Original Research

Effect of Co addition on crystallization and magnetic properties of FeSiBPCu alloy

Rui Xiang\textsuperscript{a}, Shaoxiong Zhou\textsuperscript{a,*}, Bangshao Dong\textsuperscript{a}, Guangqiang Zhang\textsuperscript{a}, Zongzhen Li\textsuperscript{a}, Yanguo Wang\textsuperscript{b}, Chuntao Chang\textsuperscript{c}

\textsuperscript{a}China Iron & Steel Research Institute Group, Advanced Technology & Materials Co., Ltd., Beijing 100081, China
\textsuperscript{b}Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, China
\textsuperscript{c}Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 519 Zhuangshi Road, Zhenhai District, Ningbo 315201, Zhejiang, China

Received 27 February 2014; accepted 1 October 2014
Available online 4 December 2014

Abstract

The effects of Co addition on the microstructure, crystallization processes and soft magnetic properties of \((\text{Fe}_{1-x}\text{Co}_x)_{83}\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_1\ (x=0.35, 0.5, 0.65)\) alloys were investigated. The experimental results demonstrated that the addition of Co decreased the thermal stability against crystallization of the amorphous phase, and thus improved the heat treatment temperature of this alloy. FeCoSiBPCu nanocrystalline alloys with a dispersed \(\alpha_0\)-FeCo phase were obtained by appropriately annealing the as-quenched ribbons at 763 K for 10 min. The \(\alpha_0\)-FeCo with grains size ranging from 9 to 28 nm was identified in primary crystallization. The coercivity \((H_c)\) markedly increased with increasing \(x\) and exhibited a minimum value at \(x=0.35\), while the saturation magnetic flux density \((B_s)\) shows a slight decrease. The \((\text{Fe}_{0.65}\text{Co}_{0.35})_{83}\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_1\) nanocrystalline alloy exhibited a high saturation magnetic flux density \(B_s\) of 1.68 T, a low coercivity, \(H_c\) of 5.4 A/m and a high effective permeability \(\mu_e\) of 29,000 at 1 kHz.

\(\text{©} 2014\) Chinese Materials Research Society. Production and hosting by Elsevier B.V. All rights reserved.

Keywords: Crystallization; Soft magnetic properties; Microstructure; High temperature; Nanocrystalline alloy

1. Introduction

The Fe-based and FeCo-based nanocrystalline alloys have been widely investigated both experimentally \([1–4]\) and theoretically \([5–7]\) in physics, materials science \([8–10]\), and engineering applications because of their excellent soft magnetic properties \([11–13]\), including high saturation magnetic flux density \((B_s)\), low coercivity \((H_c)\), high effective permeability \((\mu_e)\), and low core losses. To date, three famous types of nanocrystalline alloy systems have been developed, and these systems are known as Finemet \([14]\), Nanoperm \([9,15]\), and Hitperm \([16]\). The Fe content of these nanocrystalline alloys is always low because a large amount of metal and metalloid elements, such as Nb, Zr, B, P, and Si, are added to prepare amorphous precursors and ensure a uniform nanocrystalline structure \([2,17]\). Therefore, high Fe content (above 80 at%), Fe-based, nanocrystalline, soft magnetic alloys are desirable for practical use. As a ferromagnetic element, it is well known that a high \(B_s\) can be obtained in FeCo-based nanocrystalline alloys via the substitution of ferromagnetic element Co for Fe in Fe-based nanocrystalline alloys \([18]\). Previously, researchers have developed FeSiBCu and FeSiBPCu softmagnetic alloys with high magnetic flux densities of approximately 1.8 T and 1.9 T, respectively \([19]\). It has been found that the marked improvement in the soft magnetic behavior is due to the reduction of the effective magnetic anisotropy, which occurs when the sizes of the nano-crystals become comparable with the magnetic exchange length \([20,21]\). These findings prompted us to consider whether the substitution of Co for Fe would improve

http://dx.doi.org/10.1016/j.pmse.2014.10.002
1002-0071/© 2014 Chinese Materials Research Society. Production and hosting by Elsevier B.V. All rights reserved.
the soft magnetic properties and thermal stability of FeSiBPCu nanocrystalline alloys, thereby permitting the formation of nanocrystalline alloys. Although the Co element may increase the cost of this alloy, it is very interesting to study the effect of Co addition on the microstructure, crystallization behavior, and magnetic properties of the amorphous and nanocrystalline phases.

Therefore, in this paper, Co was substituted for Fe in the FeSiBPCu amorphous alloy system. The FeCo at% is 83%, and the present FeCoSiBPCu glassy alloys are the so-called high Fe-content ones. Soft magnetic properties including the saturation magnetic flux density, coercivity, and permeability were investigated, and the grain size of the nano-scale crystalline phases with varying Co content were also studied.

2. Materials and methods

FeCoSiBPCu alloy ingots were prepared by arc melting mixtures of Fe (99.99% by mass), Co (99.99% by mass), Si (99.99% by mass), B (99.9% by mass), Cu (99.99% by mass), and pre-melted Fe3P (99.9% by mass) in a highly purified Ar atmosphere. Amorphous (Fe1−xCo0.83)Si4B8P4Cu1 (x = 0.35, 0.5, 0.65) alloy ribbons were produced via single-roller melt spinning. The width and thickness of the ribbons were approximately 1.5 mm and 20 μm, respectively. The chemical composition of the ribbon was checked using inductively coupled plasma spectroscopy, and no detectable deviation from the nominal composition was observed. The structures of the as-quenched and annealed ribbons were identified by X-ray diffraction (XRD) with Cu Kα radiation and transmission electron microscopy (TEM). The thermal stability of the as-quenched ribbons was evaluated using differential scanning calorimetry (DSC) at the heating rate of 0.67 K/s. A crystallization treatment was applied by treating the as-quenched amorphous specimens at different temperatures for 10 min under vacuum, followed by water quenching. The average grain sizes were estimated by using Scherrer’s equation and the distribution of the grain size was obtained by analyzing more than 100 spots with statistical analysis in software Gatan Digital Microscopy Suite. The saturation magnetic flux density (B0) and coercive force (Hc) were measured under applied fields of 800 kA/m and 1 kA/m using an impendence analyzer (VSM) and a dc B–H loop tracer. The effective permeability (μe) at 1 kHz was measured under a field of 1 A/m using a vector impedance analyzer. All property measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the (Fe1−xCo)xSi4B8P4Cu1 (x = 0.35, 0.5, 0.65) as-quenched ribbons, demonstrating the microstructural evolution of the alloy as a function of Co composition. All XRD spectra show one broad peak, signifying an amorphous structure in the as-quenched state. The DSC curves measured at a heating rate of 0.67 K/s in a high-purity Ar flow for the as-quenched (Fe1−xCo)xSi4B8P4Cu1 (x = 0.35, 0.5, 0.65) ribbons are shown in Fig. 2. It is clear that the replacement of Fe by Co brings about a change in the crystallization behavior. It can be observed that the crystallization process of these ribbons occurred in two stages: in the first stage, partial transformation from the amorphous phase to the nanocrystalline α’-FeCo phase occurred, and in the second stage, complete crystallization of the remaining amorphous phase occurred. It may be noted that the initial crystallization onset temperature (T1) for (Fe0.65Co0.35)xSi4B8P4Cu1, (Fe0.5Co0.5)xSi4B8P4Cu1, and (Fe0.35Co0.65)xSi4B8P4Cu1 are 677 K, 690 K, and 730 K, respectively. However, the second crystallization onset temperatures (T12) are found to be 841 K, 849 K, and 854 K, respectively. With the additions of Co, the temperature interval ∆H(T12−T1) enlarges compared with no Co content alloys [19]. Hence, in this alloy system, the Co addition leads to a significant increase in both the initial crystallization onset temperature (T1) and the second crystallization onset temperatures (T12). Thus, Co addition reduces the thermal stability against crystallization of the amorphous phase and improves the heat treatment temperature for this alloy.
The annealing temperature ($T_a$) dependence of $H_c$ for the as-quenched ($\text{Fe}_{1-x}\text{Co}_x\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_1$ ($x=0.35, 0.5, 0.65$) alloy ribbons is shown in Fig. 3. For all alloys, $H_c$ first decreases gradually with $T_a$ up to 663 K (below $T_{x1}$) and then gradually increases. All $H_c$ have two minimum values around 663 K and 763 K. When $T_a$ is elevated to above 763 K, $H_c$ keeps slightly an increase before 803 K. For all the alloys, $H_c$ decreases at low temperature below $T_{x1}$ because the internal stress releases in the amorphous state. When $T_a$ is elevated to the vicinity of $T_{x1}$, a small amount of $\alpha'$-FeCo grains begin to precipitate from the amorphous phase, which causes the obvious increase of $H_c$. At higher temperatures just above $T_{x1}$, a large number of fine $\alpha'$-FeCo grains can form, and the increase in the number and volume fraction of nanocrystallines allows the exchange coupling between grains. That is the reason for their low values of $H_c$ at 763 K. Annealing at temperatures much higher than $T_{x1}$ leads to the precipitation of other compounds and the subsequent rapid growth of these crystals, which significantly degrade the soft magnetic properties. Therefore, $H_c$ finally increases sharply to a much higher value. The best soft magnetic properties among the ($\text{Fe}_{1-x}\text{Co}_x\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_1$ alloys was achieved when the alloys were annealed at 763 K for 10 min. Therefore, the optimum annealing treatment was determined to be at 763 K for 10 min.

Fig. 4 shows the XRD patterns of the ($\text{Fe}_{1-x}\text{Co}_x\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_1$ alloys annealed at 763 K for 10 min. It can be clearly observed from Fig. 6(a) that for the ($\text{Fe}_{1-x}\text{Co}_x$)$_{83}$Si$_4$B$_8$P$_4$Cu$_1$ alloy, the precipitated nanocrystalline grains were 9.25 nm and 11 nm was observed, and these grains were homogeneously distributed. However, the TEM image for the ($\text{Fe}_{0.35}\text{Co}_{0.65}$)$_{83}$Si$_4$B$_8$P$_4$Cu$_1$ alloy showed a uniform nanocompound structure with a fine grain size of approximately 27.8 nm. The grain size distribution of the alloy with $x=0.35$ was more uniform, and the number density was much higher than that of the alloy containing more Co. The nanocrystalline structure is nearly in agreement with the value estimated from the XRD profile of a homogeneous nanocrystalline structure. The results indicate that the Co addition helps increase the grain size in the studied alloy compositions. This increase would push the average magnetocrystalline anisotropy toward zero, as explained by the random anisotropy model [22].

Fig. 6(a)–(c) shows the Co-content dependence of the effective permeability ($\mu_e$), saturation magnetic flux density ($B_s$), and coercivity ($H_c$), respectively, for the ($\text{Fe}_{1-x}\text{Co}_x$)$_{83}$Si$_4$B$_8$P$_4$Cu$_1$ alloys annealed at 763 K for 10 min. It can be clearly observed from Fig. 6(a) that $\mu_e$ decreased from 29,200 to 21,700 as the Co content increased from $x=0.35$ to $x=0.65$. Meanwhile, $H_c$ changed in the opposite manner, as shown in Fig. 6(c); as the Co content increased from $x=0.35$ to $x=0.65$, $H_c$ increased from 5.4 to 11.9 A/m. According to the random anisotropy model [20], the soft magnetic properties of nanocrystalline materials are ascribed to the averaging-out of the magneto crystalline anisotropy due to the random distribution of the nanoscale grains. From the perspective of molecular basis, when Co was substituted for Fe in this nanocrystalline, Co partly dissolved into $\alpha'$-Fe crystallization phase, which result in $\alpha'$-FeCo crystallization phase formation. Since Co atomic radius is smaller than Fe, the substitution of Co for Fe could weakens the Cu clusters that act as nucleation sites for the formation of primary crystals during the melt-spinning process, which will result in the increase in grain size of the

---

Fig. 4. XRD patterns for the annealed ($\text{Fe}_{1-x}\text{Co}_x\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_1$ ($x=0.35, 0.5, 0.65$) alloy ribbons.

Fig. 6 (a)–(c) shows the Co-content dependence of the effective permeability ($\mu_e$), saturation magnetic flux density ($B_s$), and coercivity ($H_c$), respectively, for the ($\text{Fe}_{1-x}\text{Co}_x$)$_{83}$Si$_4$B$_8$P$_4$Cu$_1$ alloys annealed at 763 K for 10 min. It can be clearly observed from Fig. 6(a) that $\mu_e$ decreased from 29,200 to 21,700 as the Co content increased from $x=0.35$ to $x=0.65$. Meanwhile, $H_c$ changed in the opposite manner, as shown in Fig. 6(c); as the Co content increased from $x=0.35$ to $x=0.65$, $H_c$ increased from 5.4 to 11.9 A/m. According to the random anisotropy model [20], the soft magnetic properties of nanocrystalline materials are ascribed to the averaging-out of the magneto crystalline anisotropy due to the random distribution of the nanoscale grains. From the perspective of molecular basis, when Co was substituted for Fe in this nanocrystalline, Co partly dissolved into $\alpha'$-Fe crystallization phase, which result in $\alpha'$-FeCo crystallization phase formation. Since Co atomic radius is smaller than Fe, the substitution of Co for Fe could weakens the Cu clusters that act as nucleation sites for the formation of primary crystals during the melt-spinning process, which will result in the increase in grain size of the...
Fig. 5. TEM bright field images, SAED patterns and grain size distributions of the melt-spun \((\text{Fe}_{1-x}\text{Co}_x)_{83}\text{Si}_{4}\text{B}_{8}\text{P}_{4}\text{Cu}_{1})\) alloy ribbons annealed at 763 K for 10 min (a) \(x=0.35\), (b) \(x=0.5\) and (c) \(x=0.65\).
nanocrystals with increase in Co content. The coercivity and permeability are expected to roughly vary with the grain size as $H_c \propto D^6$ and $\mu \propto 1/D^6$, respectively. In the (Fe$_{0.35}$Co$_{0.65}$)$_8$Si$_4$B$_8$P$_4$Cu$_1$ alloy, as shown in Fig. 5(c), $D$ is greater than 27 nm. Because of the rather large grain size, the $H_c$ for this alloy is as large as 11.9 A/m. As the Co content decreases, $D$ decreases drastically, and the alloys begin to exhibit a fine nanocrystalline structure, which leads to a drastic decrease in $H_c$. The permeability is proportional to $D^{-6}$, and the (Fe$_{0.65}$Co$_{0.35}$)$_8$Si$_4$B$_8$P$_4$Cu$_1$ alloy has the smallest value of $D$, which explains why the (Fe$_{0.65}$Co$_{0.35}$)$_8$Si$_4$B$_8$P$_4$Cu$_1$ alloy exhibits the maximum value of $\mu_r$. Furthermore, from Fig. 6(b), it can be observed that $B_s$ decreases from 1.68 to 1.58 T as the Co content increases from $x=0.35$ to $x=0.65$. This trend occurs because of the microstructure change from an amorphous to a crystalline structure caused by the precipitation of $\alpha'$-FeCo and the changing volume fraction of the nanocrystalline phase. $B_s$ varies in proportion to the volume fraction of the nanocrystalline phase and $x=0.35$ alloy has the largest volume fraction of the nanocrystalline phase value, which result in the saturation magnetic flux density' change.

Here, we discuss the effect of Co addition on the crystallization behavior, microstructure and magnetic properties. According to recent studies, the existence of primary crystals in the as-quenched state is necessary for uniform nano-compound structure alloys, such as FeSiBCu and FeSiBPCu [18,21]. In the FeSiBPCu nanocrystalline alloy, Cu clusters form prior to nano-crystallization, leading to an increase in the local concentration of Fe in the vicinity of these clusters and the formation of bcc-Fe crystals. However, in this FeCo-SiBPCu alloy system, especially in Co-rich alloys, Co addition result in crystallization different from the FeSiBPCu nanocrystalline alloy [23–26]. The formation of a nanocrystalline $\alpha'$-FeCo phase and the increasing average grain sizes of $\alpha'$-FeCo with increasing Co content show that the Cu clusters do not act as nucleation sites for the primary crystal formation, which demonstrates that Cu is not needed for nanocrystallization in this Co-rich nanocrystalline alloy. Traditional nanocrystalline alloys are mainly due to the formation of $\alpha$-Fe (Si) or $\alpha$-Fe phases, which have good soft magnetic properties. However, because of the precipitation of $\alpha'$-FeCo phases, there is no need for the additional Cu in the Co-containing nanocrystalline alloys that will have good soft magnetic properties. Therefore, the addition of Co is effective at facilitating the formation of primary crystals during the melt-spinning process. During crystallization, large amounts of the clusters could act as nucleation sites for $\alpha'$-FeCo grains, which presumably results in an increase in $\alpha'$-FeCo grain size and the improvement of the soft magnetic properties of the nanocrystalline alloys.

4. Conclusions

In the present work, the microstructure, crystallization behavior and soft magnetic properties for (Fe$_{1-x}$Co$_x$)$_8$Si$_4$B$_8$P$_4$Cu$_1$ nanocrystalline alloys with the Co addition ranging from $x=0.35$ to $x=0.65$ have been systemically studied and results are summarized as follows: FeCoSiBPCu nanocrystalline alloys with a dispersed $\alpha'$-FeCo phase were obtained by appropriately annealing the as-quenched ribbons at 763 K for 10 min. The phase produced by primary crystallization was identified as $\alpha'$-FeCo, with grains ranging in size from 9 to 28 nm. Soft magnetic properties, such as a low $H_c$ of approximately 5.4 A/m, a high $B_s$ of 1.68 T and a high $\mu_r$ of 29,000 at 1 kHz, were obtained in the alloy with $x=0.35$. In the present alloy system, the substitution of Co for Fe can improve the heat treatment temperature and contributes to the precipitation of the $\alpha'$-FeCo phase, which weakens the Cu clusters that act as nucleation sites for the formation of primary crystals during the melt-spinning process.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 51341002) and the National Scientific and Technological Support Program (Grant no. 2013BAE08B01).

References