11 Magnetic Properties of Nanocrystalline Materials

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11.1 Introduction

It was reported in 1976 that an amorphous phase in Pd—Si, Fe—P—C and (Fe, Co, Ni)—Si—B systems is useful as a precursor to prepare a nanocrystalline structure upon crystallization.[¹] For the last two decades, a great effort has been devoted to the development of new types of high-strength or high-function materials utilizing the formation of crystallization-induced nanostructure. In the field of magnetic materials, good hard magnetic properties have been obtained in the crystallized structure of Nd₂Fe₁₄B and amorphous phases obtained from amorphous Fe—Nd—B alloys.[²] In addition for soft magnetic alloys, it has been found that crystallization of Fe—Si—B amorphous alloys containing Nb and Cu causes the formation of a nanoscale bcc structure and that the bcc alloys exhibit good soft magnetic properties with saturation magnetic flux density (Bₛ) of 1.2 to 1.4 T and effective permeability (μₑ) at 1 kHz of 10⁵.[³] These results indicate that crystallization-induced nanostructure is useful in creating hard or soft magnetic properties. Although good soft magnetic properties are obtained for nanoscale bcc Fe₇₃.₅Si₁₃.₅B₉Nb₃Cu₁, the relatively low Fe concentration leads to Bₛ being limited to less than 1.4 T. Hence, the development of a new soft magnetic alloy with high Bₛ (above 1.5 T) and high μₑ (above 10⁵) at 1 kHz has been a strongly desired goal because the simultaneous achievement of both properties enables the extension of application fields to various kinds of power transformers. It has subsequently been reported[⁴] that Fe—C thin films consisting of nanocrystalline bcc and TaC phases obtained by crystallization of a sputtered amorphous phase exhibit good soft magnetic properties (i.e., Bₛ of 1.54 T and μₑ of 5.3
× 10³ at 1 MHz), though the nanostructure cannot be synthesized by the melt spinning technique. We have previously reported that Fe-rich amorphous alloys of 90 at% Fe are formed in Fe—Zr—B and Fe—Hf—B systems by rapid solidification.\(^{[5]}\) If a nanostructure is formed in the Fe-rich alloys subjected to crystallization treatment, the nanostructured alloys are expected to exhibit high \(B_s\) exceeding 1.5 T. Based on this concept, we have examined\(^{[6–7]}\) the possibility of synthesizing a nanocrystalline structure in Fe—M—B (M = Zr, Hf or Nb) alloys and of obtaining good soft magnetic properties and we have succeeded\(^{[8–11]}\) in developing nanocrystalline Fe—Zr—Nb—B—Cu alloys with excellent soft magnetic properties (1.57 T for \(B_s\) and 16 × 10⁴ for \(\mu_e\) at 1 kHz) which had not been obtained before for any kind of soft magnetic material. It has been subsequently found\(^{[12–15]}\) that the Cu-free quaternary Fe\(_{85.5}\)Zr\(_2\)Nb\(_4\)B\(_{8.5}\) alloy exhibits high \(B_s\) of 1.64 T and high \(\mu_e\) of 6.0 × 10⁴ at 1 kHz, simultaneously. Furthermore, the Fe\(_{84.9}\)Nb\(_6\)B\(_8\)P\(_1\)Cu\(_{0.1}\) alloy combines a \(B_s\) of more than 1.6 T with good soft magnetic properties and good productivity has been developed.\(^{[15–17]}\) On the other hand, it has been found\(^{[18, 19]}\) that the dissolution of a large amount of oxygen in the remaining amorphous phase is effective in achieving a drastic increase in electrical resistivity of sputtered Fe—Hf—O and Fe—Zr—O films, leading to the achievement of good high-frequency permeability in the range 1 to 100 MHz. This paper reviews our recent results in the formation of a nanogranular bcc and amorphous structures, the development of excellent soft magnetic material by nanocrystallization in the Fe—Zr—Nb—B—Cu, Fe—Zr—Nb—B, Fe—Nb—B—P—Cu and Fe—Hf—O systems and their engineering applications.

11.2 Fe—M—B (M = Zr, Hf or Nb) Amorphous Alloys and their Crystallization-Induced Nanostructure

Iron-based amorphous alloys have been reported to be formed in a number of alloy systems such as Fe—(B, C, Si, P, Ge),\(^{[20]}\) Fe—(Zr, Hf),\(^{[21]}\) Fe—Re (Re = rare earth metal)\(^{[22]}\) and Fe—(Zr, Hf, Nb, Ta)—B.\(^{[6, 7]}\) If we pay attention to a maximum Fe concentration for formation of an amorphous phase by the melt spinning method, the previous data show that the Fe concentration increases in the order Fe—(Zr, Hf) > Fe—Re > Fe—(Zr, Hf, Nb, Ta)—B > Fe—(B, C, Si, P, Ge). This indicates the possibility that the \(B_s\) values of the resulting nanocrystalline phases also increase in the same order. Hence, the relation between the formation tendency of nanocrystalline structure and soft magnetic properties was systematically
examined for Fe—(Zr, Hf), Fe—Re and Fe—(Zr, Hf, Nb, Ta)—B amorphous ribbons prepared by melt spinning. The crystallized structure of the Fe$_{90}$Zr$_{10}$, Fe$_{90}$Hf$_{10}$ and Fe$_{90}$Nd$_{10}$ amorphous alloys consists of bcc and amorphous phases at the first-stage, and $\alpha$-Fe and compound phases at the second stage, but the grain size of the bcc and $\alpha$-Fe phases are above 40 nm and 80 nm, respectively, which are too large to obtain good soft magnetic properties.\cite{23} Therefore, it is concluded that the binary Fe-based alloys cannot be regarded as an appropriate system leading to the desired nanocrystalline structure, though high $B_s$ above 1.5 T is obtained.

Figure 11.1 summarizes the composition ranges in which an amorphous phase is formed in melt-spun Fe—Zr—B, Fe—Hf—B and Fe—Nb—B alloys containing more than 75 at% Fe and the subsequent crystallized structure consists of a nanoscale bcc-Fe and amorphous structure.\cite{24} The maximum Fe concentration for formation of an amorphous phase is about 92 at% for the Fe—Zr—B and Fe—Hf—B alloys and about 86 at% Fe for the Fe—Nb—B alloy. Besides, it is seen that a nanogranular bcc-Fe phase surrounded by the residual amorphous phase is formed in the Fe-rich concentration range above 86 at% Fe for Fe—Zr—B and Fe—Hf—B alloys. Here, it is important to describe the criteria for formation of nanoscale bcc-Fe and amorphous mixed structure in the limited Fe-rich composition ranges. Figure 11.2 shows differential thermal analysis (DTA) curves of the Fe$_{90}$Zr$_{7}$B$_{3}$ and Fe$_{89}$Hf$_{7}$B$_{4}$ amorphous alloys. Two exothermic peaks are seen on the DTA curves, indicating that the crystallization takes place through two stages. From X-ray diffraction (XRD) analysis and transmission electron microscopic (TEM) observation, the first-stage exothermic reaction is due to the precipitation of bcc-Fe phase and the second exothermic peak results from the precipitation of $\alpha$-Fe and Fe$_2$Zr or Fe$_2$Hf phases from the bcc and remaining amorphous phases. Notice that the temperature interval between the first and second exothermic peaks is as large as 150 K, indicating that the bcc-Fe and amorphous phases have a high metastability. Figure 11.3 shows a bright field electron micrograph and selected-area electron diffraction (SAED) pattern of the Fe$_{90}$Zr$_{7}$B$_{3}$ alloy annealed for 3.6 ks at 923 K, a temperature between the first and second exothermic peaks. The bcc phase has spherical equiaxed grains with a size of about 15 nm and each grain has a random orientation. Furthermore, the diffraction pattern reveals the existence of a residual amorphous phase and the absence of the second crystalline phase. Further heating to a temperature above the second exothermic peak caused the precipitation of $\alpha$-Fe and Fe$_2$Zr phases, accompanied by the complete disappearance of the remaining amorphous phase and significant grain growth of the $\alpha$-Fe phase. Borides of any kind are not observed and hence
Figure 11.1 Compositional dependence of structure for Fe—Zr—B, Fe—Hf—B and Fe—Nb—B alloys in as-quenched and annealed states.
Figure 11.2 Differential thermal analysis (DTA) curves of amorphous Fe$_{90}$Zr$_7$B$_3$ and Fe$_{90}$Hf$_7$B$_4$ alloys.

Figure 11.3 (a) Bright field transmission electron microscopy (TEM) image and (b) selected-area electron diffraction pattern of Fe$_{90}$Zr$_7$B$_3$ alloy annealed at 923 K for 3.6 ks.
the B element is thought to be preferentially dissolved into the Fe$_2$Zr phase because of the similarity of the crystal structure and chemical formula between Fe$_2$Zr and Fe$_2$B. The reason for the high thermal stability of the metastable bcc-Fe and amorphous phases is discussed in Section 11.3 on the basis of high-resolution TEM images, nanobeam electron diffraction and atom-probe field ion microscopic data.

11.3 Soft Magnetic Properties and Structural Analyses of Fe–M–B (M = Zr, Hf or Nb) Nanocrystalline Ternary Alloys

Figure 11.4 shows the composition dependence of as-quenched phase, $B_s$, and $\mu_e$ at 1 kHz for the melt-spun Fe–Zr–B and Fe–Nb–B alloy ribbons subjected to optimum annealing treatments for 3.6 ks at 873 and 923 K. The amorphous phase is formed in the wide composition range up to 92 at% Fe for the Fe–Zr–B alloys and 84 at% Fe for the Fe–Nb–B alloys. The annealed alloys exhibit good soft magnetic properties of high $B_s$ above 1.6 T and high $\mu_e$ exceeding $10^4$ around the composition of 90 at% Fe in the former system and 84 at% Fe in the latter system. It is also seen in Fig. 11.4 that the best soft magnetic properties are obtained at the upper limit of Fe concentration where the amorphous single phase is obtained in the melt-spun state. The good correspondence is because nanoscale bcc structure is obtained only from the amorphous single phase in the Fe-rich composition range. Besides, one can notice that the composition range in which the best soft magnetic properties are obtained for the Fe–Nb–B alloys shifts to the higher B concentration in comparison with that for the Fe–Zr–B alloys. The deviation is due to the extension of the formation range of the nanoscale bcc-Fe structure resulting from a decrease in the precipitation tendency of compounds, reflecting the weaker bonding nature of Nb–Fe and Nb–B pairs as compared with Zr–Fe and Zr–B pairs. Similar data to those for the Fe–Zr–B nanocrystalline alloys have been obtained in Fe–Hf–B system.\textsuperscript{[9,24]} Figure 11.5 shows the changes with annealing temperature ($T_a$) in the structure, $B_s$, $\mu_e$, mean grain size of the bcc phase ($D$) and saturation magnetostriction constant ($\lambda_s$) for the melt-spun Fe$_{90}$Zr$_7$B$_3$, Fe$_{89}$Hf$_7$B$_4$ and Fe$_{84}$Nb$_7$B$_9$ alloys. As $T_a$ increases, the amorphous phase changes to a mostly single bcc phase in the $T_a$ range of 750 to 930 K and $\alpha$-Fe plus compound in the $T_a$ range above 930 K. The $D$ value is as small as 10 to 17 nm and increases rapidly upon the phase transition to $\alpha$-Fe plus compound. The $B_s$ and $\mu_e$ have nearly zero values in the amorphous single-
phase state because of the Invar effect. The precipitation of bcc phase caused by a further increase in $T_a$ gives rise to significant increases in $B_s$ and $\mu_e$, followed by maximum values of 1.4 to 1.7 T and $2 \times 10^4$ to $3 \times 10^4$, respectively, in the $T_a$ range of 873 to 923 K just before the phase decomposition of the bcc phase. The parameter $\lambda_s$ has positive values in the amorphous single-phase state for the three alloys and changes to negative values for the Zr- and Hf-containing bcc alloys, and to slightly positive or nearly zero values for the Nb-containing bcc alloy. Considering the correspondence between structure and magnetic properties, the best soft magnetic properties are obtained in a partially crystallized structure consisting of nanoscale bcc and amorphous phases. Therefore, it is concluded that the residual existence of the amorphous phase plays an

Figure 11.4 Composition dependence of saturation magnetic flux density ($B_s$) and effective permeability ($\mu_e$) at 1 kHz for Fe—M—B (M = Zr or Nb) amorphous alloys annealed for 3.6 ks at 873 and 923 K. The data for as-quenched phase are also shown for reference.
important role in the achievement of good soft magnetic properties as a result of the formation of a nanoscale mixed structure.

Here, it is important for the understanding of the formation mechanism of the nanostructure to confirm the residual existence of the amorphous phase and to examine the solute concentrations of the bcc and amorphous phases. Figure 11.6 shows a high-resolution TEM image of Fe$_{88}$Hf$_{10}$B$_2$.
alloy annealed for 3.6 ks at 873 K, together with data from nanobeam diffract patterns and energy-dispersive X-ray spectroscopy (EDX) profiles taken from regions 1 and 2. From the fringe contrast in the TEM image and the diffraction patterns, the regions 1 and 2 are identified as bcc and amorphous phases respectively. Thus, the nanoscale bcc phase with a grain size of about 10 nm is surrounded by the remaining amorphous phase. The EDX profiles also indicate that the Hf content is

Figure 11.6 (a) High-resolution transmission electron microscopy (TEM) image, (b) and (c) nanobeam diffraction patterns and (d) and (e) energy-dispersive X-ray spectroscopy (EDX) profiles taken from the small regions (1) and (2), respectively, with a diameter of 0.6 nm for amorphous Fe$_{88}$Hf$_{10}$B$_2$ alloy annealed for 3.6 ks at 873 K.
enriched in the remaining amorphous phase. Figure 11.7 shows a high-resolution TEM image, EDX and electron energy loss spectroscopy (EELS) profiles for the Fe$_{84}$Nb$_7$B$_9$ amorphous alloy annealed for 3.6 ks at 923 K. This structural feature (that the nanogranular bcc-Fe particles with a size of about 12 nm are surrounded by the amorphous phase) is the same as that for the Fe—B alloy shown in Fig. 11.6. Similarly, the Nb is enriched in the remaining amorphous phase and no appreciable Nb is detected in the bcc particle. Furthermore, the EELS data indicate that B is also enriched in the amorphous phase. These results allow us to conclude that the structure consists of nanogranular bcc-Fe particles sur-
rounded by the remaining amorphous phase and the solute elements are significantly enriched in the amorphous phase. The enrichment is presumed to cause the increase in the thermal stability of the residual amorphous phase, leading to the maintenance of the nanogranular bcc-Fe mixed structure even in the high $T_a$ range. The redistribution of the Nb and B elements is due to an extremely low solid solubility limit of these elements in the bcc-Fe phase.

With the aim of clarifying the redistribution of the solute elements in more detail, the nanostructure was examined using atom-probe field ion microscopy techniques.\textsuperscript{[25]} Figure 11.8(a) shows the change in the numbers of detected ions across the interface between bcc-Fe and amorphous phases for Fe$_{90}$Zr$_7$B$_3$ alloy annealed for 3.6 ks at 723 K. Although the change near the interface is slight for Fe, the change in the numbers of detected Zr and B ions is significant, indicating that the concentrations of Zr and B differ significantly near the interface between the bcc-Fe and amorphous phases. Figure 11.8(b) shows the concentration profiles of Fe and Zr near the interface on the basis of the results shown in Fig. 11.8(a). It is seen that the bcc phase has higher Fe and lower Zr concentrations as compared with their nominal concentrations, while the remaining amorphous phase has lower Fe and higher Zr concentrations. Furthermore, notice that Zr is significantly enriched in the amorphous phase near the interface and has a steep concentration gradient. Because of the significant enrichment of Zr in the remaining amorphous phase near the interface, the increase in thermal stability becomes most significant in the amorphous phase region near the interface. As a result, preferential heterogeneous nucleation at the interface is suppressed, leading to the achievement of the nanoscale bcc structure. Thus, segregation of the element leading to an increase in thermal stability of the remaining amorphous phase is essential to the maintenance of the nanocrystalline structure in the high $T_a$ range. It has been pointed out that the elements leading to the segregation satisfy the following three criteria:\textsuperscript{[25]}

1. Large atomic size and high melting temperature with lower diffusivity
2. Low solid solubility limit in main constituent metal
3. Large negative heat of mixing compared to other constituent elements

Makino et al. proposed\textsuperscript{[8–10]} a mechanism for appearance of good soft magnetic properties for nanoscale bcc Fe—M—B alloys. Here, it is important to describe the mechanism because the information is thought
Figure 11.8 (a) Fractions of the numbers of Fe, Zr and B ions in the total numbers of detected ions and (b) concentration profiles of Fe and Zr elements in the region across the interface between amorphous and bcc-Fe phases for amorphous Fe$_{90}$Zr$_7$B$_3$ alloy annealed for 3.6 ks at 723 K.
to be useful in understanding a method for the improvement of soft magnetic properties. Good soft magnetic properties have been thought\(^6\)\(^\text{–}^\text{11}\) to result from the simultaneous satisfaction of the following factors:

1. The achievement of high \(B_s\) resulting from magnetic coupling between the nanoscale bcc particles via the ferromagnetic amorphous phase
2. The ease of reversion of magnetization due to achievement of magnetic homogeneity resulting from the width of magnetic domain walls which are larger than the grain size of the bcc-Fe phase
3. The retainment of nanoscale bcc structure resulting from the existence of a residual amorphous phase where the solute elements are enriched and the thermal stability increases
4. The reduction of \(\lambda_s\) resulting from the redistribution of solute elements between bcc-Fe and the remaining amorphous phase.

If this mechanism is correct, soft magnetic properties are expected to be further improved by modifications of the following four factors:

1. An increase in the Curie temperature (\(T_c\)) for the remaining amorphous phase
2. A decrease in the bcc grain size and an increase in the volume fraction of the bcc-Fe phase
3. An increase in the thermal stability of the remaining amorphous phase
4. An achievement of a nearly zero \(\lambda_s\) value.

### 11.4 Improvement of Soft Magnetic Properties by the Addition of Small Amounts of Solute Elements

Improvement of the soft magnetic properties of Fe—M—B alloys has been tried by modifying the above-described four factors by adding small amounts of various solute elements. The addition of Co has been reported to be the most effective among VIa to VIII group transition metals. Figure 11.9 shows \(B_s\), \(\mu_e\), \(T_c\) for the remaining amorphous phase, and \(D\) values as a function of \(T_a\) for (Fe\(_{0.985}\)Co\(_{0.015}\))\(_{90}\)Zr\(_7\)B\(_3\) alloy, together with the data
Figure 11.9 Changes in the structure, (a) saturation magnetic flux density ($B_s$), (b) effective permeability ($\mu_e$), (c) Curie temperature ($T_c$) of amorphous phase and (d) mean grain size ($D$) with annealing temperature ($T_a$) for amorphous ($\text{Fe}_{0.985}\text{Co}_{0.015})_{90}\text{Zr}_{7}\text{B}_{3}$ and Fe$_{90}\text{Zr}_{7}\text{B}_{3}$ alloys.

for Fe$_{90}\text{Zr}_{7}\text{B}_{3}$ alloy. Although no appreciable changes in crystallization behavior and $D$ value are seen with the addition of Co, significant increases in $B_s$ and $\mu_e$ occur, as well as the extension of the annealing temperature range leading to high $B_s$ and $\mu_e$. Notice also that high $\mu_e$ values above $2 \times 10^4$ are obtained in the wide $T_a$ range between 823 and 923 K. The extension of the $T_a$ range is also important from an engineering point
of view because the use of wide thermal treatment condition is possible. Considering that $T_c$ for the amorphous phase increases significantly for the Co-containing alloy, the improvement of soft magnetic properties seems to result from an increase in the degree of magnetic coupling between bcc particles as a result of the increase in the magnetization of the residual amorphous phase containing Co.$^{[9]}$

The effect of grain size on the soft magnetic properties for the nanoscale bcc alloys has also been examined. Figure 11.10 shows changes in $D$ and $\mu_e$ at 1 kHz and coercivity ($H_c$) with heating rate ($\alpha$) up to 923 K for
Fe\(_{90}\)Zr\(_7\)B\(_3\), Fe\(_{89}\)Hf\(_7\)B\(_4\) and Fe\(_{84}\)Nb\(_7\)B\(_9\) amorphous alloys. With increasing \(\alpha\), \(\mu_e\) increases by 2 to 10 times and \(H_c\) decreases by about 1.4 to 4 times, accompanied by a significant decrease in \(D\). It is, therefore, concluded that decreasing the \(D\) value is effective for the improvement of soft magnetic properties. The decrease in \(D\) with increasing \(\alpha\) has been interpreted\(^8\) to originate from the increase in the number of nucleation sites and the suppression of grain growth. Rapid heating is a useful technique for the production of a nanocrystalline alloy with better soft magnetic properties. Besides, the use of a rapid heating technique gives us a unique opportunity to produce a nanocrystalline structure with significantly different \(D\) values. In the relation between the logarithms of \(H_c\) and \(D\), the slope (\(n\) value) for the present bcc alloys has been measured to be 5.2\(^{[8,9]}\) which is nearly the same as the theoretically evaluated value of 6.0.\(^{[26]}\) The agreement allows us to consider that the decrease in \(H_c\) occurs as a result of the increase in the ease of reversion of magnetization resulting from the decrease in \(D\).

Figure 11.11 shows \(B_s\), \(H_c\), \(\mu_e\), \(\lambda_s\) and \(D\) values as a function of Cu content for the bcc Fe\(_{90-x}\)Zr\(_7\)B\(_3\)Cu\(_x\) and Fe\(_{84-x}\)Nb\(_7\)B\(_9\)Cu\(_x\) alloys.\(^{[27]}\) As Cu content increases from 0 to 2 at\%, the \(B_s\), \(H_c\) and \(D\) values decrease for both alloys and \(\lambda_s\) tends to increase. However, no systematic change in \(\mu_e\) with Cu content is seen. From these changes, it is seen that the addition of only 1 at\% Cu causes a decrease in \(D\), accompanying a decrease in \(H_c\). Similar decreases in \(D\) and \(H_c\) have also been recognized for Fe—Zr—B alloys containing 1 at\% Pd.\(^8\) From the atom probe field ion microscopic data, it has been confirmed\(^{[28]}\) that the decrease in \(D\) resulting from the dissolution of Cu is due to easy heterogeneous nucleation of bcc phase in the Cu-rich region of the amorphous matrix. Furthermore, it is seen that \(\lambda_s\) is negative for the Fe—Zr—B—Cu alloys and positive for the Fe—Nb—B—Cu alloys. The opposite \(\lambda_s\) values indicate the possibility that the coexistence of Zr and Nb might causes nearly zero \(\lambda_s\), leading to an improvement of soft magnetic properties. Figure 11.12 shows the relation between \(D\), \(\lambda_s\) and \(\mu_e\) or \(H_c\) for the bcc Fe—M—B and Fe—M—B—Cu (M = Zr and/or Nb) alloys. One can see a tendency for the highest \(\mu_e\) and the lowest \(H_c\) values to be obtained around the slightly positive value of \(\lambda_s\) of \(0.3 \times 10^{-6}\). Also notice that the Fe—Zr—Nb—B—Cu alloys have a grain size of 7 nm, slightly positive \(\lambda_s\) of \(0.3 \times 10^{-6}\), high \(\mu_e\) of more than \(10^5\) at 1 kHz and low \(H_c\) of less than 2 A/m. The value of \(B_s\) is also as high as 1.53 T. The simultaneous achievement of high \(\mu_e\) and \(B_s\), low \(H_c\) and nearly zero \(\lambda_s\) is the main result and exceeds those for all soft magnetic materials including Fe- and Co-based amorphous alloys and nanocrystalline Fe—Si—B—Nb—Cu\(^3\) and Fe—P—C—Ga—Cu\(^{[29]}\) alloys reported hitherto. The excellent soft magnetic properties are deduced to result from the combination of the
grain size refinement as a result of the addition of Cu and nearly zero $\lambda_s$ as a result of dissolution of Zr and Nb.

11.5 Soft Magnetic Properties and Structure of Cu-free Quaternary Fe–Zr–Nb–B Alloys

In the nanocrystalline ternary Fe–Zr–B and Fe–Nb–B alloys, the compositional range where $\mu_e$ shows a maximum does not strictly
coincide with the zero-$\lambda_s$ line. The best soft magnetic properties are obtained around the compositions of Fe$_{90}$Zr$_7$B$_3$ and Fe$_{84}$Nb$_7$B$_9$. Since $\lambda_s$ changes from negative to positive with increasing B content for the alloys, $\lambda_s$ of the Fe$_{90}$Zr$_7$B$_3$ alloy is negative whereas that of the Fe$_{84}$Nb$_7$B$_9$ alloy is positive. It is expected that the soft magnetic properties of the Fe—M—B alloys can be improved further by achieving zero-$\lambda_s$. The zero-magnetostrictive Fe—Zr—Nb—B alloys with mixed composition of Fe—Zr—B with negative $\lambda_s$ and the Fe—Nb—B alloys with positive $\lambda_s$ were studied. First, Zr, Nb and B concentrations were investigated by choosing Fe$_{90}$Zr$_7$B$_3$ and Fe$_{84}$Nb$_7$B$_9$ alloys as basic constituents and mixing them in various ratios. Figure 11.13 shows the compositional dependence of $B_s$, $\mu_e$, $D$ and $\lambda_s$ for the (Fe$_{90}$Zr$_7$B$_3$)$_{1-x}$(Fe$_{84}$Nb$_7$B$_9$)$_x$ alloys as a function of $x$. The saturation magnetic flux density, $D$, and $\lambda_s$.

**Figure 11.12** Relation between mean grain size ($D$), saturation magnetostriction constant ($\lambda_s$) and (a) effective permeability ($\mu_e$) or (b) coercivity ($H_c$) for bcc Fe—M—B(—Cu) (M = Zr and/or Nb) alloys.
of the \((\text{Fe}_{0.9} \text{Zr}_{0.1} \text{B}_{0.3})_{1-x} (\text{Fe}_{0.84} \text{Nb}_{0.16} \text{B}_{0.9})_x\) alloys show intermediate values between those of the Fe90Zr7B3 and the Fe84Nb7B9 alloys. However, \(\mu_e\) for the \((\text{Fe}_{0.9} \text{Zr}_{0.1} \text{B}_{0.3})_{1-x} (\text{Fe}_{0.84} \text{Nb}_{0.16} \text{B}_{0.9})_x\) alloys are inferior to those for the Fe90Zr7B3 and the Fe84Nb7B9 alloys. It is noted that \(\mu_e\) shows a minimum around \(x = 0.8\) where the alloy exhibits zero \(\lambda_s\). The alloy with \(x = 0.83\) results in strongly\{001\} textured microstructure in the free surface of the ribbon due to surface crystallization.\[30\] This causes inferior soft magnetic properties even though zero \(\lambda_s\) is obtained with this composition, because the magnetocrystalline anisotropy cannot be averaged out without random orientation of \(\alpha\)-Fe nanocrystals.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure11_13.png}
\caption{Compositional dependence of (a) saturation induction \((B_s)\), (b) permeability \((\mu_e)\), (c) mean grain size \((D)\) and (d) saturation magnetostriction constant \((\lambda_s)\) for nanocrystalline \((\text{Fe}_{0.9} \text{Zr}_{0.1} \text{B}_{0.3})_{1-x} (\text{Fe}_{0.84} \text{Nb}_{0.16} \text{B}_{0.9})_x\) alloys after annealing at the optimum conditions.}
\end{figure}
Next, the effect of Zr + Nb amount on the soft magnetic properties was studied.\cite{12}-\cite{15} The best soft magnetic properties were obtained at Zr + Nb = 6 at%. Figure 11.14 shows the pseudo-ternary diagram of $\mu_e$, $B_s$ and $\lambda_s$ for Fe–6%(Zr, Nb)—B alloys crystallized under optimum conditions, where the Zr + Nb amount was constant at 6 at%. A small grain size of 10–11 nm has been obtained in a compositional range of 0–3 at% Zr and 6–9 at% B. The permeability reaches a maximum value of $6.0 \times 10^4$ for the Fe$_{85.5}$Zr$_2$Nb$_4$B$_{8.5}$ alloy, which shows zero $\lambda_s$. Figure 11.15 shows the pseudo-ternary diagram of core loss ($W$) at 1.4T and 50Hz and $H_c$ for Fe–6%(Zr, Nb)—B alloys crystallized under optimum conditions. The gray region indicates where the high $\mu_e$ values more than $5.0 \times 10^4$ have been obtained. Extremely low $W$ (less than 0.09 W/kg) has been obtained in a compositional range of 1.5–2.2 at% Zr and 8–9 at% B. The compositional range where $W$ exhibits the minimum extends to lower B content from the region where the best $\mu_e$ and $H_c$ values have been obtained. This is due to increase of $B_s$ with decreasing B content. Since $W$ increases rapidly near magnetic saturation, the higher $B_s$ is favorable to obtaining low $W$.

**Figure 11.14** Pseudo-ternary diagram of permeability ($\mu_e$), saturation magnetic flux density ($B_s$) and saturation magnetostriction constant ($\lambda_s$) for nanocrystalline Fe–6%(Zr, Nb)—B alloys after annealing at the optimum conditions.
11.6 Soft Magnetic Properties and Structure of Fe—Nb—B—P—Cu Alloys Produced in Air

11.6.1 Structure and Soft Magnetic Properties

As described above, typical compositions of nanocrystalline Fe—M—B type alloys contain 7 at% M elements or 2 at% Zr and are produced by a melt-spinning technique in a controlled atmosphere (a vacuum or inert gases) because the M elements have high oxidation activity. The vacuum chamber surrounding the melt-spinning apparatus is necessary to produce typical Fe—M—B type alloys. This is a great disadvantage of the Fe—M—B type alloys for industrial applications. The production of Fe—Nb—B(—Cu) alloys is easier than for Fe—Zr(—Nb)—B(—Cu) alloys. However, Fe—Nb—B alloys exhibit the lowest $B_s$ of about 1.5 T among typical Fe—M—B(—Cu) alloys. Therefore, the development of a new nanocrystalline soft magnetic alloy with higher $B_s$ more than 1.5 T and with good productivity has been strongly desired because the simultaneous

![Pseudo-ternary diagram of core loss ($W$) and coercivity ($H_c$) for nanocrystalline Fe—6%(Zr, Nb)—B alloys after annealing at the optimum conditions. The gray area indicates the compositional range giving high permeability of more than $5 \times 10^4$.](image)
achievement of both these properties enables the extension of application fields. We tried to synthesize new Fe—Nb—B-based nanocrystalline soft magnetic alloys with high $B_s$ as well as good productivity.

Melt-pinning the Fe—Nb—B alloys with various Nb contents in air has been tried. Ductile ribbons with metallic luster were obtained for alloys with 6.5 at% Nb or less.\textsuperscript{[15]} Figure 11.16 shows the as-quenched structure and the compositional dependence of $\mu_e$ in the crystallized state of Fe—Nb—B(—Cu) alloys with 6 at% Nb as a function of B content.\textsuperscript{[15]} For all the alloys, a B content of more than 10–11 at% is necessary to obtain a single amorphous structure in the as-quenched state. When the B content is less than this value, a mixed structure of $\alpha$-Fe and amorphous phases is formed in the as-quenched state. The addition of Cu scarcely changes the glass-forming ability of the alloys. Figure 11.17 shows the XRD patterns taken from the free surface in the as-quenched state of Fe$_{85-x}$Nb$_6$B$_9$Cu$_x$ ($x = 0 - 1$) alloys. The diffraction peak corresponding to $\alpha$-Fe 110 accompanied by a halo from an amorphous phase is observed in the profile around $2\theta \approx 52^\circ$ for all the alloys. The values for the mean grain size of the $\alpha$-Fe phase ($D_q$) roughly estimated from the $\alpha$-Fe diffraction peak are about 45, 25 and 50 nm for the Cu-free, 0.5 at% Cu-

![Figure 11.16 Compositional dependence of effective permeability ($\mu_e$) in crystallized state of Fe—Nb—B(—Cu) alloys with 6 at% Nb as a function of B content. The as-quenched structure evaluated from the X-ray diffraction patterns is also shown.](image-url)
added and 1 at% Cu-added alloy, respectively. On the other hand, \( D_q \) of 0.1 at% Cu alloy is not estimated because the diffraction peak is too broad and unclear. Therefore, we can assume that \( D_q \) for the 0.1 at% Cu alloy is extremely small. This result indicates that the addition of 0.1 at% Cu to the Fe\textsubscript{85}Nb\textsubscript{6}B\textsubscript{9} alloy should suppress coarsening of the \( \alpha \)-Fe grains in the as-quenched state around the glass-formation limit.

As shown in Fig. 11.16, a maximum value of \( \mu_e \) for crystalline alloys without Cu and with 1 at% Cu is obtained at the compositions where a single amorphous structure in the as-quenched state is formed. On the other hand, for 0.1 at% Cu-added alloy, the maximum \( \mu_e \) of \( 2.8 \times 10^4 \) in the crystalline state is obtained at 9 at% B where a structure of an amorphous phase and extremely small \( \alpha \)-Fe grains is formed in the as-quenched state. Therefore, it can be said that the addition of 0.1 at% Cu changes the as-quenched structure, and results in the expansion of the compositional range where good soft magnetic properties are obtained in the crystalline state to high Fe content.

Next, the addition of P to Fe—Nb—B(—Cu) alloys with 6 at% Nb has been studied to improve the soft magnetic properties of the alloys\textsuperscript{[15]} Figure 11.18 shows the as-quenched structure and \( \mu_e \) in the crystalline state of Fe—Nb—B(—P—Cu) alloys as a function of (B + P) content.
The effective permeability is improved by replacing B by 1 at% P around 9–10 at% (B + P). The maximum value of $\mu_e$ is $4.1 \times 10^4$ obtained with crystalline Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy. This alloy also exhibits a high $B_s$ of 1.61 T, which is considerably higher than that of the Fe$_{84.7}$B$_7$ alloy.

Figures 11.19 and 11.20 show the changes in the XRD patterns taken from the free surface in the as-quenched state for Fe$_{85-x}$Nb$_6$B$_8$P$_x$Cu$_x$ and Fe$_{84.9}$Nb$_6$B$_9-y$P$_y$Cu$_{0.1}$ alloys, respectively.$^{[15,16]}$ The diffraction peak corresponding to $\alpha$-Fe 110 is observed in the profile for the alloys except for Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy. The values of $D_q$ are estimated to be about 20–60 nm for the alloys. On the other hand, the as-quenched structure of Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy evaluated from the XRD pattern seemed to be a single amorphous phase. Figure 11.21 shows (a) the TEM image, (b) the SAED patterns, (c) a high-resolution TEM image and nanobeam electron diffraction pattern of the as-quenched Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy taken from the inner part of the ribbon. A large number of the nanoscale $\alpha$-Fe grains are observed in all the TEM images.$^{[16,17]}$ The simultaneous addition of P and Cu to the Fe$_{85}$Nb$_6$B$_9$ alloy makes a drastic change in the as-quenched structure including the nanoscale $\alpha$-Fe grains. From TEM observation of the crystallized Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy, it is clear that the nanocrystalline

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**Figure 11.18** Compositional dependence of effective permeability ($\mu_e$) in crystallized state of Fe—Nb—B(—P—Cu) alloys with 6 at% Nb as a function of B + P content. The as-quenched structure evaluated from the X-ray diffraction patterns is also shown.
Figure 11.19 Changes of X-ray diffraction patterns taken from free surface in the as-quenched state of Fe$_{85-x}$Nb$_6$B$_6$P$_1$Cu$_x$ alloys as a function of Cu content. Values of mean grain size ($D_q$) of $\alpha$-Fe phase estimated by the broadening of the diffraction peak are also shown.

Figure 11.20 Changes of X-ray diffraction patterns taken from free surface in the as-quenched state of Fe$_{84.9}$Nb$_{6}$B$_{9-y}$P$_y$Cu$_{0.1}$ alloys as a function of P content. Values of mean grain size ($D_q$) of $\alpha$-Fe phase estimated by the broadening of the diffraction peak are also shown.
structure of the alloy does not include the coarse $\alpha$-Fe grains and is as uniform as that of the typical Fe$_{84}$Nb$_6$B$_9$ alloy obtained by crystallizing a fully amorphous phase produced in a controlled atmosphere.

Figure 11.22 shows the relation between $\mu_e$ in a crystallized state and $D_q$ in an as-quenched state of the Fe$_{85-x}$Nb$_6$B$_{9-y}$P$_y$Cu$_x$ ($x = 0 - 1$, $y = 0 - 2$) alloys.$^{[16]}$ The permeability in a crystallized state increases with decreasing
This result indicates that the precursor to the uniform nanostructure with high $\mu_e$ is not always a fully amorphous phase, and there is a possibility of realizing higher $B_s$ materials with higher Fe contents.

11.6.2 Effect of Grain-Size Distribution and Curie Temperature of Intergranular Amorphous Phase on Soft Magnetic Properties

Figure 11.22 Relation between effective permeability ($\mu_e$) in a crystallized state and mean $\alpha$-Fe grain size ($D_q$) in as-quenched state for Fe$_{85-x}$Nb$_y$B$_{9-y}$Cu$_x$ ($x = 0 - 1$, $y = 0 - 2$) alloys.

Figure 11.23 Transmission electron microscopy (TEM) images and selected-area electron diffraction patterns taken from inner part of the ribbon of as-quenched and crystallized (923K for 300s) Fe$_{85}$Nb$_6$B$_9$ alloy.

$D_q$. This result indicates that the precursor to the uniform nanostructure with high $\mu_e$ is not always a fully amorphous phase, and there is a possibility of realizing higher $B_s$ materials with higher Fe contents.

11.6.2 Effect of Grain-Size Distribution and Curie Temperature of Intergranular Amorphous Phase on Soft Magnetic Properties

Figure 11.23 shows TEM images and SAED patterns taken from the inner part of the ribbon of as-quenched and crystallized Fe$_{85}$Nb$_6$B$_9$ alloy.\textsuperscript{[16, 31]} The Fe$_{85}$Nb$_6$B$_9$ alloy has a mixed as-quenched structure composed of an amorphous phase and $\alpha$-Fe grains with 10–25 nm in size as
shown in Section 11.6.1. These grains grow to a size of about 40 nm during the annealing treatment, and remain in the nanostructure after crystallization as shown in Fig. 11.23(b). It is considered that such structural inhomogeneities will result in remarkable effects on the soft magnetic properties. Here, the effect of the grain-size distribution on the magnetic softness of nanocrystalline soft magnetic alloys is discussed based on the random anisotropy model (RAM).\[26, 32\]

For simplicity, let us consider that the maximum grain size ($D_m$) does not exceed the exchange correlation length ($L_{ex}$). Then the fluctuating part of the magnetocrystalline anisotropy ($\langle K_1 \rangle$) is given by using a distribution function of the grain size ($f(D)$), as\[31\]

$$\langle K_1 \rangle = (1 - v_a)^2 \frac{K_1}{K_0^6} \left\{ \int_0^{D_0} \frac{D^3 f(D) dD}{D} \right\}^2,$$  \hspace{1cm} Eq. (11-1)

where $v_a$ is the volume fraction of the intergranular amorphous phase, $K_1$ is the intrinsic magnetocrystalline anisotropy constant and $L_0$ is the intrinsic exchange correlation length.\[32\] We further assume a log-normal distribution function as the grain-size distribution:

$$f(D_r) = \frac{1}{\sqrt{2\pi}\sigma_D D_r} \exp\left(-\frac{\ln^2 D_r}{2\sigma_D^2}\right),$$  \hspace{1cm} Eq. (11-2)

where $D_r = D/D_0$ is the reduced grain size, $D_0$ is the median and $\sigma_D$ is the geometric standard deviation. If $f(D_r)$ is negligibly small at $D_r > D_m$, then $D_m$ can be regarded as infinity and we obtain $L_{ex} = L_0^4/\{ (1 - v_a) \langle D \rangle^3 \exp(3\sigma_D^2) \}$ and

$$\langle K_1 \rangle = (1 - v_a)^2 K_1 \left( \frac{\langle D \rangle}{L_0} \right)^6 \exp(6\sigma_D^2),$$  \hspace{1cm} Eq. (11-3)

where $\langle D \rangle = D_0 \exp(\sigma_D^2/2)$ is the mean grain size. Then eqn (11.3) indicates that $\langle K_1 \rangle$ increases with increasing $\sigma_D$, i.e., soft magnetic properties of nanocrystalline alloys deteriorate with increasing $\sigma_D$, even if $\langle D \rangle$ is constant. It should be noted that this result is essentially established in other distribution functions.Naturally, the effective anisotropy in nanocrystalline alloys may have contributions from induced anisotropies such as magnetoelastic anisotropy other than the random magnetocrystalline anisotropy and hence the effective anisotropy constant in actual materials is more correctly $\langle K \rangle = \sqrt{K_u^2 + \langle K_1 \rangle^2}$,\[33\] where $K_u$ is the induced uniaxial anisotropy constant and $\langle K_1 \rangle = (1 - v_a) K_1/\sqrt{N} = K_1 \sqrt{(1 - v_a) \int D^3 f(D) dD/L_{ex}^3}$.
$N$ is the number of grains in a magnetically coupled volume). Most of the nanocrystalline Fe—M—B (M = Zr, Hf, Nb) alloys with good soft magnetic properties exhibit a remanence ratio ($J_r/J_s$) of around 0.5. This means that the magnetization process of the alloys is mostly governed by the induced anisotropies, i.e., $K_u > \langle K_1 \rangle$. In a limiting condition of $K_u^2 >> \langle K_1 \rangle^2$ enables us to arrive at 

$$L_{ex} = L_0\sqrt{\langle K_1 \rangle/K_u}$$

and

$$\langle K \rangle = K_u + (1 - v_a)\frac{\sqrt{K_u K_1}}{2} \left(\frac{\langle D \rangle}{L_0}\right)^3 \exp(3\sigma_D^2). \quad \text{Eq. (11-4)}$$

The $D^3$ behavior of $H_c$ is observed for nanocrystalline Fe—Zr—B(—Cu) alloys with sufficiently small $D$.[33]

The grain-size distribution evaluated by counting $\alpha$-Fe grains in TEM images is shown in Fig. 11.24.[31] The log-normal distribution function reproduces well the observed grain-size distribution. In order to reproduce the grain-size distribution of the Fe$_{85}$Nb$_6$B$_9$ alloy more accurately, we consider the bimodal distribution function ($f_b(D)$) expressed by superimposing the two log-normal distribution functions with different medians ($D_0$ and $d_bD_0$, $d_b > 1$), the geometric standard deviations ($\sigma_D$ and $\sigma_b$) and the ratio of the distribution function for the large grains to that of the small grains ($r_b$).[31] When the induced anisotropies are dominant, the coercivity is given as $H_c = 0.64(\langle K \rangle - K_u)/J_s$,[34] where $J_s$ is the saturation magnetization.

The calculated results are also shown in Fig. 11.24.[31] Here, $v_a$ values are determined by X-ray diffraction profiles.[31] The calculated $H_c$ with the unimodal log-normal distribution function for the Fe$_{84}$Nb$_7$B$_9$ and Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloys are in good agreement with the measured ones. On the other hand, the calculated $H_c$ for the Fe$_{85}$Nb$_6$B$_9$ alloy is $2/3$ as large as the experimental one. This large difference originates in disregarding the existence of the coarse grains with about 40 nm in size. The calculated $H_c$ is consistent with the experimental one when the existence of the coarse grains is considered. Therefore, it can be said that our model explains well the dependence of $H_c$ on the grain-size distribution for the nanocrystalline Fe—Nb—B(—P—Cu) alloys. These results also suggest that one should pay attention not only to the mean grain size but also to the grain-size distribution since inhomogeneity of the grain size increases $H_c$.

Figure 11.25 shows $J_s^{1/\beta}$ vs. temperature plots for the crystallized (at 823 K) Fe$_{84}$Nb$_7$B$_9$ and the Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloys. Here, $\beta$ (= 0.36) is the critical exponent for spontaneous magnetization.[35] It should be noted that the Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy exhibits the higher Curie temperature for the intergranular amorphous phase ($T_c^{am}$) than the Fe$_{84}$Nb$_7$B$_9$ alloy. In order
to discuss the effect of $v_a$ and $T_c^{\text{am}}$ on the soft magnetic properties, the extended random anisotropy model (RAM) proposed by Löffler et al.\textsuperscript{[36]} was applied. The model takes into account the reduction of the ferromagnetic exchange interaction between adjacent grains. Here, we assume that the crystalline and inter-granular amorphous phases have different exchange stiffness constants, i.e., $A_c$ and $A_a$, respectively. Let us consider that $L_{\text{ex}}$ is determined by $K_u$ instead of $\langle K_1 \rangle$, i.e., $L_{\text{ex}} = \varphi \sqrt{A_{\text{eff}} / K_u}$, where $\varphi$ is a parameter which reflects both the sym-

Figure 11.24 Grain-size distribution of Fe—Nb—B(—P—Cu) alloys. The histograms and mean grain size ($D$) were obtained from transmission electron microscopy (TEM) images. The solid lines indicate fitting (a), (b) and (d) unimodal or (c) bimodal log-normal distribution functions. The inset in (c) is an enlarged view of 30–50 nm grain size. The fitting parameters and calculated results are also shown.
Figure 11.25 $J^{1/\beta}$ vs. temperature plot for crystallized (at 823 K) Fe$_{84}$Nb$_7$B$_9$ and Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy, where $J$ is the magnetization and $\beta$ is the critical exponent for the spontaneous magnetization. The arrows indicate the Curie temperature of the inter-granular amorphous phase ($T_{c_{am}}$).

The symmetry of $K_1$ and the total spin rotation angle over the exchange-correlated coupling chain,$^{[37]}$

$$A_{\text{eff}} = A_c \left(1 + \frac{\Lambda}{D}\right) \left(1 + \frac{A_c \Lambda}{A_D D}\right)^{-1}$$

Eq. (11-5)

is the effective exchange stiffness constant proposed by Löffler et al.$^{[36]}$ and $\Lambda \approx D \{(1 - v_a)^{-1/3} - 1\}$ is the thickness of the amorphous matrix.$^{[38]}$

Equations (11.4) and (11.5) yield

$$\langle K \rangle \approx K_u + (1 - v_a) \frac{3}{2} \sqrt{K_u K_1^2 D^3}{2 \varphi^3 A_c^{3/2}}$$

Eq. (11-6)

$$\left[1 + \frac{A_c}{A_a} \left(\frac{1}{(1 - v_a)^{1/3}} - 1\right)\right]^{3/2} \exp(3\sigma_D^2).$$
Since the exchange stiffness constant is proportional to the Curie temperature and the square of the spin, $A_c/A_a$ can be written as $A_c/A_a \approx S_c^2T_{c cr}/(S_a^2T_{c am})$, where $T_{c cr}$ is the Curie temperature of the crystalline phase, $S_c$ and $S_a$ are the spin of the crystalline and inter-granular amorphous phases, respectively.

Figure 11.26 shows the calculated $H_c$ (relative value for $H_c(\nu_a = 0) = 0.64\sqrt{K_uK_i}D/(2\varphi^3A_c^{3/2}J_s)$) as a function of $T_{c am}$. Here, $S_a$ is assumed to be 1/2 because the magnetic hyperfine field of the inter-granular amorphous phase is about 1/2 as large as that of the $\alpha$-Fe phase. The closed circles show the relative values of observed $H_c$ for Fe$_{84}$Nb$_7$B$_9$ and Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloys annealed at 823 K. The coercivity increases with increasing $\nu_a$ and decreasing $T_{c am}$. Especially, the effect of $T_{c am}$ on $H_c$ is considerably greater for the alloys with large $\nu_a$. Furthermore, the calculated results are in good agreement with the observed values. Therefore, it can be concluded that the small $\nu_a$ and high $T_{c am}$ of the Fe$_{84.9}$Nb$_6$B$_8$P$_1$Cu$_{0.1}$ alloy are the main factors contributing to good soft magnetic properties even in the low $T_a$ region around 800 K.

Table 11.1 summarizes soft magnetic properties of $B_s$, $\mu_e$, $H_c$, $\lambda_s$, electrical resistivity ($\rho$) and core losses ($W$) for the bcc Fe—M—B and Fe—M—B—Cu alloys, together with the data of sample thickness ($t$) and $D$, in comparison with those for amorphous Fe—Si—B$^{[40]}$ and Co—
Table 11.1 Sample thickness ($t$), mean grain size ($D$), electrical resistivity ($\rho$), and magnetic properties ($B_s$: saturation magnetic flux density, $\mu_e$: effective permeability, $H_c$: coercivity, $\lambda_s$: saturation magnetostriction constant, and $W$: core loss) for the nanogranular bcc Fe—M—B(—Cu) alloys, Fe—Si—B—Nb—Cu alloys and amorphous alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>$t$ (µm)</th>
<th>$D$ (nm)</th>
<th>$B_s$ (T)</th>
<th>$\mu_e$*</th>
<th>$H_c$ (A/m)</th>
<th>$\lambda_s$ (10^-6)</th>
<th>$\rho$ (µΩm)</th>
<th>$W_{14/50}$** (W/kg)</th>
<th>$W_{2/100\text{kHz}}$** (W/kg)</th>
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<td>Fe$_{91}$Zr$_7$B$_2$</td>
<td>18</td>
<td>16</td>
<td>1.67</td>
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<td></td>
<td>0.21</td>
<td>79.7</td>
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<td>16</td>
<td>1.63</td>
<td>29 000</td>
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<td>-1.1</td>
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<td>0.21</td>
<td>79.7</td>
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<td>1.64</td>
<td>34 000</td>
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<td>-1.1</td>
<td>0.51</td>
<td>185.4</td>
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<td>(Fe$_{0.985}$Co$_0.015$)$_9$Zr$_7$B$_3$</td>
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<td>16</td>
<td>1.64</td>
<td>27 000</td>
<td>4.2</td>
<td>0</td>
<td>0.12</td>
<td>63.7</td>
<td></td>
</tr>
<tr>
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<td>12</td>
<td>1.70</td>
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<td>4.2</td>
<td>-0.1</td>
<td>0.53</td>
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<td>1.62</td>
<td>34 000</td>
<td>3.5</td>
<td></td>
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<td>3.2</td>
<td></td>
<td></td>
<td>27.5</td>
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<td>32 000</td>
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<td>36 000</td>
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<td>0.58</td>
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<td>+1.1</td>
<td>0.64</td>
<td>54.7</td>
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<td>41 000</td>
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<tr>
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<td>9</td>
<td>1.61</td>
<td>110 000</td>
<td>2.0</td>
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<td>0.56</td>
<td>60.0</td>
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<td>8</td>
<td>1.57</td>
<td>160 000</td>
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<td>-0.3</td>
<td>0.56</td>
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<td>8</td>
<td>1.53</td>
<td>120 000</td>
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<td>+0.3</td>
<td>0.61</td>
<td>0.06</td>
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<td>60 000</td>
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<td>10 000</td>
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<td>0.88</td>
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<td>85 000</td>
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<td></td>
<td>49.4</td>
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<td></td>
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<td>100 000</td>
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<td>+2.1</td>
<td>1.15</td>
<td>39.1</td>
<td></td>
</tr>
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</table>

* $f = 1$ kHz, ** $W_{a/b}$ is the core loss at $a \times 10^{-1}$ T and $b$ Hz, *** Ref. (3).
Fe—Si—B\[40\] and nanoscale bcc Fe—Si—B—Nb—Cu\[3\] alloys. It is confirmed that soft magnetic properties combined with high \(B_s\) and low \(W\) for the present nanoscale bcc alloys are superior to those for the other magnetic materials. Based on the data summarized in Table 11.1, the relation between \(B_s\) and \(\mu_e\) for soft magnetic materials is shown in Fig. 11.27, where the data of silicon steels and Mn—Zn ferrites are also presented for comparison. It is seen that the Fe—M—B type alloys possess much better soft magnetic properties which had not been achieved for all other soft magnetic materials.

11.7 Improvement of High-frequency Permeability by the Dissolution of Oxygen in the Surrounding Amorphous Phase

11.7.1 As-sputtered Structure

As described above, the permeability (\(\mu'\)) of the nanocrystalline Fe—M—B alloys (\(t = 20 \mu \text{m}\)) is as high as \(10^5\) at 1 kHz, but decreases to about \(2 \times 10^3\) at 1 MHz (\(7 \times 10^2\) at 3 MHz). For the future development of high-performance and miniaturized electronic devices, it is important to
improve the high-frequency permeability characteristics. It is generally known that an increase in electrical resistivity and a decrease in sample thickness are effective for the improvement of high-frequency permeability because these changes cause a decrease in eddy current loss which becomes significant in a high frequency range. As one of the methods to increase the electrical resistivity, the B content in Fe—M—B alloys was increased to about 20 at%. However, the increase in B content causes the disappearance of the nanocrystalline bcc structure by the simultaneous precipitation of bcc and compound, though an amorphous single phase is obtained in the melt-spun state.\cite{40} Subsequently, Hayakawa et al.,\cite{41} examined the effect of the addition of oxygen on the formation and soft magnetic properties of nanogranular bcc alloys for Fe—M base alloys. As an effective method to dissolve a large amount of oxygen and to prepare a thin sample, we used a sputtering method in a mixed atmosphere of argon and oxygen. It has been reported\cite{18,19} that as-deposited Fe_{46-88}Hf_{2-20}O_{7-41} films have four types of structure which consist of a bcc single phase, mixed bcc and amorphous phases, an amorphous single phase and an oxide phase, depending on the film composition. Useful soft magnetic properties are obtained in the films which have mixed bcc and amorphous phases. Figure 11.28 shows the XRD patterns of as-deposited Fe—M—O [M = Ti, Zr, Hf, V, Nb, Ta, W, rare earth metals (Re)]\cite{42} films. In the Zr-, Hf- and Re-containing alloys, a broad peak due to an amorphous phase and diffraction peaks due to a bcc phase are observed. In contrast to these results, only the diffraction peaks corresponding to a bcc phase are observed for the Ti-, V-, Ta-, Nb- and W-containing alloys and no appreciable broad peak is seen. Furthermore, one can notice that the diffraction angle of bcc 110 peak shifts to a lower angle than that of pure bcc-Fe marked with a dashed line in Fig. 11.28, indicating that the bcc phase includes a larger amount of M and oxygen.

Figures 11.29 and 11.30 show high-resolution TEM images, nanobeam electron diffraction patterns and EDX profiles for the as-deposited Fe_{55}Hf_{11}O_{34} and Fe_{49}Hf_{16}O_{35} films, respectively, together with data of electrical resistivity at room temperature ($\rho_{RT}$). The electron diffraction patterns and the EDX profiles were taken from the points marked in the figure. Both films are composed of very fine-grained crystals less than 10 nm in diameter, which were surrounded by the amorphous phase. Grains with diameter less than 5 nm in size are fewer and the region of amorphous phase becomes larger for Fe_{49}Hf_{16}O_{35} film compared with Fe_{55}Hf_{11}O_{34} film. These crystals are identified as bcc-Fe phase supersaturated with Hf and O from the nanobeam diffraction pattern and the EDX profile of the crystal (region 1). The $\rho_{RT}$ value increases from 10.5 to 492 $\mu\Omega$m with an increase in the amorphous region of the film.
Figure 11.28 X-ray diffraction patterns of as-deposited Fe—M—O films.

Figure 11.31 shows the X-ray photoelectron spectroscopy (XPS) profiles of Fe_{2p3/2}, Hf_{4f7/2}, Y_{3d5/2} and Ta_{4f7/2} for as-deposited Fe_{55}Hf_{11}O_{34}, Fe_{68}Y_{22}O_{10} and Fe_{55}Ta_{18}O_{27} films. Each profile is indicated with solid triangles in the figure. In all systems, the binding energy of Fe_{2p3/2} agrees with that of pure Fe. In contrast, the binding energies of Hf_{4f7/2} and Y_{3d5/2} are close to those of HfO_{2} and Y_{2}O_{3}, respectively. Therefore, O preferentially combines with Hf and Y in the Fe_{55}Hf_{11}O_{34} and Fe_{68}Y_{22}O_{10} films consisting of bcc and amorphous phases, as shown in Figs. 11.28 and 11.29. Then, these elements are mainly dissolved in the amorphous phase and probably form M-oxide like structure. In contrast, for the Fe_{55}Ta_{18}O_{27} film consisting of a mostly single bcc phase, the binding energy of Ta_{4f7/2} is close to that of metallic Ta and there is no evidence of chemical binding.
Figure 11.29 High-resolution transmission electron microscopy (TEM) images, nanobeam electron diffraction patterns and energy-dispersive X-ray spectroscopy (EDX) profiles taken from each microregion for as-deposited Fe$_{55}$Hf$_{11}$O$_{34}$ film.

Figure 11.30 High-resolution transmission electron microscopy (TEM) images, nanobeam electron diffraction patterns and energy-dispersive X-ray spectroscopy (EDX) profiles taken from each microregion for as-deposited Fe$_{49}$Hf$_{16}$O$_{35}$ film.
between Ta and O elements. They are presumed to be supersaturated in the bcc phase, which results in the diffraction peak shift of bcc 110 as shown in Fig. 11.28. As a result, it is considered that the rapid increase in $\rho_{RT}$ results from the highly resistive amorphous region including M—O atomic pairs for the Fe—(Hf, Zr, Re)—O films. The formation of the mixed structure is due to a combination of three factors:

1. A low solid solubility limit of Hf in the bcc-Fe phase
2. Preferential interaction of oxygen with Hf
3. Large solubility of oxygen in an amorphous phase.

### 11.7.2 Magnetic Properties

Figure 11.32 shows the compositional dependence of $B_s$ and $H_c$ of as-deposited Fe—Hf—O films which were sputtered under no applied...
magnetic field. Open and solid circles represent the single bcc phase and the single amorphous phase, respectively. Double open and half solid circles indicate the oxide phase and the mixed bcc and amorphous phases, respectively. The value of $B_s$ tends to decrease with increasing Hf and O contents and has a ridge around Hf content of 10 to 15 at%. The value of $H_c$ decreases with increasing Hf and O contents and has a valley around the same Hf content as the ridge of $B_s$. Therefore, the ridge of $B_s$ approximately agrees with the valley of $H_c$, and there is a region in which $B_s$ above 1.0 T and $H_c$ below 160 A/m are simultaneously obtained. In this region, the real part of the initial permeability ($\mu'$) is about $4 \times 10^2$ even in the as-deposited state and the film structure is composed of fine bcc and amorphous phases as indicated by shading.

Figure 11.33 shows the temperature dependence of $B_s$ for as-deposited Fe—Hf—O films in comparison with a Fe—Hf amorphous alloy film. The Fe—Hf—O films with the mixed amorphous and bcc structure exhibit two-stage crystallization behavior. The arrows indicate the first crystallization temperature corresponding to grain growth of the bcc phase,
Properties which was measured by DSC. The value of $B_s$ for both films decreases with increasing temperature with bending points in the course of changes, at 500 and 750 K for the Fe$_{49}$Hf$_{16}$O$_{35}$ and Fe$_{55}$Hf$_{11}$O$_{34}$ films, respectively. An amorphous Fe$_{76}$Hf$_{24}$ film has a low $T_c$ (below room temperature) owing to the Invar effect.\[43\] For the Fe$_{49}$Hf$_{16}$O$_{35}$ film, the bending point is thought to result from the $T_c$ of the amorphous phase not from crystallization, because the temperature is lower than that of the first crystallization. It is difficult to conclude certainly that the bending point is attributed to the $T_c$ of the amorphous phase for the Fe$_{55}$Hf$_{11}$O$_{34}$ film, because the temperature of the bending point is close to the first crystallization temperature. However, there is no bending point below that temperature, and the $T_c$ of the amorphous phase for the Fe$_{55}$Hf$_{11}$O$_{34}$ film can be regarded as higher than 700 K. As a consequence, the $T_c$ of the amorphous phase including Fe and Hf increases with the dissolution of O in the Fe—Hf—O films. Furthermore, we confirmed\[44\] that the $T_c$ of the amorphous phase for the Fe—Hf—O films increased after annealing. The magnetic properties and $\rho_{RT}$ values for as-deposited Fe—M—O (M = group IVa–VIa transition metals and Re) films are summarized in Table 11.2, together with their film structures. The film compositions are the same as those of the films shown in Fig. 11.28. In all systems, $B_s$ above 0.9 T and high $\rho_{RT}$ above 4 $\mu\Omega$m are simultaneously obtained. The $\lambda_s$ values were 0.1–2.9 $\times$ 10$^{-6}$. Relatively low $H_c$ values below 400 A/m are obtained in M = Hf, Zr and Re systems, which have mixed structure of nanogranular bcc and amorphous phases.

![Figure 11.33](image-url) Temperature dependence of saturation magnetic flux density ($B_s$) for as-deposited Fe$_{76}$Hf$_{24}$, Fe$_{55}$Hf$_{11}$O$_{34}$ and Fe$_{49}$Hf$_{16}$O$_{35}$ films. The arrows indicate the first crystallization temperature ($T_x$) of the films.
As shown in Fig. 11.28, no amorphous phase is formed in the Ti-, V-, Ta- and W-containing alloys. In these alloys, $H_c$ is relatively large and sufficient soft magnetic properties are not obtained. Therefore, the formation of a mixed structure consisting of the nanoscale bcc and amorphous phases is required for the achievement of good magnetic softness in the as-deposited state. The soft magnetic properties in as-deposited Fe—(Hf, Zr, Re)—O films are probably due to the nanoscale grain size and the intergrain ferromagnetic coupling through the high-$T_c$ amorphous phase. Furthermore, it should be noted that good soft magnetic properties are obtained even in the films including rare earth (Re) elements, which have a large magnetocrystalline anisotropy and usually inhibit soft magnetic properties. This is due to the decrease in magnetic interaction between Fe and Re resulting from the preferential binding with O.

The soft magnetic properties of the Fe—(Hf, Zr, Re)—O films are improved by sputtering under a uniaxial magnetic field, or uniaxial field annealing (UFA) treatment after deposition under no applied magnetic field. Furthermore, we tried to improve the frequency characteristics by enhancing uniaxial anisotropy ($H_K$) by the addition of Co to the

<table>
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<th>Structure</th>
<th>$B_s$ (T)</th>
<th>$H_c$ (A/m)</th>
<th>$\rho$ ((\mu\Omega)m)</th>
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<td>9.3</td>
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Fe—M—O films. Figure 11.34 shows the $B-H$ curve for an as-deposited Co$_{44.3}$Fe$_{19.1}$Hf$_{14.5}$O$_{22.1}$ film, together with the data for the Fe$_{61}$Hf$_{13}$O$_{26}$ film. The former was deposited under a static magnetic field and the latter was UFA treated after deposition under no applied magnetic field. The $H_K$ value of 1.15 kA/m for the Fe$_{61}$Hf$_{13}$O$_{26}$ film is the largest of all the Fe—Hf—O films. However, the $H_K$ of the Co$_{44.3}$Fe$_{19.1}$Hf$_{14.5}$O$_{22.1}$ film exhibits 4.8 kA/m which is approximately four times larger than that of the Fe$_{61}$Hf$_{13}$O$_{26}$ film. This film exhibits a high $B_s$ of 1.1 T and a high $\rho_{RT}$ of 15.1 $\mu$Ωm simultaneously, and moreover, the angle dispersion of magnetic anisotropy becomes small. Therefore, excellent high-frequency characteristics are expected to be obtained for the Co$_{44.3}$Fe$_{19.1}$Hf$_{14.5}$O$_{22.1}$ film owing to its significant high $\rho_{RT}$ and large $H_K$ values.

Figure 11.35 shows the frequency dependence of $\mu$ and the quality factor ($Q = \mu'/\mu''$) of the Fe—Hf—O and Co—Fe—Hf—O films prepared by various methods, together with the data on other metallic soft magnetic alloy films developed to date. The $Q$ value is a very important factor from
the viewpoint of applications. Actually, conventional soft magnetic films exhibit high permeability at 1 MHz, in particular, approximately $10^4$ has been obtained for nanocrystalline soft magnetic films such as Fe—Si—Al—Hf—C film. However, $\mu'$ decreases with increasing frequency because of low $\rho_{RT}$ values. On the other hand, the $\mu'$ of the Fe—Hf—O films is lower than that of conventional films in the range below 30 MHz, while in the frequency range higher than that, the Fe—Hf—O films exhibit higher and flat $\mu'$ characteristics over 100 MHz because of their high $\rho_{RT}$ values and moderate $H_K$. Fe$_{62}$Hf$_{17}$O$_{27}$ film exhibits a $B_s$ of 1.3 T and a high $\mu'$ of $1.4 \times 10^3$ at 100 MHz in an as-deposited state. Moreover, the $Q$ values
are also higher than those of the conventional films. The highest $Q$ value of 61 at 100 MHz is obtained for the $\text{Co}_{44.3}\text{Fe}_{19.1}\text{Hf}_{14.5}\text{O}_{22.1}$ film. Needless to say, these films have higher $Q$ values than other metallic films even in a low-frequency range. In the other M systems, similar high-frequency characteristics are observed, so that the Fe—M—O and Co—Fe—Hf—O films can be regarded as low-loss soft magnetic films in a wide frequency range from MHz to around GHz.

### 11.8 Applications

Figure 11.36 summarizes expected application fields for the soft magnetic Fe—M—B(—Cu) type alloys, together with the magnetic characteristics which are required for their applications. Application fields include power transformers, data communication interface components, electromagnetic interference (EMI) prevention components, magnetic heads, sensors, magnetic shielding and reactors. The expectation of applications to power transformers comes from the lower core losses over a wide maximum induction range as compared with oriented Si-steels and amorphous Fe$_{78}$Si$_{9}$B$_{13}$ alloy as shown in Fig. 11.37.$^{[9,10]}$ In addition, the efficiency of the power transformer was examined as a function of output

![Figure 11.36](image-url)
current for the bcc Fe—Zr—Nb—B—Cu alloys and clarified to be much higher than those for the Fe—Si—B amorphous alloys and oriented Si-steels (Fig. 11.38),\textsuperscript{[10]} in agreement with the tendency for core losses. We have also evaluated noise attenuation characteristics which are important for the common mode choke coil. Figure 11.39 shows that the bcc Fe—Zr—Nb—B—Cu alloys had better noise attenuation values over the whole frequency range when compared with Fe—Si—B amorphous alloys.\textsuperscript{[10]} The better performance as power transformers and common mode choke coils allows us to expect that the newly developed nanocrystalline Fe—M—B alloys are practical soft magnetic materials. Finally, it is important to note that the Fe—Zr—Nb—B—Cu alloys have already been used as pulse transformers in ISDN terminal adapters.

Figure 11.35 also summarizes typical application items and characteristics required for their applications for Fe—M—O and Co—Fe—Hf—O films. In the frequency range around 10 MHz, we postulate thin-film inductors or transformers for microswitching converters\textsuperscript{[46]} for portable electrical equipment. Microswitching dc–dc converters using Co-based amorphous alloy film as the core material in thin-film inductors have

Figure 11.37 Core losses at 50 Hz as a function of maximum induction for bcc Fe—Zr—Nb—B—Cu alloy. The data for amorphous Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} and oriented Si-steel are also shown for comparison.
already been reported,[47] but they will be operated at higher frequency for further miniaturization and improvement of power supplies. For such high-frequency switching converters operating around 10 MHz, the Fe—M—O films exhibit their ability as a core material.

In the high frequency range up to 100 MHz, the Fe—M—O films are useful for magnetic heads for ultrahigh-density recording exceeding 1 Gbit/in². High $B_s$ soft magnetic films such as Fe—M—N[48] are studied for high-density recording heads, but high-frequency characteristics around 100 MHz are required. In the further high-frequency range around GHz, noise filters, thin-film transformers or other micromagnetic devices dealing with electromagnetic waves are proposed.

For other examples of applications, Figs. 11.40 (a) and (b) show a schematic illustration of a planar inductor for microswitching converters and the frequency dependence of $Q = \omega L/R$ values of a planar Cu coil using each magnetic film, respectively. The inductor is made up of a planar coil sandwiched with two magnetic films facing each other as shown in Fig. 11.40 (a). In the case of the inductor, we use one side of the Cu coil
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as a conductor. As can be seen in Fig. 11.40 (b), an inductor using Fe—Hf—O film shows a maximum. High $Q$ values of 12.3 at 5 MHz and 21.8 at 20 MHz are obtained for an inductor using the Co—Fe—Hf—O film. Therefore, these planar inductors using the Fe—Hf—O and Co—Fe—Hf—O films enable higher frequency operation and higher efficiency than an inductor using Co—Ta—Hf films for microswitching converters because of the loss characteristics of the magnetic films.

11.9 Conclusions

The development of new soft magnetic materials with excellent characteristics of high $B_s$ of more than 1.5 T combined with high $\mu_e$ of more than $10^5$ at 1 kHz was achieved by nanocrystallization of Fe—Zr—Nb—B—Cu amorphous alloys. The Cu-free quaternary Fe$_{85.5}$Zr$_2$Nb$_4$B$_{8.5}$ alloy which exhibits high $B_s$ of 1.64 T and high $\mu_e$ of $6.0 \times 10^4$ at 1 kHz simultaneously, was also developed. In addition, it was found that the simultaneous addition of 1 at% P and 0.1 at% Cu to the Nb-poor Fe$_{85}$Nb$_6$B$_9$ alloy results in good magnetic properties of high $B_s$ of more than 1.6 T.
and high $\mu_e$ of more than $4 \times 10^4$ at 1 kHz as well as good productivity. Furthermore, the dissolution of oxygen in the remaining amorphous phase caused significant improvement of high-frequency permeability of $10^3$ in the frequency range 1 to 100 MHz by a drastic increase in $\rho_{RT}$ to $10^3 \mu \Omega m$. Considering that these characteristics had not been previously reported, nanostructure control is concluded to be a useful method for the development of new types of high functional materials. The future progress of nanostructure-controlled materials is expected to enable the fabrication of new materials exhibiting useful characteristics which have not been achieved for conventional materials.

References