Effect of Cu Addition on Soft Magnetic Properties of Fe–Zr–Si Amorphous Alloy

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The effect of Cu addition on the soft magnetic properties of Fe–Zr–Si amorphous alloy was investigated by X-ray analysis, TEM observation, and B–H curve tracer. As a melt-spun amorphous ribbon sample was annealed above the crystallization onset temperature, very fine α-Fe particles smaller than ~15 nm were precipitated and uniformly distributed in an amorphous matrix. Cu addition to Fe–Zr–Si amorphous alloy annealed above the crystallization onset temperature resulted in decreased coercivity and increased saturation magnetization and permeability. [doi:10.2320/matertrans.M2014168]

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1. Introduction

Over the past few decades amorphous and nanocrystalline Fe-based soft magnetic alloys have been widely investigated because of their superior soft magnetic properties and wide applicability.1–5 Soft magnetic alloys possess higher saturation magnetization (B_s) and permeability (μ) with lower coercivity (H_c) than crystalline alloys. Fe-based soft magnetic alloys such as FINEMET (Fe–Si–Cu–Nb–B),6,7 NANOPERM (Fe–Zr–Cu–B),7 and HITPERM ((Fe,Co)–M–B–Cu)8 have been commercialized. A common microstructure of these alloys is nanocrystalline grains that are homogeneously dispersed in amorphous matrix. In particular, the FINEMET alloy is extensively used for electronic devices, transformers, sensors, and inductors due to its high saturation magnetization over 1.2 T and lower coercivity of 0.5–1.0 A/m. Boron and niobium are key alloying elements of the FINEMET alloy that enhance the glass-forming ability (GFA) and the formation of nanocrystalline grains, but they are relatively expensive compared to other alloying elements. Therefore, some studies have investigated alternative soft magnetic alloys excluding B and Nb, and amorphous Fe–Zr–Si–Cu alloy has been highly favored.9,10 Zr addition increases the GFA, and a small amount of Cu addition improves the soft magnetic properties in amorphous Fe–Zr–Si–Cu alloys. Although previous works demonstrated the advantage of Cu addition fixed at 1.0 at%9,10 there has been little research on changes in soft magnetic properties caused by the amount of Cu addition. The present study investigates the effect of Cu addition on the soft magnetic properties of amorphous Fe–Zr–Si alloy by systematically changing the amount of Cu added.

2. Experimental Procedure

Commercial metal powders of Fe, Zr, Si, and Cu (purity greater than 99.9%) were used to prepare Fe_{79.5-x}Zr_{8.5},Si_{12}Cu_{x} (x = 0.5, 1.5, and 2.5) alloys. Weighted metal powders were mixed for 180 min and melted with an arc-melting furnace in an Ar atmosphere to produce alloy ingots. The ingots were pulverized and placed in a quartz crucible for melt spinning. Melt spun ribbon samples (about 25 μm thick and 1 mm wide) were produced using a single roller melt spinning method.11 The crystallization onset temperature (T_c) of ribbon samples was measured by differential scanning calorimetry (DSC, SDT Q600) during continuous heating at a heating rate of 0.33°C s⁻¹. Isothermal heat treatment to form nanocrystalline particles was carried out at a temperature of T_c + 50°C for 3 and 10 min. The microstructure of ribbon samples was observed by transmission electron microscopy (TEM, JEM-2010) and X-ray diffraction (XRD, RIGAKU MAX-2500) with Cu Kα radiation. The hysteresis loop and soft magnetic properties of ribbon samples were measured using a B–H curve tracer with an AC magnetic field of 1 kA m⁻¹ and a frequency of 10 kHz.

3. Results and Discussion

Figure 1 compares the XRD patterns of as-quenched Fe_{79.5-x}Zr_{8.5},Si_{12}Cu_{x} ribbon samples according to the amount of Cu added. All XRD patterns of as-quenched ribbon samples only show broad diffuse peaks due to an amorphous phase. Jia et al.12 reported that Cu addition improved the GFA and reduced the oxygen content of Fe–Co

![Fig. 1 XRD patterns of Fe_{79.5-x}Zr_{8.5},Si_{12}Cu_{x} melt-spun ribbons.](Image)
based alloy. The addition of Cu was confirmed to be effective at depressing phase separation during cooling and heating.

Figure 2 shows the DSC curves of as-quenched Fe$_{79.5-x}$Zr$_{8.5}$Si$_{12}$-Cu$_x$ ribbon samples ($x = 0.5$, 1.5, and 2.5) that were measured during continuous heating up to 690°C at a heating rate of 0.33°C s$^{-1}$. An exothermic peak appeared, indicating the crystallization onset temperature. The $T_x$ of as-quenched Fe$_{79.5-x}$Zr$_{8.5}$Si$_{12}$-Cu$_x$ ribbon samples decreased from 587 to 549°C with increasing Cu content. The two-stage crystallization behavior is typically observed in Fe-Zr-Si alloys. As shown in Fig. 2, the crystallization onset temperature related to the first crystallization step ($T_{x1}$) was only observed because the second crystallization onset temperature ($T_{x2}$) was higher than 690°C. Recently, Xue et al.$^{13}$ reported that an increase of Cu content simultaneously decreased $T_{x1}$ and increased $T_{x2}$. Their experimental results of the Cu effect on variations in crystallization onset temperature correspond with the experimental results of present work. Namely, the thermal stability of Fe-Zr-Si amorphous alloy improved with the Cu addition.

The XRD patterns of Fe$_{78}$Zr$_{8.5}$Si$_{12}$-Cu$_{1.5}$ ribbon samples annealed at 617°C are shown in Fig. 3. This is 50°C higher than its $T_x$, as indicated in Fig. 2. The three peaks of crystalline $\alpha$-Fe were exhibited at diffraction angles of 44, 65, and 82°. Similar crystalline peaks were also observed for the other annealed ribbon sample containing different Cu contents.

Figure 4 shows a TEM image with the selected area electron diffraction (SAED) pattern of the Fe$_{78}$Zr$_{8.5}$Si$_{12}$-Cu$_{1.5}$ ribbon sample annealed at 617°C for 10 min. Very fine particles smaller than ~15 nm were observed to be precipitated uniformly within the amorphous matrix. From the SAED pattern, crystalline particles were identified as the $\alpha$-Fe(Si) phase without any compound phases.

The effects of crystallization annealing and Cu addition on the hysteresis loop measured using a $B$-$H$ curve tracer with an AC magnetic field are shown in Fig. 5. Figure 5(a) shows changes in the hysteresis loop of the Fe$_{78}$Zr$_{8.5}$Si$_{12}$-Cu$_{1.5}$ ribbon sample annealed at 617°C for 10 min. Very fine particles smaller than ~15 nm were observed to be precipitated uniformly within the amorphous matrix. From the SAED pattern, crystalline particles were identified as the $\alpha$-Fe(Si) phase without any compound phases.

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is due to higher residual stress, and heat treatment relieves stress to lower the coercivity.\textsuperscript{14)} Increased coercivity or decreased permeability with longer heat treatment is reportedly related to an increase in the volume fraction of crystalline $\alpha$-Fe or increased average grain size.\textsuperscript{15,16)} Figure 5(b) shows changes in the hysteresis loop of Fe$_{79.5}$Zr$_{8.5}$Si$_{12}$-Cu ribbon samples annealed at $T_a+50^\circ C$ for 3 min according to the amount of Cu added. Coercivity decreased slightly from 75.1 A m$^{-1}$ for the sample with 0.5 at\% Cu to 72.1 A m$^{-1}$ for the sample with 1.5 at\% Cu. Saturation magnetization and permeability also increased with increasing Cu content. Improvement in the soft magnetic properties due to Cu addition is also observed in Fe–B based alloys.\textsuperscript{17)} However, by adding 2.5 at\% Cu, coercivity increased to 81.8 A m$^{-1}$ while saturation magnetization and permeability drastically decreased. Excessive Cu addition is thought to cause a sudden increase in the volume fraction of the crystalline $\alpha$-Fe phase during annealing. After considering the overall magnetic properties influenced by crystallization annealing and Cu addition, the Fe$_{79.5}$Zr$_{8.5}$Si$_{12}$-Cu$_{1.5}$ ribbon sample annealed at 617$^\circ C$ for 3 min was determined to exhibit superior soft magnetic behavior.

4. Conclusions

The effect of Cu addition on the improvement of soft magnetic properties in Fe–Zr–Si amorphous alloys was investigated. A melt-spun amorphous ribbon of the Fe–Zr–Si alloy was easily obtained by adding Cu to enhance the GFA. Annealing above $T_a$ induced $\alpha$-Fe particles smaller than $\sim$15 nm that were uniformly distributed in an amorphous matrix. It was determined that Fe–Zr–Si amorphous alloy with 1.5 at\% Cu added showed superior soft magnetic properties after annealing at $T_a+50^\circ C$ for 3 min.

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