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Structural and Magnetic Properties of P Microalloyed Fe$_{76}$Cu$_{0.8}$Nb$_{2.2}$B$_9$Si$_{12}$ Alloys

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Abstract: The development of Fe-based nanocrystalline alloys with high saturation magnetization ($B_s$), excellent magnetic softness and good manufacturability is highly desirable. Here, the effect of substituting 1 at% P for B and Si on the thermal stability, microstructure and magnetic properties of Fe$_{76}$Cu$_{0.8}$Nb$_{2.2}$B$_9$Si$_{12}$ alloy has been studied in detail. It was found that replacing B with P effectively reduces the coercivity ($H_c$) of the alloy without deteriorating the $B_s$ and permeability ($\mu$). However, replacing Si with P has little effect on the $H_c$ and $B_s$, yet significantly reduces the $\mu$. The variation in the magnetic properties can be well understood from the evolution of the microstructure and magnetic anisotropy induced by P microalloying. The Fe$_{76}$Cu$_{0.8}$Nb$_{2.2}$B$_9$Si$_{12}$ alloy with a good processing window, a high $B_s$ of 1.41 T, a great $\mu$ of 29,000 at 1 kHz and a low $H_c$ of 0.6 A/m is suitable for high-power electronic devices.

Keywords: nanocrystalline alloys; microstructure; magnetic properties; microalloying; magnetic anisotropy

1. Introduction

Fe-Si-B-Nb-Cu nanocrystalline alloys first, demonstrated by Yoshizawa et al. in 1988 [1], have been the most widely studied and used nanocrystalline soft magnetic alloys. The nanocrystalline soft magnetic alloys have an amorphous/nanocrystalline dual-phase structure, comprising α-Fe(Si) crystallites of less than 20 nm in diameter, uniformly embedded in a residual amorphous matrix that is approximately 1–2 nm thick [2–4]. This structure possesses large magnetization, small magnetocrystalline anisotropy and low magnetostrictive coefficient, which makes the Fe-Si-B-Nb-Cu nanocrystalline alloys present high permeability ($\mu$) and ultra-low coercivity ($H_c$) values [5–7]. However, the Fe-Si-B-Nb-Cu alloys currently in commercial use (named Finemet, with a typical composition of Fe$_{73.5}$Si$_{13.5}$B$_8$Nb$_3$Cu$_1$) have a low saturation magnetization ($B_s$) of around 1.24 T, which struggles to meet the development needs of the miniaturization and high power of electronic devices.

Increasing the quantity of Fe and Co elements is the most effective way to increase the $B_s$ of Fe-based nanocrystalline alloys [8–11]. In addition, reducing the content of non-magnetic metallicoids [12], large early transition metals (Nb, Mo, Zr, etc.) [13–16] and post-transition metals such as Cu [17,18] is also beneficial to improve $B_s$. However, a high content of ferromagnetic elements usually leads to an increase in the magnetic anisotropy and a decrease in the amorphous-forming ability, which would deteriorate the soft magnetic properties of Fe-based nanocrystalline alloys [6,13,19]. Several studies have attempted to increase $B_s$ without degrading the soft magnetic properties and amorphous-forming
ability of the nanocrystalline alloys with high Fe content by microalloying P [20,21], Al [22], Nb [10,23], Sn [24], Mo [25–27] and C [28]. Among them, P has less negative impact on $B_s$ than early transition metals such as Nb [29], and is more effective than metalloids such as B [30] and Si [31] in inhibiting the growth of $\alpha$-Fe(Si) grains.

Recently, we fabricated an Fe$_{76}$Cu$_1$Nb$_2$B$_8$Si$_{13}$ nanocrystalline alloy with good soft magnetic properties and manufacturability [10,32]. However, the low $\mu$ limits its application. It was found that the addition of Mn effectively enhances the high-frequency permeability of the alloy, but reduces $B_s$, and requires a harsh rapid heating annealing process [33]. In addition, P microalloying also improves the $\mu$ of the alloy. However, the optimal annealing temperature range for this P-doped alloy is narrow and the corresponding annealing time is short (10 min) [21]. Therefore, the manufacturability of these alloys needs to be further improved for large-scale production.

It was reported that the optimized Cu content required for nanocrystalline alloys with high Fe content to obtain the highest $\mu$ is about 0.6 at% [18]. Based on this work, we have recently optimized the composition of Fe$_{76}$Cu$_1$Nb$_2$B$_8$Si$_{13}$ alloy, and unexpectedly found that the annealing window of Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$ alloy is very wide, that is, the difference between the first and second onset crystallization temperatures is as high as 207 °C and the annealing time can be as long as 1 h or more. Unfortunately, although the $\mu$ of the Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$ alloy is as high as 29,000 at 1 kHz, the coercivity $H_C$ is larger than 3 A/m, which would lead to high hysteresis loss [3].

The aim of this work is to evaluate the effectiveness of P microalloying in reducing the $H_C$ without decreasing the $B_s$ and $\mu$ of the Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$ alloy, and to reveal why slight changes in P, B and Si contents have a significant impact on the soft magnetic properties of the alloy. It was found that although the addition of 1 at% P significantly reduces the annealing temperature range of the alloy, it still has greater manufacturability than that of the Mn-doped and P-doped Fe$_{76}$Cu$_1$Nb$_2$B$_8$Si$_{13}$ alloys. In addition, substituting 1 at% P for B and Si has significantly different effects on the microstructure and magnetic properties of the alloys. We have explored this interesting phenomenon by studying the evolution of microstructure and magnetic anisotropy. The developed Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$P$_1$ alloy exhibits a high $B_s$ of 1.41 T, a great $\mu$ of 29,000 at 1 kHz and a low $H_C$ of 0.6 A/m, making it suitable for high-power electronic devices.

2. Experimental

Master alloy ingots with nominal compositions of Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$, Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$P$_1$ and Fe$_{76}$Cu$_{0.8}$Nb$_2$B$_8$Si$_{12}$P$_1$ (at%) were prepared by induction melting with highly pure raw materials of Fe (99.99 wt%), Cu (99.99 wt%), Nb (99.99 wt%), B (99.95 wt%), Si (99.99 wt%) and pre-alloyed FeP (99.99 wt%) under a pure argon atmosphere. Melt-spun ribbons with a thickness of approximately 27–30 µm and a width about 1 mm were produced by a single-roller melt-spinning method with a copper roller speed of 35 m/s in an argon atmosphere. Nanocrystalline ribbons were prepared by annealing the melt-spun ribbons at 510–590 °C for 60 min in an isothermal tube annealing furnace (Shanghai Y-feng electrical furnace Co., Ltd., Shanghai, China) under a vacuum degree of 5 × 10$^{-3}$ Pa followed by water quenching.

Thermal parameters, including the onset crystallization temperatures of the melt-spun ribbons, were evaluated by differential scanning calorimetry (DSC, NETZSCH 404C, Selb, Germany) at a heating rate of 0.67 °C/s under high-purity argon flow. Magnetic properties such as $B_s$, $H_C$ and $\mu$ were measured by a vibrating sample magnetometer (VSM, Lakeshore 7410, Columbus, OH, USA) under a maximum applied field of 800 kA/m, a DC B-H loop tracer (EXPH-100, Riken Deshi Co., Ltd., Saitama, Japan) under a maximum applied field of 800 A/m and an HP4294A impedance analyzer with a frequency from 1 kHz to 110 MHz in a field of 1 A/m, respectively. The amorphous structure of the melt-spin ribbons and the precipitates of the annealed ribbons were identified by X-ray diffraction (XRD, Bruker D8 Advance, Karlsruhe, Germany) with Cu-Kα radiation and transmission electron microscopy (TEM, TF20, Hillsboro, OR, USA).
3. Results and Discussion

Figure 1 shows the XRD patterns of the melt-spun Fe\textsubscript{76}Cu\textsubscript{0.8}Nb\textsubscript{2.2}B\textsubscript{9}Si\textsubscript{12}, Fe\textsubscript{76}Cu\textsubscript{0.8}Nb\textsubscript{2.2}B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1} and Fe\textsubscript{76}Cu\textsubscript{0.8}Nb\textsubscript{2.2}B\textsubscript{9}Si\textsubscript{11}P\textsubscript{1} ribbons. For convenience, we abbreviate the chemical formulas of the above alloys as B\textsubscript{9}Si\textsubscript{12}, B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1} and B\textsubscript{9}Si\textsubscript{11}P\textsubscript{1}, respectively. The melt-spun ribbons have typical diffraction peaks of an amorphous structure, that is, broad diffuse reflection peaks, and no sharp crystal diffraction peaks can be seen. The fully amorphous structure of the 30 μm thick ribbons indicates the good amorphous-forming ability of the present alloys, which is beneficial to obtain homogeneous and fine nanocrystalline grains [2].

![Figure 1. XRD patterns of melt-spun Fe\textsubscript{76}Cu\textsubscript{0.8}Nb\textsubscript{2.2}B\textsubscript{9}Si\textsubscript{12} (B\textsubscript{9}Si\textsubscript{12}), Fe\textsubscript{76}Cu\textsubscript{0.8}Nb\textsubscript{2.2}B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1} (B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1}) and Fe\textsubscript{76}Cu\textsubscript{0.8}Nb\textsubscript{2.2}B\textsubscript{9}Si\textsubscript{11}P\textsubscript{1} (B\textsubscript{9}Si\textsubscript{11}P\textsubscript{1}) ribbons.](image)

Figure 2 shows the DSC curves of the melt-spun B\textsubscript{9}Si\textsubscript{12}, B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1} and B\textsubscript{9}Si\textsubscript{11}P\textsubscript{1} ribbons. All ribbons have two distinct exothermic peaks, and the first and second crystallization peaks represent the precipitation of α-Fe(Si) and Fe-boride phases, respectively [21,33]. The difference between the first and second onset crystallization temperatures (ΔT = T\textsubscript{x2} − T\textsubscript{x1}) of the B\textsubscript{9}Si\textsubscript{12} ribbon is as high as 207 °C, which is much greater than that of the previously developed Fe\textsubscript{76}Cu\textsubscript{1}Nb\textsubscript{2}B\textsubscript{9}Si\textsubscript{13} (163 °C) alloy [10]. It should be pointed out that the DSC results of the ribbons obtained by re-preparing the master alloy all confirm that the ΔT of B\textsubscript{9}Si\textsubscript{12} is 207 ± 2 °C. The large ΔT can extend the processing window, so that single α-Fe(Si) nanocrystalline grains can be formed in a wider annealing temperature range and a longer annealing time [2]. It is clearly seen that the addition of 1 at% P has little effect on T\textsubscript{x1}, whereas it significantly decreases T\textsubscript{x2}, resulting in the ΔT of B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1} and B\textsubscript{9}Si\textsubscript{11}P\textsubscript{1} alloys decreasing to 158 °C and 149 °C, respectively. The phenomenon that P doping leads to a decrease in T\textsubscript{x2} is consistent with previous results [13,20,21]. It is reasonable to deduce that since the mixing enthalpy of P and B is positive (0.5 kJ/mol [34]), when P and B are excluded from the α-Fe(Si) grains during crystallization, the mutual repulsion of P and B may promote the precipitation of Fe-B phase, resulting in the decrease in T\textsubscript{x2}. Nevertheless, the ΔT of B\textsubscript{9}Si\textsubscript{12}P\textsubscript{1} is still larger than that of typical Finemet alloys (140 °C) [35], and recently developed Fe\textsubscript{73}Cu\textsubscript{1}Nb\textsubscript{2}B\textsubscript{9}Si\textsubscript{13}Mn\textsubscript{3} (149 °C) [33], Fe\textsubscript{76}Cu\textsubscript{1}Nb\textsubscript{2}B\textsubscript{9}Si\textsubscript{13}P\textsubscript{1} (152 °C) and Fe\textsubscript{76}Cu\textsubscript{1}Nb\textsubscript{2}B\textsubscript{9}Si\textsubscript{13}Mo\textsubscript{0.5} (151 °C) alloys [21], implying the good annealing process window of the present alloys.
ample, in the FeSi content also has a remarkable effect on the netoelastic anisotropy of Fe

The reduced $H_{c}$ of $B_8Si_{12}P_1$ increases significantly. This result may originate from the reduced $\Delta H_c$ of the P-doped alloys, which easily precipitate Fe-boride compounds with high magnetocrystalline anisotropy during high-temperature and long-term annealing [3]. Nevertheless, the $H_c$ of $B_8Si_{12}P_1$ in the annealing temperature range of 510–570 °C is less than 2 A/m, which is advantageous compared with the $B_9Si_{12}$ and $B_9Si_{11}P_1$ alloys.

Figure 4 shows the $\mu$ of the melt-spun $B_9Si_{12}$, $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ ribbons as a function of annealing temperature. The $\mu$ was obtained by measuring the magnetic spectrum of the 50 mm long ribbons by an HP4294A impedance analyzer in a field of 1 A/m. The $\mu$ of $B_9Si_{12}$ increases gradually with the increase in annealing temperature, reaching 29,000 at 590 °C. The $\mu$ of $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ first increases and then decreases with increasing annealing temperature. However, $B_8Si_{12}P_1$ has a $\mu$ comparable to that of $B_9Si_{12}$ in the temperature range of 510–570 °C, while the $\mu$ of $B_9Si_{11}P_1$ is very low, less than 18,000. Except for $B_8Si_{12}P_1$, the $\mu$ of $B_9Si_{12}$ and $B_9Si_{11}P_1$ does not change inversely to the $H_c$. Similar phenomena can also be found in other nanocrystalline alloy systems [22,36]. It is well known that the magnetoelastic anisotropy of Fe-Cu-Nb-B-Si nanocrystalline alloys is sensitive to Si content, which significantly affects the $\mu$ of the alloys. When the Si content is around 15 at%, the magnetoelastic anisotropy of the alloys is close to zero [36]. Moreover, a slight

Figure 2. DSC curves of melt-spun $B_9Si_{12}$, $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ ribbons at a heating rate of 0.67 °C/s. $T_{x1}$ and $T_{x2}$ denote the first and second onset crystallization temperatures, respectively. $\Delta T = T_{x2} - T_{x1}$, reflecting the annealing temperature range for obtaining single fine nanocrystalline grains.
change in Si content also has a remarkable effect on the μ of nanocrystalline alloys [36,37]. For example, in the Fe-Si-B-P-Cu system, the μ of alloys that differ only by 1 at% Si differs by more than 3000. Therefore, B₉Si₁₁P₁ with less Si content has a smaller μ than B₈Si₁₂ and B₈Si₁₂P₁, which may be related to the increased magnetoelastic anisotropy [3,36].

Figure 3. \( H_c \) of B₉Si₁₂, B₈Si₁₂P₁ and B₉Si₁₁P₁ ribbons as a function of annealing temperature. The annealing time is 60 min.

Figure 4. \( \mu \) of B₉Si₁₂, B₈Si₁₂P₁ and B₉Si₁₁P₁ ribbons at 1 kHz as a function of annealing temperature. The annealing time is 60 min.

Figure 5 shows typical hysteresis loops of the B₉Si₁₂, B₈Si₁₂P₁ and B₉Si₁₁P₁ ribbons after annealing at 550 °C for 60 min. The \( B_s \) of the samples (a total of eight 3 mm long ribbons) was obtained by a VSM at a maximum field strength of 800 kA/m. All samples show a slender hysteresis loop, and the curves have a high slope under a small applied magnetic field, typical characteristics of soft magnetic materials. The \( B_s \) values of the annealed B₉Si₁₂, B₈Si₁₂P₁ and B₉Si₁₁P₁ ribbons are 1.36 T, 1.41 T and 1.42 T, respectively, implying that the substitution of 1 at% P for metalloids has little effect on the \( B_s \) of the alloys. Therefore, the above results demonstrate the effectiveness of P microalloying in reducing the \( H_c \) without decreasing the \( B_s \) and \( \mu \) of the Fe₇₆Cu₁₀₈Nb₂₂B₉Si₁₂ alloy. In addition, the annealing time can be over 60 min in the optimal temperature range of 510–570 °C, indicating the good annealing process window of the alloys. Compared with the previously reported Fe₇₆Cu₁₁Nb₂B₈Si₁₃ [10,32], Fe₇₆₋ₓCu₁₁Nb₂B₈Si₁₃Mnx [33], Fe₇₆Cu₁₁Nb₂B₇Si₁₃P₁
and Fe₇₆Cu₁₁Nb₁₂₅B₈Si₁₃Mo₀₅ alloys [21], the present Fe₇₆Cu₁₁₂₅Nb₂₂₂B₈Si₁₂P₁ alloy has better annealing processability and superior overall magnetic properties.

According to Herzer’s random anisotropy model, the $H_c$ of nanocrystalline alloys is proportional to the sixth power of grain size for grain sizes below about 50 nm [36]. Thus, we investigated the influence of P microalloying on the $H_c$ of the alloys in terms of the variation in grain size and its distribution. Figure 6 shows the XRD patterns of the $B_9Si_{12}$, $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ ribbons annealed at 550 °C for 60 min. The XRD patterns show one main diffraction peak at about $2\theta = 45^\circ$ and two sub-diffraction peaks at about $2\theta = 65^\circ$ and $83^\circ$. The sharp diffraction peaks indicate that the annealed ribbons have undergone obvious crystallization, and only $\alpha$-Fe(Si) grains are precipitated in the amorphous matrix. The full width at half maximum of the diffraction peaks of $B_9Si_{12}P_1$ ($0.65^\circ$) is larger than that of $B_9Si_{12}$ ($0.64^\circ$) and $B_9Si_{11}P_1$ ($0.71^\circ$). The crystallite size can be calculated using the following equation: $L = K\lambda/(B\cos\theta)$, where $L$ is the linear dimension of crystallite, $K$ is the numerical constant (0.9), $\lambda$ is the wave-length of the incident X-ray, and $B$ is the full width at half maximum [38–40]. The crystallite sizes of $B_9Si_{12}$, $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ obtained from the XRD patterns are about 13 nm, 12 nm and 13 nm, respectively. Thus, $B_8Si_{12}P_1$ has the smallest grain size.

In order to further confirm the influence of P microalloying on the crystalline phase and its size and distribution, we observed the TEM micrographs, selected-area electron diffraction (SAED) and characteristic grain size distribution of the $B_9Si_{12}$, $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ ribbons annealed at 550 °C. As shown in Figure 7, all ribbons exhibit a typical nanocrystalline structure where $\alpha$-Fe(Si) grains (confirmed by the SAED) are randomly embedded in the residual amorphous matrix, which is consistent with the XRD results. The $\alpha$-Fe(Si) grains of $B_9Si_{12}$, $B_8Si_{12}P_1$ and $B_9Si_{11}P_1$ have an average size of approximately 12 nm, 11 nm and 12 nm, respectively. The XRD and TEM results indicate that substituting 1 at% P for B and Si is beneficial for reducing the size of $\alpha$-Fe(Si) grains. In particular, the substitution of P for B is more beneficial to refine grain size than that of P for Si. Since the mixing enthalpies of the P-B atomic pair, P-Si atomic pair and Si-B atomic pair are 0.5 kJ/mol, $-25.5$ kJ/mol and $-14$ kJ/mol, respectively [34], the substitution of P for B effectively improved the negative mixing enthalpies of atomic pairs, which helps to inhibit long-range diffusion between atoms [41], making the grain size of $B_8Si_{12}P_1$ the smallest. In addition, the grain size of $B_8Si_{12}P_1$ is rarely above 22 nm and mainly distributed around...
10 nm. Based on the random anisotropy model [36], the smaller the average grain size of \( \alpha \)-Fe(Si) grains, the smaller the \( H_c \). Therefore, the reduced grain size of \( B_8Si_{12}P_1 \) is the main factor for achieving the minimum \( H_c \).

Figure 5. Typical hysteresis loops of \( B_9Si_{12} \), \( B_8Si_{12}P_1 \) and \( B_9Si_{11}P_1 \) ribbons annealed at 550 °C for 60 min.

Figure 6. XRD patterns of \( B_9Si_{12} \), \( B_8Si_{12}P_1 \) and \( B_9Si_{11}P_1 \) ribbons annealed at 550 °C for 60 min.

Figure 7. TEM micrographs, SAED and characteristic grain size distribution of (a) \( B_9Si_{12} \), (b) \( B_8Si_{12}P_1 \) and (c) \( B_9Si_{11}P_1 \) ribbons annealed at 550 °C for 60 min.

Figure 7. Cont.
4. Conclusions

The effect of P microalloying on the thermal stability, microstructure and magnetic properties of Fe$_{76}$Cu$_{0.8}$Nb$_{2.2}$B$_9$Si$_{12}$ alloy has been investigated. The slight changes in P, B and Si contents have little effect on $B_s$, but significantly affect the $H_c$ and $\mu$ of the alloy. Substituting 1 at% P for Si has a limited effect in reducing $H_c$, yet significantly reduces $\mu$. On the other hand, substituting 1 at% P for B can effectively decrease $H_c$ and keep $\mu$ basically unchanged. The Fe$_{76}$Cu$_{0.8}$Nb$_{2.2}$B$_8$Si$_{12}$P$_1$ alloy exhibits good annealing processability, a high $B_s$ of 1.41 T, a great $\mu$ of 29,000 at 1 kHz and a low $H_c$ of 0.6 A/m, which can be mainly attributed to the formation of more homogeneous and finer $\alpha$-Fe(Si) grains.

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