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New Fe-metalloids based nanocrystalline alloys with high B_s of 1.9 T and excellent magnetic softness

Akihiro Makino,[1,a] He Men,[2] Takeshi Kubota,[1] Kunio Yubuta,[1] and Akihisa Inoue[1]
[1]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[2]*Graduate School of Engineering, Tohoku University, Sendai 980-8577, Japan*

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The melt-spun $Fe_{83.3-84.3}Si_4B_8P_{3-4}Cu_{0.7}$ alloys have a heterogeneous amorphous structure including a large amount of α-Fe-like clusters. Compared with the FeSiB alloys, the particle size rapidly decreases from several hundred nanometers to 2–3 nm due to the proper amounts of simultaneous P and Cu additions. By controlling the crystallization process, a homogeneous nanocrystalline structure composed by small α-Fe grains with size of 10–17 nm in diameter can be realized from the heterogeneous amorphous alloys. The nanocrystallized $Fe_{83.3-84.3}Si_4B_8P_{3-4}Cu_{0.7}$ alloys show the extremely high saturation magnetic flux density of 1.88–1.94 T sufficiently near to 1.97 T of Fe-3.5 mass % Si crystalline soft magnetic alloys, and exhibit low coercivity of less than 10 A/m and higher effective permeability of 16 000–25 000 at 1 kHz due to the simultaneous realization of the homogeneous nanocrystalline structure and the small magnetostriction of $(2-3)\times10^{-6}$. In addition, the nanocrystalline alloys exhibit the superior core loss to the representative $Fe_{78}Si_9B_{13}$ amorphous alloy at 50 Hz. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3058624]

INTRODUCTION

Nanocrystalline soft magnetic alloys[1–3] produced by crystallizing amorphous phases have a great potential for electromagnetic applications due to their excellent soft magnetic properties and rather high magnetic flux density. Up to now, the developed nanocrystalline soft magnetic alloys always include a large amount of metal elements such as Nb, Zr, Mo, Cu, and so forth to realize the uniform nanocrystalline structure.[4–8] During heating, an apparent short-medium range ordering[9] or a nanoscale phase separation[10] in the amorphous precursor with the metal elements acts as the nucleation site for the primary crystal and leads to the refinement of the grains. Therefore the precursor for nanocrystalline structure is needed to be an amorphous phase essentially including the metal elements, however, they cause a remarkable decrease of the saturation magnetic flux density ($\boldsymbol{B}_s$) (Ref. 11) and a significant increase of the material cost. Considering current energy problems, higher $\boldsymbol{B}_s$ accompanied with excellent magnetic softness is strongly required for the magnetic materials used in electrical power supplies. This paper intends to present new Fe-metalloids based nanocrystalline alloys with high $\boldsymbol{B}_s$ of 1.9 T and excellent magnetic softness.

EXPERIMENTAL PROCEDURE

FeSiB(PCu) alloy ingots were prepared by induction-melting mixtures of Fe (99.98 mass %), Si (99.998 mass %), B (99.5 mass %), Cu (99.99 mass %), and premelted Fe–P(99.9 mass %) in a high purity argon atmosphere. A single-roller melt-spinning method in air was used to produce the rapidly solidified ribbons with about 20 μm in thickness. The alloy compositions represent nominally atomic percent. The structure was identified by x-ray diffractometry (XRD) and transmission electron microscopy (TEM). Mean grain size of a crystalline phase was estimated by using Scherrer's equation from the full width at half maximum of the bcc (110) reflection peak from the specimens. Thermal property of melt-spun alloys was evaluated with a differential scanning calorimeter at a heating rate of 0.67 K/s under an argon flow. The melt-spun specimens were subjected to annealing for 600 s at various temperatures at a heating rate of 6.7 K/s in a vacuum atmosphere. Saturation magnetic flux density ($\boldsymbol{B}_s$) and coercivity ($\boldsymbol{H}_c$) were measured by a vibrating sample magnetometer (VSM) and a dc $\boldsymbol{B}$-$\boldsymbol{H}$ loop tracer, respectively. Effective permeability ($\boldsymbol{\mu}_e$) at 1 kHz and core loss ($\boldsymbol{W}$) at 50 Hz were measured with a vector impedance analyzer under a field of 0.4 A/m and an ac $\boldsymbol{B}$-$\boldsymbol{H}$ analyzer operated under sinusoidal input voltage, respectively, by using the wounded toroidal cores with a diameter of about 20 mm. Magnetostriction was measured by strain gauge method. Density was measured by the Archimedean method with *n*-tridecane.

RESULTS AND DISCUSSION

Figure 1 shows annealing temperature dependencies of coercivity ($\boldsymbol{H}_c$) for melt-spun $Fe_{84-y+z}Si_4B_{12-x}P_{x-y}Cu_y$ (x: 0 and 4, y: 0, and 0.7. z: 0 and 1). All the alloys were found to be completely ductile and confirmed to have heteroamorphous structures with small amounts of α-Fe particles by XRD measurement. The Cu- and/or P-added alloys exhibit the low $\boldsymbol{H}_c$ of 7–9 A/m, and the $Fe_{84}Si_4B_{12}$ alloy with rather large α-Fe grains with diameter of several 10 nm shows relatively high $\boldsymbol{H}_c$ of 15 A/m. The $\boldsymbol{H}_c$ of $Fe_{84}Si_4B_{12}$ and $Fe_{83.3}Si_4B_{12}Cu_{0.7}$ alloys monotonically increased with increasing annealing temperature due to the grain growth of

[a]Electronic mail: amakino@imr.tohoku.ac.jp.

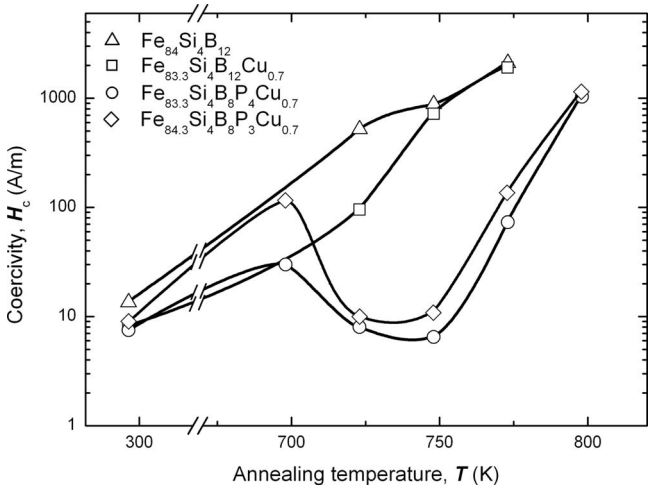

FIG. 1. Annealing temperature dependencies of coercivity ($\boldsymbol{H}_c$) for melt-spun $Fe_{84-y+z}Si_4B_{12-x}P_{x-z}Cu_y$ (x: 0 and 4, y: 0 and 0.7, z: 0 and 1) alloys.

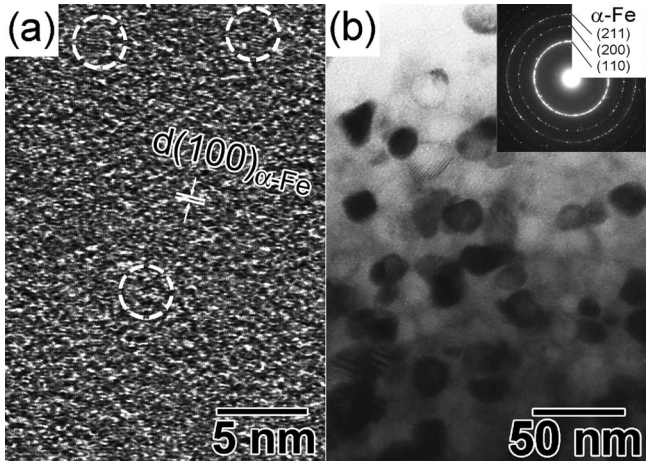

FIG. 2. TEM observation images of melt-spun $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ alloy; (a) high resolution image for a specimen at as-quenched state and (b) bright field image and SAED pattern for a specimen crystallized at 748 K.

α-Fe grains. On the contrary, the $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloys exhibited lower values than 10 A/m in the temperature range of 723–748 K within the interval ($\Delta \boldsymbol{T}$) between primary crystallization temperatures ($\boldsymbol{T}_{x1}$) and secondary one ($\boldsymbol{T}_{x2}$), which are shown in Table I. The P- and Cu-added alloys have wide $\Delta \boldsymbol{T}$ probably due to the additions, which should be favorable for forming the α-Fe structure without some compounds.

The high resolution TEM image for the as-quenched alloy revealed that the alloy is not fully amorphous, but a heteroamorphous structure consisting of an extremely small crystalline phase with 2–3 nm in diameter, randomly dispersed within the amorphous matrix as shown in Fig. 2(a). Judging from the lattice fringes as indicated by white bars, corresponding to the bcc (110) plane distance of α-Fe crystalline, the phase is revealed to be α-Fe crystal. Figure 2(b) shows a uniform nanocrystallized structure with the grain size of approximately 10 nm from the heteroamorphous phase. From the selected area electron diffraction (SAED) pattern, the crystalline phase was identified as an α-Fe phase. Almost the same nanostructure composed of α-Fe grains with diameter of about 17 nm was obtained for $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloy. The structures are very similar to the previously developed nanocrystallized alloys with excellent magnetic softness,[1,2,12,13] in spite of not containing a large amount of the metal elements. For the $Fe_{84}Si_4B_{12}$ and $Fe_{83.3}Si_4B_{12}Cu_{0.7}$ alloys without simultaneous addition of P and Cu annealed at 723 K, the coarse α-Fe grains with mean grain size of 96 and 70 nm in diameter were formed, respectively. Here, these values were estimated from XRD profiles.

TABLE I. $\boldsymbol{T}_{x1}$, $\boldsymbol{T}_{x2}$ and $\Delta \boldsymbol{T}$ for the melt-spun $Fe_{84-y+z}Si_4B_{12-x}P_{x-z}Cu_y$ (x: 0 and 0.7, y: 0 and 4, z: 0 and 1) alloys.

Composition (at%)	$\boldsymbol{T}_{x1}$ (K)	$\boldsymbol{T}_{x2}$ (K)	$\Delta \boldsymbol{T}$ (K)
$Fe_{84}Si_4B_{12}$	728	809	81
$Fe_{83.3}Si_4B_{12}Cu_{0.7}$	698	801	103
$Fe_{83.3}Si_4B_8P_4Cu_{0.7}$	669	823	154
$Fe_{84.3}Si_4B_8P_4Cu_{0.7}$	684	1820	136

It is well known that the magnetic softness for the nanocrystalline alloys strongly depends on the grain size.[14] Thus, the crystallized $Fe_{84}Si_4B_{12}$ and $Fe_{83.3}Si_4B_{12}Cu_{0.7}$ alloys consisting α-Fe grains with larger than 70 nm in diameter exhibit much higher $\boldsymbol{H}_c$ of 880 and 720 A/m than nanocrystallized $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloys consisting of α-Fe grains with 10–17 nm in diameter as shown Fig. 1. It has already been reported that Cu addition is effective for refinement of the α-Fe(Si) grains at crystallized structure.[1,2,15] However, for the FeSiB alloys with high Fe content exceeding the limit for single amorphous formation, the Cu addition is not effective enough to exhibit excellent magnetic softness. It should be noticed that the simultaneous addition of P and Cu can realize the refinement of the α-Fe grains in the crystallized structure.

We discuss on the origin of the remarkable effect of the simultaneous addition of P and Cu on the nanocrystallization. Taking account of the result that the effect is observed only for the simultaneous addition of the proper amounts of P and Cu, the mixing enthalpy ($\Delta \boldsymbol{H}$) (Ref. 16) between the constituent elements is considered. It is noted that $\Delta \boldsymbol{H}$ is positive (+13 kJ/mol) between Fe and Cu and negative (−9 kJ/mol) between Cu and P, suggesting that there are repulsive and attractive interactions existing between Fe and Cu, and Cu and P atoms, respectively. Therefore, during melt-spinning process, an extremely small region including enriched Cu and P elements could separate from the Fe–Si–B–P amorphous phase and possibly initiates the α-Fe-like clusters, which should result in the refinement of the grains. During the crystallization, large amounts of the clusters could act as the nucleation site for the α-Fe grains. Thus, uniform nanocrystalline structures were realized by crystallizing the heteroamorphous phase for $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloys, which results in extremely low $\boldsymbol{H}_c$ of 7 and 10 A/m.

Table II summarizes the grain size ($\boldsymbol{D}$) of precipitated phase and magnetic properties ($\boldsymbol{B}_s$, $\boldsymbol{H}_c$, $\boldsymbol{\mu}_e$, and $\boldsymbol{\lambda}_s$) for $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$, and nanocrystalline, amorphous, and crystalline alloys previously developed. The $\boldsymbol{B}_s$ of the nanocrystalline $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and

TABLE II. Grain size (D) and magnetic properties (B_s, H_c, μ_e, and λ_s) of $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ nanocrystalline soft magnetic alloys. Data of representative nanocrystalline, amorphous, and crystalline alloys are also shown for comparison.(Refs. 1, 2, 15, and 17–19).

Composition (at. %)	D (nm)	B_s (T)	H_c (A/m)	μ_e (at 1 kHz)	λ_s (10^{-6})
$Fe_{83.3}Si_4B_8P_4Cu_{0.7}$	10	1.88	7	25 000	2
$Fe_{84.3}Si_4B_8P_3Cu_{0.7}$	17	1.94	10	16 000	3
$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$	20	1.24	0.5	150 000	2.1
$Fe_{90}Zr_7B_3$	13	1.7	5.8	30 000	−1.1
$Fe_{85.5}Zr_2Nb_4B_{8.5}$	11	1.64	3.0	60 000	−0.1
$Fe_{82.7}Si_2B_{14}Cu_{1.3}$	22	1.85	6.5	···	···
$Fe_{78}Si_9B_{13}$	Amo.	1.53	8.0	10 000	27
Fe-3.5 mass % Si	···	1.97	41	770	6.8

$Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloys is much higher than the conventional nanocrystalline and amorphous alloys.[1,2,15,17,18] The H_c and the μ_e of these alloys are 7–10 A/m and 16 000–25 000 due to the simultaneous realization of the homogeneous nanocrystalline structure and the much smaller saturation magnetostriction (λ_s) of $(+2-3)\times10^{-6}$, which are inferior to the previous reported nanocrystalline alloys, but are much superior to the $Fe_{78}Si_9B_{13}$ amorphous and Fe-3.5 mass % Si alloys.

Core loss (W) is an important characteristic for the materials in power devices. Figure 3 shows the W at 50 Hz of the nanocrystalline $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloys as a function of maximum magnetic flux density (B_m), in comparison with the data of the optimal annealed $Fe_{78}Si_9B_{13}$ amorphous alloy. Comparing to the commercial nonoriented and the oriented Fe-3 mass % Si, W at B_m of 1 T for the nanocrystalline alloys is much smaller than those measured by using punched ring samples for the Fe–Si alloys.[17] Although the W of the nanocrystalline and the amorphous alloys increase with increasing B_m, the nanocrystalline alloys exhibit the superior W to the amorphous alloy over the whole B_m range. The rapid increase of W takes place at higher B_m of 1.7–1.8 T for the nanocrystalline alloys than that of 1.4 T for the amorphous alloy. Here, the very low W in the B_m range up to 1.7–1.8 T of the nanocrystalline alloy should be an outstanding feature never seen in the other soft magnetic materials.

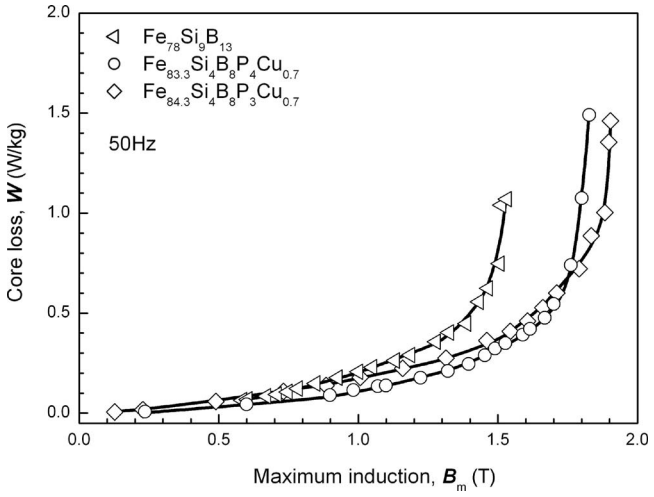

FIG. 3. Core loss (W) of nanocrystalline $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ alloys as a function of maximum magnetic flux density (B_m). The data of $Fe_{78}Si_9B_{13}$ amorphous alloy annealed at 653 K for 7.2 ks are also shown for comparison.

CONCLUSIONS

Structure and magnetic properties of the as-quenched and the crystallized Fe-rich FeSiBPCu alloys were studied. The uniform nanocrystalline structure composed of α-Fe grains is found to be realized by annealing the heteroamorphous structure with the extremely small α-Fe grains formed by an unusual effect of the simultaneous addition of P and Cu. The conclusions obtained are summarized as follows:

(1) The uniform nanocrystallized structures from the heteroamorphous alloys consist of small α-Fe grains with about 10 and 17 nm in size for $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$, respectively. With the structural change from the amorphous to the nanocrystalline structure, the B_s rapidly increases to 1.88–1.94 T.
(2) The B_s of the nanocrystalline alloys is considerably higher than those of any soft magnetic amorphous and nanocrystalline alloys previously reported.
(3) $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ and $Fe_{84.3}Si_4B_8P_3Cu_{0.7}$ nanocrystalline alloys exhibit excellent magnetic softness, H_c of 7 and 10 A/m, and μ_e of 25 000 and 16 000 at 1 kHz, due to the simultaneous realization of the uniform nanostructure composed by small α-Fe grains and small magnetostriction of $(2-3)\times10^{-6}$.

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