Magnetic properties of nanocrystalline Fe-Cu-Si-B alloys

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Abstract. Recently, nanocrystalline Fe-Cu-B and Fe-Cu-Si-B soft magnetic alloys with high saturation magnetic flux density more than 1.8 T and low coercivity of about 6 A m⁻¹ were developed by annealing melt-quenched alloys containing 1.3 -1.5 at % Cu and 0 - 7 at % Si. In this work, the magnetic properties of annealed Fe₇₇.₅₋ₓCuₓSi₁₅.₅B₇ alloys with high Si content prepared by melt spinning are reported. The appropriate Cu content in this alloy system shifted to Cu content higher than that of the reported Fe-Cu-Si-B alloys with high Bₛ. The annealed alloy with x = 2.0 showed the Hc of about 10 A m⁻¹, the B₈₀₀₀ of 1.47 T, and low magnetostriction of +4.8 x 10⁻⁶.

1. Introduction

Fe-based nanocrystalline soft magnetic materials such as Fe-Cu-Nb-Si-B and Fe-Zr-B alloys are produced by crystallizing amorphous ribbons prepared by a single roller melt spinning process, and exhibit excellent magnetic properties such as high saturation magnetic flux density (Bₛ), low coercivity (Hc), high permeability (μ), and low core loss [1][2]. Therefore, the nanocrystalline Fe-Cu-Nb-Si-B soft magnetic alloys have been widely used for industrial applications [3][4]. Recently, downsizing and energy saving have been required for electrical machinery and apparatus from an environmental standpoint. Accordingly, the demand of high Bₛ and low core loss becomes greater for soft magnetic materials. However, the Bₛ of the conventional Fe-based nanocrystalline alloys is at most 1.7 T, because they contain non-magnetic elements of from 2 to 7 atomic % such as Nb and Zr. It is well known that the substitution of Co for Fe in Fe-based nanocrystalline alloys increases Bₛ [5][6]. However, the substitution of Co for Fe increases material cost markedly. Therefore, Co-free nanocrystalline soft magnetic alloys are desirable for practical use. Recently, for these requirements, nanocrystalline Fe-Cu-B and Fe-Cu-Si-B soft magnetic alloys with high Bₛ have been developed [7][9]. These nanocrystalline alloys are fabricated by annealing melt-quenched alloys containing 1.3 -1.5 at % Cu and 0 - 7 at % Si. The as-quenched alloys consist of primary crystals, Cu clusters and amorphous matrix phase. The nanocrystalline structure of the Fe-based alloys can be obtained by annealing the quenched amorphous alloys consisting of primary crystals and Cu clusters, which act as heterogeneous nucleation sites of bcc Fe-Si grains. Thus, in these alloys, the substitution of Cu for Fe plays an important role for nanocrystalline structure and excellent soft magnetic properties. It is well known that increasing Si content in Fe-Cu-Nb-Si-B alloy decreases magnetostriction. Hence, increasing Si content appears to decrease magnetostriction and improve soft magnetic properties for Fe-Cu-Si-B alloy system. In this work, the magnetic properties and microstructure of annealed Fe-Cu-Si-B alloys prepared by melt spinning are reported.
2. Experimental procedure

Amorphous Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ ($x = 0, 0.5, 1.0, 1.35, 1.5, 2.0$) alloy ribbons were prepared by a single-roller melt spinning technique. The width and thickness of the ribbons were 5 mm and 21 $\mu$m, respectively. Toroidal core specimens with 19 mm outer diameter and 15 mm inner diameter were fabricated by winding the ribbons. These core samples were annealed to induce nanocrystallization without a magnetic field. Typical annealing conditions were at 743 K for 3.6 ks in a nitrogen gas atmosphere. D.C. B-H loops of the samples were measured with an automatic hysteresis loop tracer. Crystallization temperature was measured at a heating rate of 0.167 K s$^{-1}$ with a differential scanning calorimetry (DSC). The phases present in these alloys were identified by X-ray diffraction (XRD) using Cu-K$_\alpha$. The microstructure was observed by transmission electron microscopy (TEM).

3. Results and discussion

The Cu content dependence of $H_c$ for Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ alloys ($x = 0, 0.5, 1.0, 1.35, 1.5, 2.0$) annealed at 743 K for 3.6 ks is shown in Fig. 1. The $H_c$ for the alloys with $x = 0 - 1.5$ is larger than 200 A m$^{-1}$. However, a drastic decrease occurs between $x = 1.5$ and 2.0. The alloy with $x = 2$ shows the low $H_c$ of about 10 A m$^{-1}$. Thus, addition of Cu more than 1.5 at % is very effective to decrease $H_c$ in this alloy system, and the appropriate Cu content shifts to Cu content higher than that of the reported Fe-Cu-Si-B alloys with lower Si, higher B, and higher Fe content [7]-[9]. The $B_s$ of the alloy with $x = 2$ is 1.47 T lower than that of the reported nanocrystalline Fe-Cu-Si-B alloys with low Si content. However, this is higher than that of the conventional nanocrystalline Fe-Cu-Nb-Si-B alloys.

Figure 2 shows the dependence of $H_c$ on annealing temperature for Fe$_{75.5}$Cu$_2$Si$_{15.5}$B$_7$ alloy. The $H_c$ of the Fe$_{75.5}$Cu$_2$Si$_{15.5}$B$_7$ alloy shows the small peak around 683 K, and decreases slightly up to 743 K with annealing temperature. Thus, the $H_c$ of the Fe$_{75.5}$Cu$_2$Si$_{15.5}$B$_7$ alloy does not increase by annealing over crystallization temperature and below 743 K. However, between 743 K and 773 K, the $H_c$ increases drastically and becomes more than 2000 A m$^{-1}$ over 773 K. To clarify the behaviour on magnetic properties described above, thermal analysis and microstructure were investigated. The DSC curves for as-quenched Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ alloys are shown in Fig. 3. The crystallization temperature ($T_x$) decreases by Cu substitution. The exothermic peak for crystallization is sharp in the alloys with $x = 0 - 1.5$. On the other hand, it shifts to lower temperature and broadens in the alloy with $x = 2.0$. This suggests that a large number of crystalline nuclei form easily and the crystallization progresses slowly in the alloy with $x = 2.0$. According to a previous study [10], it is known that the Cu clustering behaviour affects the nanocrystallization and nanostructure in Fe-Cu-Nb-Si-B alloys. Hence, in this alloy system, the change of the exothermic peak due to crystallization appears to concern the formation of a large number of Cu-enriched clusters during preparing the
Figure 2. Dependence of coercivity $H_c$ on annealing temperature for Fe$_{75.5}$Cu$_2$Si$_{15.5}$B$_7$ alloy.

ribbons by a single roller melt quenching.

Figure 4 shows the XRD patterns for as-quenched Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ alloys. The XRD patterns for the as-quenched alloys with $x = 0 - 1.5$ shows hallow pattern typical to amorphous phase. On the other hand, in the alloy with $x = 2$, the small crystalline peak corresponding to bcc Fe-Si phase is seen on hallo-pattern. Accordingly, the as-quenched alloy with $x = 2$ consists of the amorphous phase as main phase and primary crystalline bcc Fe-Si phase.

The XRD patterns for the annealed Fe$_{75.5}$Cu$_2$Si$_{15.5}$B$_7$ alloys are shown in Fig. 5. From the XRD pattern for the alloy annealed at 743 K, it is considered that the alloy consists of bcc Fe-Si phase as main phase and residual amorphous phase. In addition, the peaks corresponding to ordered lattice (Fe$_3$Si) are confirmed. On the other hand, the XRD pattern for the alloy annealed at 823 K indicates that the Fe$_2$B phase with high magnetocrystalline anisotropy forms in this alloy. From the XRD results, the degradation of soft magnetic properties in the alloy annealed over 743 K appears to be mainly due to the formation of Fe$_2$B.

Figure 6 shows TEM bright field micrographs of the as-spun Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ alloys ($x = 1.0, 2.0$). The TEM image for the as-spun alloy with $x = 1.0$ shows that the alloy consists of amorphous single phase. On the other hand, from the TEM image, the as-spun alloy with $x = 2.0$ consists of an amorphous matrix phase and primary nanocrystals. The difference of a number density of crystal grains between the as-spun alloys with $x = 1.0$ and with $x = 2.0$ influences the microstructure and soft magnetic properties in the annealed alloys. However, the number of bcc grains is smaller than that of the Fe$_{83.7}$Cu$_{1.5}$B$_{14.8}$ alloys. This result suggests that the number of primary crystals decreases with increasing Si and decreasing Fe if the Cu content is comparable.

Figure 7 shows TEM bright field micrographs of the annealed Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ alloys ($x = 1.0, 2.0$). The average grain size of the alloy with $x = 2.0$ is about 20 – 50 nm smaller than that of the alloy with $x = 1.0$. The origin of the soft magnetic behaviour in nanocrystalline alloys has been theoretically explained [11], based on the so-called random anisotropy model [12]. According to this model, when the grain size is smaller than magnetic exchange length $L_x$, the origin of the soft magnetic properties in the nanocrystalline materials is ascribed to average out the magnetocrystalline anisotropy. From the TEM observation, it is concluded that the decrease $H_c$ of the alloy with $x = 2$ is mainly attributed to the decrease in grain size. However, the grain size is larger than the reported Fe- Cu-B alloys. It is suggested that the increase in grain size results from the decrease of B content in a residual amorphous matrix phase as compared with the Fe$_{83.7}$Cu$_{1.5}$B$_{14.8}$ alloys with high B content.
Fig. 3. DSC curves for as-quenched Fe\(_{77.5-x}\)Cu\(_x\)Si\(_{15.5}\)B\(_7\) alloys.

Table 1 presents the properties of various nanocrystalline and conventional Fe-based soft magnetic alloys. The nanocrystalline Fe-Cu-Si-B alloys and Fe-Cu-B exhibits high \(B_s\) of about 1.8 T, since they contain over 80 at% Fe. However, since the volume fraction of residual amorphous phase is about 50%, the \(\lambda_s\) is about one-half of Fe-based amorphous alloys. The other hand, the \(\lambda_s\) in the present Fe\(_{75.5}\)Cu\(_2\)Si\(_{15.5}\)B\(_7\) alloy is +4.8 \times 10^{-6}, which is below quarter of that in Fe-based amorphous alloys and below one-half of that in the reported nanocrystalline Fe-Cu-Si-B alloys with high \(B_s\). Thus, the increase of Si content decreases magnetostriction in the nanocrystalline Fe-Cu-Si-B alloy system.

Fig. 4. XRD patterns for as-quenched Fe\(_{77.5-x}\)Cu\(_x\)Si\(_{15.5}\)B\(_7\) alloys.
Fig. 5. XRD patterns for annealed Fe$_{75.5}$Cu$_{2}$Si$_{15.5}$B$_{7}$ alloy.

Fig. 6. TEM bright field micrographs of as-spun Fe$_{77.5-x}$Cu$_{x}$Si$_{15.5}$B$_{7}$ alloys ($x = 1.0, 2.0$).

Fig. 7. TEM bright field micrographs of annealed Fe$_{77.5-x}$Cu$_{x}$Si$_{15.5}$B$_{7}$ alloys ($x = 1.0, 2.0$).
Table 1. Properties of nanocrystalline and conventional Fe-based soft magnetic alloys.

| Alloy                          | $B_s$ (T) | $H_c$ (A m$^{-1}$) | $\rho$ ($\mu\Omega$ m) | $\lambda_s$ ($10^4$) |
|-------------------------------|----------|--------------------|------------------------|----------------------|
| Fe$_{78}$Cu$_1$Zr$_7$B$_6$    | 1.20     | 0.5                | 1.2                    | +2.1                 |
| Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ | 1.23    | 0.4                | 1.2                    | ~0                   |
| Fe$_{80.6}$Cu$_1.4$Si$_5$B$_{13}$ | 1.52   | 3.2                | 0.56                   | +1.0                 |
| Oriented Si-steel             | 2.03     | 8.0                | 0.48                   | -                    |
| Non-oriented Si-steel         | 1.96     | 4.0                | 0.57                   | +7.8                 |
| 6.5 mass % Si-Fe              | 1.80     | 4.5                | 0.82                   | +0.1                 |
| Amorphous Fe$_{78}$Si$_9$B$_{13}$ | 1.56  | 1.7                | 1.3                    | +27                  |

The $\lambda_s$ is given as the balance of the $\lambda_s$ of a residual Fe-based amorphous matrix phase (positive value) and nano-scale bcc Fe-Si grains. This appears to be due to the increase of Si content in the bcc Fe-Si grains with negative $\lambda_s$.

4. Summary

The magnetic properties and microstructure of the annealed Fe$_{77.5-x}$Cu$_x$Si$_{15.5}$B$_7$ alloys were studied. The appropriate Cu content in this alloy with high Si content shifts to Cu content higher than that of the reported high $B_s$ Fe-Cu-Si-B alloys with low Si content, higher B, and higher Fe content. The annealed alloy with $x = 2.0$ shows the $H_c$ of about 10 A m$^{-1}$ and the $B_s$ of 1.47 T. These magnetic properties arise from the formation of nano-scale bcc Fe-Si grains. In the present alloys with high Si content, Cu plays an important role for the nanostructure and soft magnetic properties after annealing, and the formation of the primary crystals and Cu clusters in the as-quenched alloys. The $\lambda_s$ of this alloy decreases below one-half of that of the reported nanocrystalline Fe-Cu-Si-B alloys with high $B_s$ more than 1.8 T.

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