e$ at 1 kHz</th>
<th>$H_C$ (A/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;Nb&lt;sub&gt;6&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>923</td>
<td>802</td>
<td>1.50</td>
<td>3500</td>
<td>15.9</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;Nb&lt;sub&gt;6&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Ni&lt;sub&gt;2&lt;/sub&gt;</td>
<td>923</td>
<td>757</td>
<td>1.54</td>
<td>18000</td>
<td>3.7</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;Nb&lt;sub&gt;6&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Pd&lt;sub&gt;2&lt;/sub&gt;</td>
<td>923</td>
<td>778</td>
<td>1.56</td>
<td>9300</td>
<td>5.7</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;Nb&lt;sub&gt;6&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Pt&lt;sub&gt;2&lt;/sub&gt;</td>
<td>923</td>
<td>771</td>
<td>1.54</td>
<td>9800</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;Nb&lt;sub&gt;6&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Au&lt;sub&gt;2&lt;/sub&gt;</td>
<td>873</td>
<td>782</td>
<td>1.47</td>
<td>10000</td>
<td>7.7</td>
</tr>
</tbody>
</table>

**Table 2: Magnetic properties ($B$, $\mu_e$ and $H_C$) for the Fe-Zr-B and Fe-Zr-B-Cu alloys and other soft magnetic materials.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Structure</th>
<th>$t$ ($\mu$m)</th>
<th>$B_r$ (T)</th>
<th>$\mu_e$ at 1 kHz</th>
<th>$H_C$ (A/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>bcc</td>
<td>18</td>
<td>1.70</td>
<td>11000</td>
<td>7.2</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Mn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>bcc</td>
<td>19</td>
<td>1.65</td>
<td>15000</td>
<td>7.4</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Ni&lt;sub&gt;2&lt;/sub&gt;</td>
<td>bcc</td>
<td>18</td>
<td>1.65</td>
<td>17000</td>
<td>2.4</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66&lt;/sub&gt;Zr&lt;sub&gt;14&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;Ni&lt;sub&gt;2&lt;/sub&gt;Mn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>bcc</td>
<td>17</td>
<td>1.55</td>
<td>20000</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe-6.5mass%Si</td>
<td>Ordered bcc</td>
<td>300</td>
<td>1.80</td>
<td>2400</td>
<td>9.6</td>
</tr>
<tr>
<td>Fe-Si-B*</td>
<td>Amorphous</td>
<td>20</td>
<td>1.41</td>
<td>6000**</td>
<td>6.9</td>
</tr>
<tr>
<td>Co-Fe-Si-B*</td>
<td>Amorphous</td>
<td>18</td>
<td>0.53</td>
<td>80000**</td>
<td>0.32</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;57&lt;/sub&gt;Si&lt;sub&gt;15&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Nb&lt;sub&gt;2&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;*</td>
<td>bcc</td>
<td>18</td>
<td>1.24</td>
<td>100000**</td>
<td>0.53</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;57&lt;/sub&gt;Si&lt;sub&gt;15&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;Nb&lt;sub&gt;2&lt;/sub&gt;Cu&lt;sub&gt;4&lt;/sub&gt;*</td>
<td>bcc</td>
<td>18</td>
<td>1.55</td>
<td>90000**</td>
<td>12.8</td>
</tr>
</tbody>
</table>

*Ref. (24) **$H_m=0.4$ A·m⁻¹
for comparison. The $B_r$ values of the bcc Fe-Zr-B and Fe-Zr-B-Cu alloys are considerably higher than those of bcc Fe-Si-B-Nb-Cu alloys and amorphous Co-based alloys and the $\mu_c$ at 1 kHz is also much higher than those of Fe-6.5 mass% Si and Fe-based amorphous alloys. Furthermore, the alloy components in the bcc phase and hence the origin for the appearance of the small magnetostriiction are also different between the Fe-Zr-B alloys and the Fe-Si-B-Nb-Cu alloys, because the simultaneous dissolution of Nb and Cu elements is essential to cause the small magnetostriiction for the latter alloys. It is therefore said that the soft magnetic properties of the bcc Fe-Zr-B and Fe-Zr-B-Cu alloys with nanoscale grain sizes are different from those of the other soft magnetic alloys and hence the newly developed Fe-Zr-B base alloys can be classified into a new soft magnetic material and are expected to be particularly used as a core material in electric transformer which requires a high $B_r$ value.

IV. Discussion

The reason why the bcc Fe-Zr-B alloys obtained by crystallization of the amorphous phase exhibit good soft magnetic properties is presumably due to the formation of homogeneous bcc structure with nanoscale grain sizes ranging from 10 to 20 nm. Accordingly, it is important to clarify the mechanism for the formation of the bcc phase with nanoscale grain sizes in the simple Fe-Zr-B system without Cu and Nb elements. The formation seems to have the necessity of the following two factors; (1) the homogeneous nucleation of nanoscale bcc grains at an incipient stage of crystallization, and (2) the difficulty of grain growth of the nanoscale bcc phase.

As shown in Fig. 7, the high $\mu_c$ values in Fe-Zr-B ternary alloys are obtained in the low solute concentration range along the boundary between an amorphous single phase and coexisting amorphous and bcc phases. The compositional limitation is probably because the compositional range in which the bcc phase precipitates as a primary crystalline phase is limited to the range of 5 to 7% Zr and 1 to 8% B in the Fe-Zr-B ternary system. The addition of Cu results in an extension of the composition and temperature ranges in which the bcc phase appears as a primary crystalline phase. Such a significant effect caused by the addition of Cu is thought to originate from the following three reasons. That is, (1) the increase in the ease of nucleation and the number of nucleation sites for the bcc phase resulting from the increase of the degree of the compositional fluctuation in the Fe-base amorphous structure containing the immiscible Cu element, (2) the increase in the difficulty of grain growth of the bcc phase resulting from the lowering of the precipitation temperature of the bcc phase, and (3) the increase of the ease of formation of the bcc phase due to the difficulty of formation of the Fe$_2$(Zr, B) compound resulting from the dissolution of additional B element. The enhancement of compositional fluctuation (or structural inhomogeneity) in the amorphous phase and the ease of precipitation of fine bcc grains from the amorphous phase for the Cu-containing alloys have been reported in Fe-Si-B-Cu$^{(23)}$ and Fe-Si-B-Nb-Cu$^{(25)}$ alloys.

As shown in Fig. 3, no distinct broad peak revealing the existence of an amorphous phase is seen in the X-ray diffraction pattern obtained from the amorphous Fe$_8$Zr$_5$B$_2$ alloy annealed for 3.6 ks at 723 K. However, the $B_{\text{req}}$ value shown in Fig. 4(a) increases gradually even in the temperature range above 723 K, indicating that the amorphous phase remains at temperatures above 723 K. In addition, from the change in the lattice spacing of (110)$_\text{bcc}$ with $T_s$ shown in Fig. 6(a), the solute content in the bcc phase seems to decrease with increasing $T_s$, leading to an increase of the solute content in the remaining amorphous phase. Considering the previous result$^{(10)}$ that the $T_s$ value of the Fe-Zr-B amorphous alloys increases significantly with increasing solute content and exceeds 1000 K in the Zr concentration range above 11 at.%, the remaining amorphous phase with high solute contents seems to exist up to rather high temperatures and to act as a resistant phase for the suppression of grain growth of the bcc phase. The microstructural data shown in Fig. 6 indicate that the grain size of the bcc phase remains almost constant in the temperature range below 923 K and increases rapidly in the range of 923 to 973 K where the remaining amorphous phase disappears completely and the Fe$_2$(Zr, B) begins to precipitate. The rapid increase in the grain size in the limited temperature range is presumably due to the phase transition of the supersaturated bcc solution to α-Fe + Fe$_2$(Zr, B) + Fe$_3$(Zr, B). It is thus presumed that the amorphous thin layer exists along the grain boundaries of the bcc phase and acts as an effective resistant barrier against the grain growth of the bcc phase.

Finally, the volume fraction of the amorphous phase which appears to exist along the grain boundary of the bcc phase was evaluated from the change of the magnetization ($\sigma$) with heating temperature. Figure 17 shows the magnetization-temperature relation for the amorphous Fe$_{56}$Zr$_5$B$_{19}$Cu$_{3}$ alloy, along with the data of the onset temperatures ($T_{\text{c1}}$ and $T_{\text{c2}}$) of the first and the second exothermic peaks on the DTA curve. As the

![Fig. 17 Change in the magnetization (\(\sigma\)) of an amorphous Fe$_{56}$Zr$_5$B$_{19}$Cu$_{3}$ alloy upon continuous heating at a rate of 0.17 K/s. The $T_{\text{c1}}$ and $T_{\text{c2}}$ represent the onset temperatures of the first and the second exothermic peaks on the DTA curve measured at the same heating rate.](image-url)
temperature increases, the magnetization decreases remarkably and approaches nearly zero value at 390 K which is Curie temperature for the amorphous alloy. The further rise of heating temperature results in a significant increase of $\sigma$ in the vicinity of $T_c$, because of the precipitation of the bcc phase from the amorphous matrix. It is notable that the discontinuous increase of $\sigma$ is also recognized at $T_z$. The increase of $\sigma$ at $T_z$ is presumably because the remaining amorphous phase translates to $\alpha$-Fe + Fe$_3$(Zr, B) + Fe$_6$(Zr, B) and the $\alpha$-Fe has the $T_c$ value higher than $T_z$. In the assumption that the increase of $\sigma$ at $T_z$ is due to the $\alpha$-Fe resulting from the decomposition of the remaining amorphous phase to $\alpha$-Fe + Fe$_3$(Zr, B) + Fe$_6$(Zr, B), the volume fraction of the amorphous phase which is thought to remain along the grain boundary of the bcc phase is evaluated to be 20 to 30% for the Fe$_{86}$Zr$_{14}$B$_8$Cu alloy.

V. Summary

The annealing-induced changes in microstructure and soft magnetic properties were examined for Fe–Zr–B amorphous alloys, with the aim of developing a new soft magnetic material combined with a high saturation magnetization. In addition, the effect of additional transition metals (M and X) on the crystallized microstructure and soft magnetic properties was also investigated for Fe–Zr–B–Cu, Fe–Zr–B–Cu–M (M = Ti, Hf, V, Nb, Ta, Cr, Mo, or W) and Fe–Zr–B–N–X (X = Ni, Pd, Pt or Au) amorphous alloys. The results obtained are summarized as follows.

(1) The crystallized structure obtained by annealing of amorphous Fe–Zr–B ternary alloys for 3.6 ks at 923 K consists of a bcc phase with a nanoscale grain size of about 20 nm in the range of 5 to 7%Zr and 1 to 8%B. The bcc Fe$_{90}$Zr$_{10}$B alloy exhibits novel soft magnetic properties of 1.7 T for $B$, and 14000 for $\mu_0$ at 1 kHz.

(2) The increase of B content from 2 to 6% in Fe–Zr–B amorphous alloys gives rise to a decrease of structural homogeneity in the bcc phase and the $\mu_0$ value decreases from 14000 to 3000.

(3) The addition of 1 to 3%Cu to the Fe–Zr–B alloys ranging from 5 to 7%Zr and 2 to 6%B is very effective for the formation of a homogeneous bcc structure leading to remarkably enhanced $\mu_0$ values. Furthermore, the addition of 1%Cu results in the formation of the bcc phase with a nanoscale grain size of about 10 nm even for the Fe–Zr–B alloys with high B contents of 4 to 6%. Accordingly, the compositional range in which the high $\mu_0$ values above 10000 at 1 kHz are obtained is significantly extended in the Cu-containing Fe–Zr–B–Cu alloys.

(4) The partial replacement of Zr in Fe$_{86}$Zr$_{1-x}$B$_x$Cu$_3$M$_y$ by 3%M (M = Hf, Nb or Ta) was also found to bring about the bcc alloys exhibiting high $\mu_0$ values above 10000 at 1 kHz and high $B$, values above 1.5 T. In addition to Cu, the addition of Ni, Pd, Pt and Au elements is also effective for the increase of $\mu_0$ to high values above 10000 for the bcc Fe–Zr–N–B alloys.

(5) The bcc phase with the nanoscale grain sizes remains almost unchanged in the wide temperature range from 750 to 900 K. The rather high thermal stability of the nanoscale bcc structure is presumably because the remaining amorphous thin layer along the grain boundary of the bcc phase has a high thermal stability due to the dissolution of a large amount of solute elements and acts as an effective barrier against the grain growth of the bcc phase.

Acknowledgments

The authors wish to thank Prof. H. Fujimori for generous permission to use equipment for the measurement of magnetic properties and Mr. M. Kikuchi for identifying the microstructures by the TEM technique.

REFERENCES

(17) Binary Alloy Phase Diagrams, ed. by T. B. Massalski, ASM, Ohio (1986).