Magnetic Properties of $\text{Fe}_{77.5-x}\text{Si}_{13.5}\text{B}_9\text{Cu}_x$ As-Cast Ribbons

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The $\text{Fe}_{77.5-x}\text{Si}_{13.5}\text{B}_9$ as-cast ribbons are amorphous. Without any annealing processes, partial crystallization can be obtained in Cu-doped $\text{Fe}_{77.5-x}\text{Si}_{13.5}\text{B}_9\text{Cu}_x$ as-cast ribbons. Cu addition improves the nucleation of $\alpha$-$\text{Fe(Si)}$ in the as-cast ribbons. Some soft magnetic properties of $\text{Fe}_{77.5-x}\text{Si}_{13.5}\text{B}_9\text{Cu}_x$ as-cast ribbons are measured. Results indicate that $\text{Fe}_{77.5-x}\text{Si}_{13.5}\text{B}_9\text{Cu}_x$ as-cast ribbons exhibit a saturation magnetization $\mu_0\text{Ms}$ of 1.55 T, a saturation magnetostriction $\lambda_s$ of $1 \times 10^{-6}$, and an effective permeability $\mu_{\text{eff}}$ (at 1 kHz) of 5000, which may be of potential applications in some fields. [doi:10.2320/matertrans.M2009246]

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1. Introduction

By combined addition of Nb and Cu elements to Fe-Si-B alloys, Yoshizawa et al.$^{1}$ in 1988 found that Fe-Cu-Nb-Si-B annealed nanocrystalline ribbons (FINEMET) show excellent soft magnetic properties, due to the microstructure consisting of $\alpha$-$\text{Fe(Si)}$ nanograins (about 10–12 nm) and remaining amorphous matrix. FINEMET alloys show high permeability, high saturation induction, low saturation magnetostriction and lower core loss (almost the same core loss as Co based amorphous alloys).$^{1}$ It was also showed that Fe-Cu-M-Si-B ($M = \text{Nb, Mo, Ta, W, V and Cr}$) annealed ribbons have analogous nano-structures but different sizes of $\alpha$-$\text{Fe(Si)}$ nanograins.$^{3}$ The conventional composition of FINEMET alloys is $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_1\text{Si}_{13.5}\text{B}_9$, and primary as-cast states are mainly amorphous. Extended X-ray absorption fine structure analysis (EXAFS) showed that small Cu clusters appear in $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_1\text{Si}_{13.5}\text{B}_9$ (x = 1) as-cast ribbon.$^{3}$ Investigations of high resolution transmission electron microscopy (HRTEM) and the atom-probe field ion microscopy (APFIM) indicated that in $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_1\text{Si}_{13.5}\text{B}_9$ annealed ribbons the Cu clusters possibly serve the nucleation sites for $\alpha$-$\text{Fe(Si)}$, accelerating primary crystallization.$^{4,5}$ Three-dimensional atom probe (3DAP) analysis of various stages of crystallized $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_1\text{Si}_{13.5}\text{B}_9$ alloy gave more complete information on the microstructural feature.$^{6}$ It was unambiguously showed that Cu clusters form in the amorphous state prior to the onset of the crystallization reaction. Some of Cu clusters were observed in direct contact with $\alpha$-Fe primary particles, suggesting that Cu clusters indeed serve as heterogeneous nucleation sites for the primary crystals.$^{6}$ It has been found that Nd-Fe-B hardmagnetic nanocrystalline ribbons with high performance can be prepared directly by melt-spinning technique without annealing processes.$^{7}$ We showed that Fe-Cu-Nb-Si-B nanocrystalline alloys with appropriate high Cu contents, having good soft magnetic properties, could be prepared directly by melt-spinning technique without any annealing processes.$^{8}$ Our results confirmed that Cu addition in $\text{Fe}_{74.5-x}\text{Cu}_1\text{M}_x\text{Si}_{13.5}\text{B}_9$ ($M = \text{Nb, Mo, V and Ta}$) improved the nucleation of $\alpha$-$\text{Fe(Si)}$.$^{9-11}$ Supporting the conclusions derived from microstructure observations$^{3-6}$ Lee et al.$^{12}$ recently found that as-cast Fe$_{76.4}$Si$_{13.5}$B$_{14}$TaN$_{0.1}$ nanocrystalline ribbons with good soft magnetic performance could be directly prepared by melt-spinning technique without annealing, where Ta plays a similar role like Nb, Ag atom was supposed to provide nucleation sites for $\alpha$-$\text{Fe(Si)}$

On the other hand, Ohta and Yoshizawa$^{13,14}$ recently reported that Fe$_{83.7}$Cu$_1$Si$_{13.5}$B$_{14.8}$ and Fe$_{82.7}$Cu$_1$Si$_{13.5}$B$_{14.8}$ annealed ribbons were nanostructured with bcc $\alpha$-Fe nanocrystals, and showed saturation magnetic induction $B_s$ larger than 1.8 T. By transmission electron microscopy (TEM) observation, they found that nanocrystalline grains were precipitated in Fe$_{83.7}$Cu$_1$Si$_{13.5}$B$_{14.8}$ as-cast ribbons, and suggested that the existence of primary crystals in the as-cast ribbons was necessary for the appearance of high-number-density nanocrystals in Fe-Cu-B and Fe-Cu-Si-B annealed ribbons. It was further presumed that Cu clusters helped the nucleation of primary crystals.$^{13,14}$ Chen et al.$^{15}$ observed by TEM that $\alpha$-Fe nanocrystals appeared in Fe$_{72.6}$Cu$_1$Si$_{13.5}$B$_{16.5}$ ($y = 0.2$ and 5) as-cast ribbons, and found by three-dimensional atom probe (3DAP) that Cu clusters located at the amorphous/$\alpha$-Fe interface. They suggested that Cu clusters with size of 4–6 nm served as heterogeneous nucleation sites for the $\alpha$-Fe crystals in Fe-Cu-B and Fe-Cu-Si-B alloys.

For Fe$_{73.5}$Cu$_1$Nb$_1$Si$_{13.5}$B$_9$ annealed ribbons, Nb element was found to exist in the remaining intergranular amorphous phases, which suppressed the growth of $\alpha$-$\text{Fe(Si)}$. Without addition of Nb, what happens when only Cu element adds to $\text{Fe}_{77.5}\text{Si}_{13.5}\text{B}_9$ as-cast ribbons? In the present work, influences of Cu addition on magnetic properties of $\text{Fe}_{77.5}\text{Si}_{13.5}\text{B}_9$ as-cast ribbons were investigated. X-ray diffraction results clearly indicated that the Cu addition improved the crystallization of $\alpha$-$\text{Fe(Si)}$ in Cu-doped as-cast ribbons. The $\text{Fe}_{77.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_2.5$ as-cast ribbons have a saturation magnetization $\mu_0\text{Ms}$ = 1.55 T, an effective permeability $\mu_{\text{eff}}$ (at 1 kHz) = 5000 and a saturation magnetostriction $\lambda_s$ = $1 \times 10^{-6}$, which could be of potential applications in some fields such as magnetic composite powder materials.

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2. Experiments

Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} alloys were prepared by amelting under argon atmosphere. The buttons were melted four times to ensure homogeneity. Ribbons of about 20 \(\mu\)m thickness and 2 mm width were prepared by the single roller melt-spinning technique with a wheel speed of 40 m/s. The structure of as-cast ribbons was examined by X-ray diffraction using Cu \(K\alpha\) radiation. The real permeability \(\mu_r\) at 1 kHz and 0.8 A/m was measured by the equivalent impedance method using a coil with an impedance analyzer, where toroids (Cu free) or four pieces of ribbons (Cu doped) were used to form a closed magnetic path. The inner and outer diameters of Fe\textsubscript{77.5}Si\textsubscript{13.5}B\textsubscript{9} toroids were 8 and 7.8 mm, respectively. The saturation magnetization \(\mu_0M_s\) was measured by vibrating sample magnetometer at room temperature. The measurement of effective saturation magnetization \(J_{\text{S}}\) was performed using a strain gauge method, through measuring the strains along the ribbon axis in parallel and perpendicular (in plane) fields up to 1035 kA/m.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of Fe\textsubscript{77.5-x}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons with a wheel speed \(V = 40\) m/s. The Fe\textsubscript{77.5}Si\textsubscript{13.5}B\textsubscript{9} as-cast ribbons consist of mainly amorphous structure. However, diffraction peaks of \(\alpha\)-Fe(Si) phase can be clearly observed for Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} (1 \(\leq x \leq 3.5\)) as-cast ribbons. Without any annealing processes, partial crystallization can be obtained in Cu-doped Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons. Such results strongly indicate that addition of Cu to Fe\textsubscript{77.5}Si\textsubscript{13.5}B\textsubscript{9} alloy improves the nucleation of \(\alpha\)-Fe(Si) in as-cast ribbons, similar to the cases of Fe\textsubscript{74.5-x}Cu\textsubscript{3}M\textsubscript{2}Si\textsubscript{13.5}B\textsubscript{x} (M = Nb, Mo, V and Ta) as-cast ribbons.\textsuperscript{8-11} Our results are consistent with the conclusions derived from microstructure observations on Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} annealed ribbons that Cu clusters serve the nucleation sites for \(\alpha\)-Fe(Si), accelerating primary crystallization.\textsuperscript{4,6,9} For Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} annealed ribbons, the grain size of fcc-Cu was about 5 nm, which was so small that Cu reflections were not recognized even by the selected area electron diffraction (SAD) but were detectable by the nanobeam diffraction and 3DAP methods.\textsuperscript{5} It can be assumed that Cu cluster plays the role of nucleation site in Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons, even though no diffraction peaks corresponding to fcc-Cu can be observed from X-ray diffraction patterns (Fig. 1). The concentration of Cu is very small (no more than 4%), which are dispersed in the microstructure composed of \(\alpha\)-Fe(Si) nanograins and residual amorphous phase.

It has been found that Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} as-cast ribbon consists of mainly amorphous structure,\textsuperscript{1,6,8} even though EXAFS showed that small Cu clusters appeared in the as-cast Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} (\(x = 1\)) ribbon.\textsuperscript{1} However, X-ray diffraction peaks of \(\alpha\)-Fe(Si) can be clearly observed from Fe\textsubscript{77.5}Si\textsubscript{13.5}B\textsubscript{9}Cu\textsubscript{3} (\(x = 1\)) as-cast ribbons, as shown in Fig. 1. Such results indicate that only Cu addition to Fe\textsubscript{77.5}Si\textsubscript{13.5}B\textsubscript{9} alloy accelerates the primary crystallization more effectively than the combined addition of Cu and Nb.

The grain sizes D of \(\alpha\)-Fe(Si) in Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons were estimated based on the Scherrer’s method, and results were shown in Fig. 2(a). The grain size D of \(\alpha\)-Fe(Si) is about 29 nm for \(x = 1\), and decreases to 16 nm with an increase of Cu content up to \(x = 2.5\). The appropriate Cu addition refines the grain size D of \(\alpha\)-Fe(Si). However, the grain size D becomes larger again for high Cu additions. For example, D is 31 nm for \(x = 3\) and 27 nm for \(x = 3.5\). In addition, the grain size D (about 16–31 nm) of \(\alpha\)-Fe(Si) for Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} (\(x = 1–3.5\)) as-cast ribbons are much larger than those (6–8 nm) for Fe\textsubscript{74.5-\textsubscript{x}}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} as-cast ones.\textsuperscript{8} It shows that without Nb addition, the refinement of \(\alpha\)-Fe(Si) due to the Cu addition in Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons is limited. It also suggests that Nb addition plays a role in reducing the grain size of \(\alpha\)-Fe(Si) in the as-cast ribbons. It has been found that the grain sizes of \(\alpha\)-Fe(Si) are about 10–12 nm for Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} ribbons annealed at 550°C for 1 h,\textsuperscript{13} which are even smaller than those for Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons. For the former, Hono et al.\textsuperscript{14} indicated that the element of Nb was expelled from \(\alpha\)-Fe(Si) to the intergranular amorphous phases, suppressing the growth of \(\alpha\)-Fe(Si) grains.

With an increase of Cu addition, besides the \(\alpha\)-Fe(Si), diffraction peaks of Fe\textsubscript{2}B and Fe\textsubscript{3}B phases occur gradually in Fe\textsubscript{77.5-\textsubscript{x}}Si\textsubscript{13.5}B\textsubscript{x}Cu\textsubscript{3} as-cast ribbons (see Fig. 1). Annealing at high temperatures (above 600°C) also leads to the precipitation of Fe-B phases in Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} annealed ribbons.\textsuperscript{17} For Fe\textsubscript{77.5}Cu\textsubscript{3}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} annealed ribbons, it has been found that in the process of primary crystallization, B element is also expelled from \(\alpha\)-Fe(Si) to intergranular amorphous phase.\textsuperscript{16} Fe-B phases precipitate from the B-rich
intergranular amorphous phase in the secondary crystallization. The addition of Nb retards the secondary crystallization temperature in Fe73.5Cu5Nb5Si9B9. Different from the case of Fe73.5Cu5Si13.5B9 as-cast ribbons, evident diffraction peaks of Fe-B phases were not observed in Fe74.5Cu5Si13.5B9 as-cast ribbons. 8) It means that the addition of Nb stabilizes the intergranular amorphous phase surrounding α-Fe(Si). The crystallization of amorphous Fe77.5Si13.5B9 was investigated by Zhang and Ramanujan. 16) They found that for Fe77.5Si13.5B9 ribbon, α-Fe(Si) appeared after annealing at 490°C for 1 h and Fe-B phases (Fe3B and Fe2B) occurred after annealing at 550°C for 1 h.

We measured some soft magnetic properties of as-cast Fe77.5Si13.5B9 amorphous ribbons: The saturation magnetization $\mu_0M_s$ is 1.35 T, the saturation magnetization $\lambda S$ is 38 $\times$ 10$^{-6}$, the effective permeability $\mu_{eff}$ (real permeability in experimental) at 1 kHz and 0.8 A/m is about 4800 (See Fig. 2(b)). The similar value (1.3 T) of saturation magnetization $\mu_0M_s$ of Fe77.5Si13.5B9 amorphous ribbon was previously reported. 18) As shown in Fig. 2(b), with an increase of Cu addition, there is an increase of saturation magnetization $\mu_0M_s$ for Fe77.5Si13.5B9 as-cast ribbons, due to the increasing amount of α-Fe(Si). The maximum of $\mu_0M_s$ (1.55 T) occurs at about $x = 2.5$ (Fe75Si13.5B9Cu2.5) as-cast ribbons. It is interesting to note that the saturation magnetization $\mu_0M_s$ of Fe77.5Si13.5B9 ribbon annealed at 490°C for 1 h was 1.55 T, where α-Fe(Si) phase crystallized from the amorphous ribbon. 16) It can be seen from Fig. 2(c) that with increasing Cu content, the saturation magnetostriiction $\lambda S$ of Fe77.5Si13.5B9Cu, as-cast ribbons drops at first, undergoes a minimum value ($3 \times 10^{-6}$) at $x = 2.5$, and then increases slightly. As shown in Fig. 2(d), there is an enhancement of effective permeability $\mu_{eff}$ at 1 kHz with an increase of Cu content. The maximum of effective permeability $\mu_{eff} = 5000$ at 1 kHz also occurs at $x = 2.5$ (Fe75Si13.5B9Cu2.5) as-cast ribbons, accompanying the maximum of $\mu_0M_s$ and minimum of $\lambda S$. At low Cu contents, the effective permeability $\mu_{eff}$ increases due to the combined effects of the increase of fraction of α-Fe(Si) nanograins, the decrease of their grain size D, and the reduction of saturation magnetostriiction $\lambda S$. It is now widely accepted that the change of $\lambda S$ is due to the competition among the contributions from amorphous, nanocrystalline and interfacial phases. 20,21) The reduction of positive $\lambda S$ with an increase of Cu content is due to increase amount of Fe-Fe(Si) in Fe77.5Si13.5B9Cu, as-cast ribbons, since the amorphous Fe77.5Si13.5B9 has positive $\lambda S$ but α-Fe(Si) crystals have negative $\lambda S$. Due to the same reason, the positive $\lambda S$ decreases with increasing annealing temperature up to 560°C for Fe73.5Cu5Si13.5B9 annealed ribbons. 1 The observed increase of $\mu_0M_s$ with addition of Cu content may be attributed to the increasing amount of α-Fe(Si) in as-cast ribbons. At first glance, one might attribute the drop of $\mu_0M_s$ at high Cu addition to the dilute effect, since Cu is a non-magnetic element. However, what is the mechanism of the increase of $\lambda S$ at high Cu doping? In fact, the increase of $\lambda S$ at high Cu content has been also found in Fe74.5Cu5Si13.5B9 (M = Nb, Mo, V and Ta) as-cast ribbons. 8-11) For annealed Fe74.5Cu5Si13.5B9Nb5Cu9 (x = 0, 0.5, 1 and 1.5) nanocrystalline ribbons, Ohnuma et al. 22) found that an optimal Cu content for obtaining the largest permeability was $x = 1$, corresponding to the largest effective number-density of Cu clusters. The excess Cu addition results in the coarsening of Cu clusters and the decrease of the effective number-density of Cu clusters. 22) It has been suggested that for Fe74.5Cu5Si13.5B9 as-cast ribbons, with increasing Cu content the effective number-density of Cu clusters increases at first, undergoes a maximum at an optimal Cu content, and finally decreases with excess Cu addition due to the coarsening of Cu clusters. 9-11) Similar phenomenon may also occur in Fe77.5Si13.5B9Cu as-cast ribbons. The increase of $\lambda S$ at high Cu doping may be mainly attributed to the reduction of nucleation for α-Fe(Si) originated from the coarsening of Cu clusters. The reduction of saturation magnetization $\mu_0M_s$ at high Cu dopants may be explained as the combined effects: (1) the dilution effect of non-magnetic element Cu and (2) drop of nucleation of α-Fe(Si). There are several mechanisms responsible for low effective permeability $\mu_{eff}$ for Fe77.5Si13.5B9Cu as-cast ribbons with high Cu contents: (1) the reduction of nucleation for α-Fe(Si); (2) the precipitation of Fe-B phase with larger crystalline magneto-anisotropies; (3) the increase of saturation magnetostriiction $\lambda S$ and (4) larger grain size of α-Fe(Si).
4. Conclusions

In the present work, the influence of Cu addition upon magnetic properties of Fe$_{77.5}$Si$_{13.5}$B$_9$ as-cast ribbons was investigated. The Fe$_{77.5}$Si$_{13.5}$B$_9$ as-cast ribbons are amorphous. For as-cast Fe$_{77.5}$Si$_{13.5}$B$_9$ amorphous ribbons, the saturation magnetization $\mu_0M_s$ is 1.35 T, the saturation magnetostriction $\lambda_s$ is $38 \times 10^{-6}$, the effective permeability $\mu_{eff}$ at 1 kHz and 0.8 A/m is about 4800. Without any annealing processes, partial crystallization can be obtained in Fe$_{77.5-x}$Si$_{13.5}$B$_9$Cu$_x$ as-cast ribbons. The Cu addition improves the nucleation of Fe(Si) in Fe$_{77.5-x}$Si$_{13.5}$B$_9$Cu$_x$ as-cast ribbons. The grain sizes of Fe(Si) are no less than 16 nm in Fe$_{77.5-x}$Si$_{13.5}$B$_9$Cu$_x$ ($x < 3.5$). For Fe$_{75}$Si$_{13}$B$_9$Cu$_{2.5}$ as-cast ribbons, the saturation magnetization $\mu_0M_s$ can reach 1.55 T, the saturation magnetostriction $\lambda_s$ is $1 \times 10^{-6}$, the effective permeability $\mu_{eff}$ at 1 kHz is about 5000. In addition, Fe$_{75}$Si$_{13}$B$_9$Cu$_{2.5}$ as-cast ribbons are brittle. Fe$_{75}$Si$_{13}$B$_9$Cu$_{2.5}$ as-cast ribbons having high saturation magnetization, low saturation magnetostriction and cheap cost, may be of potential applications in some fields such as composite powder materials having complex-shape.

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