Effect of Fe Content on the Crystallization Behavior and Magnetic Properties of Amorphous FeSiBPCu Alloy Postprint

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Abstract

FeSiBPCu amorphous alloys with different Fe contents were prepared by melt-spinning and subjected to rapid annealing treatment, and their crystallization behavior and magnetic properties were investigated in depth. The results show that with increasing Fe content, the apparent crystallization activation energy of FeSiBPCu alloys gradually decreased; the precipitated phases throughout the entire crystallization process were consistent and independent of Fe content; Fex(SiB)96-xP3Cu1 (x=80, 83 and 85) alloys developed a uniform nanocrystalline structure after annealing, with grain sizes less than 20 nm; however, the annealed Fe78Si6B12P3Cu1 and Fe75Si8B13P3Cu1 alloys exhibited highly non-uniform grain sizes ranging from 5-50 nm; the annealed Fe85Si3B8P3Cu1 alloy exhibited excellent soft magnetic properties: a coercivity of 12 A · m-1, a saturation magnetic polarization of 1.87 T, and a core loss still below 1.0 at a maximum magnetic flux density of 1.7 T, which is far superior to the widely used annealed Fe78Si9B13 and non-oriented silicon steel.

Full Text

Preamble

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Effect of Fe Content on Crystallization Behaviors and Magnetic Properties of FeSiBPCu Amorphous Alloys

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Abstract

The crystallization behavior and soft magnetic properties of amorphous alloys with composition Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85, atomic fraction, %) were systematically investigated. The results demonstrate that the apparent activation energy for crystallization gradually decreases with increasing Fe content. The precipitation phases remain consistent throughout the entire crystallization process, independent of Fe content. Annealed Fex(SiB)96-xP3Cu1 alloys with x = 80, 83, and 85 exhibit uniform nanocrystalline structures with grain sizes smaller than 20 nm. In contrast, annealed Fe78Si6B12P3Cu1 and Fe75Si8B13P3Cu1 alloys show highly non-uniform grain size distributions ranging from 5–50 nm. The annealed Fe85Si3B8P3Cu1 alloy demonstrates excellent soft magnetic properties: a coercivity of 12 $A \cdot m^{-1}$, a saturation magnetization of 1.87 T, and core losses remaining below 1.0 $W \cdot kg^{-1}$ even at a maximum magnetic induction of 1.7 T, which far surpasses the performance of widely used annealed Fe78Si9B13 alloy and non-oriented silicon steel.

Keywords: metallic materials, Fe-based amorphous alloy, nanocrystallization, soft magnetic property, activation energy

Introduction

Fe-based soft magnetic alloys have been widely utilized due to their superior magnetic properties and low cost [1-5]. Fe-based amorphous nanocrystalline alloys, characterized by high saturation magnetic polarization (Js) and low core losses (W), exhibit better soft magnetic performance than silicon steel and are recognized as environmentally friendly materials from energy-saving and environmental protection perspectives [6]. Developing Fe-based amorphous nanocrystalline alloys with enhanced soft magnetic properties has been a major research focus. For FeSiB alloys, amorphous ribbons with good soft magnetic properties can be prepared when the Fe content (atomic fraction) is between 70%–80%; however, when Fe content exceeds 80%, coarse α-Fe phases appear in the amorphous ribbons, deteriorating the magnetic properties [7,8]. The microstructure and precipitate types after crystallization heat treatment directly influence magnetic performance. In Fe85Nb6B9 alloys, co-addition of 1% P (atomic fraction) and 0.1% Cu reduces the grain size of α-Fe phase from 45 nm to 2–3 nm [9]. Simultaneous addition of P and Cu to FeSiB alloys also yields uniform nanocrystalline structures after heat treatment, resulting in excellent soft magnetic properties [10,11]. Since Fe element plays a dominant role in the magnetic properties of Fe-based magnetic materials, this study focuses on the effect of Fe content on the crystallization behavior and magnetic properties of FeSiBPCu alloys. Alloys with composition Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) were selected for investigation using DSC, XRD, TEM, and various magnetic property testing equipment to study the thermodynamic properties, microstructural evolution, and magnetic characteristics.

Experimental Methods

Sample Preparation

Master alloys with composition Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) were prepared from high-purity raw materials: Fe (99.98 wt%), Si (99.98 wt%), Cu (99.99 wt%), B (99.5 wt%), and pre-alloyed ferrophosphorus. The raw materials were melted in a high-frequency induction furnace under high-purity argon atmosphere to obtain homogeneous master alloys. Amorphous ribbons with widths of 1–2 mm and thicknesses of 20 m were produced by single-roller melt-spinning. The ribbons were annealed using a ULVAC Mila-3000 furnace at a vacuum level of 10^{-4} Pa and a heating rate of 0.17 K/s.

Sample Characterization

The structure of the samples was analyzed using Rigaku Geigerflex and RINT 2100 X-ray diffractometers (XRD) with Cu Kα radiation, scanning ranges of 20°–80° and 20°–140°, and a scan rate of 1°/min. Crystallization kinetics were studied using a DSC 6200 differential scanning calorimeter in both non-isothermal and isothermal modes. Non-isothermal tests were conducted at heating rates of 0.083, 0.17, 0.34, 0.67, 1.00, and 1.33 K/s. Isothermal test temperatures were selected to be 30 K below the onset temperature of the first crystallization peak (Tx1), with a heating rate of 0.17 K/s and high-purity argon flow of 100 mL/min throughout the tests. Transmission electron microscopy (TEM) specimens were prepared using a Fischione 1010 ion mill and observed using a JEM-2000 high-resolution TEM at an accelerating voltage of 200 kV.

The most important soft magnetic properties for transformer applications are coercivity (Hc), saturation magnetization (Js), and core loss (W). Coercivity was measured using a Riken Denshi BHH-50 hysteresis loop tracer under an applied field of 2 $\mathrm{kA \cdot m^{-1}}$. Saturation magnetization was determined using a

VSM-5-10 vibrating sample magnetometer under an applied field of 800 kA $\cdot$ m^{-1}. Core losses were measured using a SY-8217 B-H analyzer at a frequency of 50 Hz. The density of the melt-spun ribbons was measured by Archimedes' method in n-tridecane. All magnetic property tests were conducted at room temperature.

Results and Discussion

2.1 Thermal Analysis

[Figure 1: see original paper] shows the DSC curves of the as-quenched FeSiBPCu alloy ribbons, indicating the Curie temperature (Tc), initial crystallization temperature (Tx), peak temperature (Tp), and the temperature difference between the first and second exothermic peaks (ΔT). All curves exhibit two exothermic peaks, characteristic of primary crystallization behavior [12]. The two exothermic peaks correspond to the precipitation of α-Fe phase and Fe-B compounds, respectively [13,14]. The apparent activation energy for crystallization of the as-quenched Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys was calculated using the Kissinger method [15]. The thermal physical parameters are listed in .

For FeSiBPCu alloys, the apparent activation energy for crystallization gradually decreases with increasing Fe content. The Tc, Tx1, and Tp1 values decrease progressively with Fe content, while Tx2 and Tp2 remain essentially unchanged. Consequently, the ΔT value increases with Fe content. Previous studies [3,16,17] have indicated that amorphous alloys with high ΔT values tend to form uniform nanocrystalline structures during annealing between the two peak temperatures, while suppressing the precipitation of compounds with large magnetocrystalline anisotropy. The high ΔT values in high-Fe-content FeSiBPCu alloys provide favorable conditions for achieving excellent magnetic properties during annealing.

Isothermal DSC analysis was performed on all alloys, and the JMA equation was used to calculate the Avrami exponent (n) for the as-quenched Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys to determine the crystallization mechanism. The n values are listed in . Despite variations in Fe content, the n values for FeSiBPCu alloys range from 2.3 to 2.5, indicating that isothermal crystallization is a diffusion-controlled three-dimensional growth process with different nucleation rates [18].

The thermodynamic calculations reveal significant differences in the apparent activation energy for crystallization among FeSiBPCu alloys with different Fe contents. As Fe content increases, the apparent activation energy decreases, indicating reduced stability of the as-quenched alloys. The Fe85Si3B8P3Cu1 alloy is the most susceptible to crystallization. However, isothermal DSC analysis shows that changes in Fe content do not alter the crystallization mechanism of FeSiBPCu alloys.

2.2 Microstructural Evolution

[Figure 2: see original paper] presents the XRD patterns and microstructural observations of as-quenched Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloy ribbons. All ribbons exhibit characteristic amorphous peaks in the as-quenched state. For alloys with Fe content >80%, the selected-area electron diffraction (SAED) patterns show sharp rings, indicating the presence of nanocrystalline phases. Bright-field images reveal crystal-like clusters 2–5 nm in size distributed within the amorphous matrix. However, the SAED patterns of Fe78Si6B12P3Cu1 and Fe75Si8B13P3Cu1 alloys show only typical amorphous halos, consistent with the XRD results.

Based on the DSC results, rapid heat treatments were performed on the ribbons. For convenience, Ta1 is defined as the annealing temperature between the two exothermic peaks, and Ta2 as the annealing temperature above Tp2. [Figure 3: see original paper] shows the XRD patterns and TEM results of the annealed FeSiBPCu alloys. After annealing at Ta1, only α-Fe phase is detected in all alloys, with no other phases present. TEM observations confirm this through SAED patterns, which show only α-Fe phase, consistent with XRD results.

Grain sizes in the annealed alloys were calculated from XRD results using the Scherrer equation. summarizes the grain sizes and lattice constants of annealed Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys. The lattice constant increases with Fe content, while the grain size decreases from 28 nm to 14 nm. The annealed Fe85Si3B8P3Cu1, Fe83Si4B9P3Cu1, and Fe80Si5B11P3Cu1 alloys exhibit relatively uniform grains: approximately 10 nm, 15 nm, and 20 nm, respectively. In contrast, the annealed Fe78Si6B12P3Cu1 and Fe75Si8B13P3Cu1 alloys show highly non-uniform grain sizes. The Fe78Si6B12P3Cu1 alloy exhibits grain sizes ranging from 5–30 nm with some remaining amorphous matrix (indicated by arrows in [Figure 3: see original paper]), while the Fe75Si8B13P3Cu1 alloy shows an even broader grain size distribution of 5–50 nm with substantial amorphous regions (also indicated by arrows).

Overall, for Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys, the optimal annealing temperature decreases with increasing Fe content. The volume fraction of amorphous phase in the annealed microstructure decreases, while the grain size becomes smaller and more uniform. The Fe75Si8B13P3Cu1 alloy requires the highest annealing temperature (823 K), yet still retains considerable amorphous matrix. In contrast, the Fe85Si3B8P3Cu1 alloy annealed at 773 K for 600 s shows a uniform grain size of ~10 nm with almost no observable amorphous matrix.

XRD patterns of alloys annealed at Ta2 reveal precipitation of α-Fe, Fe2B, and Fe3B phases in all alloys, indicating that the crystallization sequence is independent of Fe content. However, the co-addition of P and Cu [11] modifies the precipitate types during crystallization. Variations in Fe content do not affect the types of Fe-B compound precipitates.

For alloys with Fe content $ $80%, numerous nanoscale clusters were observed in the amorphous matrix of as-quenched ribbons. Similar clusters have been reported in other alloy systems [19,20] and are attributed to the opposite mixing enthalpies of P and Cu with Fe. During rapid solidification, the melt-spun ribbons develop P- and Cu-enriched regions that serve as nucleation sites for α-Fe phase during subsequent annealing, increasing the nucleation density. Additionally, the atomic radius of Fe is significantly larger than that of Si and B, so higher Fe content reduces atomic spacing and hinders long-range diffusion [21]. Thermodynamic calculations also show that both the initial apparent activation energy (nucleation barrier) and peak apparent activation energy (growth barrier) decrease with increasing Fe content. In high-Fe FeSiBPCu alloys, the lowest nucleation barrier results in the highest nucleation rate, while the lowest growth barrier facilitates rapid grain growth. This leads to competitive growth among nuclei, producing smaller and more uniform final grain sizes. This mechanism is confirmed by both XRD calculations and TEM observations.

For Fex(SiB)96-xP3Cu1 (x = 75 and 78) alloys, both nucleation and growth barriers are high, indicating high stability in the as-quenched state and resistance to crystallization. No clusters were observed in the as-quenched ribbons, requiring substantial energy to overcome the nucleation barrier during annealing. The formed nuclei must also overcome high growth barriers. Moreover, lower Fe content results in larger atomic spacing, facilitating long-range diffusion. Composition and energy fluctuations cause preferential nucleation and growth in localized regions, leading to broad grain size distributions. TEM observations confirm this and reveal substantial amorphous phases between nonuniform grains.

These analyses demonstrate that Fe atomic fraction in as-quenched FeSiBPCu alloys can reach 85%, substantially exceeding the conventional 80% limit. The precipitate types during crystallization are consistent across Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys, independent of Fe content. However, Fe content significantly affects the annealed microstructure: increasing Fe content reduces grain size and improves uniformity. The annealed Fe75Si8B13P3Cu1 alloy shows grain sizes of 5–50 nm with substantial residual amorphous phase, while the annealed Fe85Si3B8P3Cu1 alloy exhibits uniform ~10 nm grains with minimal amorphous phase.

The lattice constant of annealed alloys increases with Fe content, approaching that of pure α-Fe. This indicates decreasing solute element content in the α-Fe phase after crystallization, which is beneficial for achieving excellent soft magnetic properties [2,3]. The microstructure of nanoscale ferromagnetic grains embedded in an amorphous matrix favors superior soft magnetic performance in Fe-based alloys [10,11].

2.3 Magnetic Properties

[Figure 4: see original paper] presents the soft magnetic properties of Fex(SiB)96-

xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys. [Figure 4: see original paper]a shows the relationship between coercivity (Hc) and annealing temperature. For alloys with Fe content <80%, Hc increases continuously with annealing temperature without showing any decreasing trend. For alloys with Fe content $ 80^{-1}$ at 773 K.

[Figure 4: see original paper]b shows the saturation magnetization (Js) values. For as-quenched FeSiBPCu alloys, Js initially increases with Fe content but decreases when Fe content exceeds 83%. This reduction may be attributed to metalloid element electrons occupying Fe 3d orbitals in high-Fe-content alloys [22], reducing the effective magnetic moment and saturation magnetization. For annealed alloys (both Ta1 and Ta2), Js increases monotonically with Fe content, reaching a maximum value of 1.87 T for the Fe85Si3B8P3Cu1 alloy annealed at Ta1.

Core loss (W) is a critical performance metric for transformer soft magnetic materials. Core loss measurements were performed on annealed Fe83Si4B9P3Cu1 and Fe85Si3B8P3Cu1 alloys, which exhibited low coercivity and high saturation magnetization. [Figure 4: see original paper]c shows the relationship between W and maximum magnetic induction (Bm) for these nanocrystalline soft magnetic alloys. Although W increases continuously with Bm for each alloy, both Fe83Si4B9P3Cu1 and Fe85Si3B8P3Cu1 nanocrystalline alloys exhibit extremely low W values compared to commercial non-oriented silicon steel, even at Bm = 1.0 T. Compared to the widely used Fe78Si9B13 alloy, the W1.7T/50Hz values remain below $1.0\ \mathrm{W \cdot kg^{-1}}$ even at Bm up to 1.7 T. Such low core loss values are exceptionally rare among soft magnetic materials.

In summary, higher Fe content in FeSiBPCu alloys correlates with better soft magnetic properties. The annealed Fe85Si3B8P3Cu1 alloy exhibits excellent comprehensive soft magnetic properties: Js = 1.87 T, Hc $< 12\ \mathrm{A \cdot m^{-1}}$, and W $< 1.0\ \mathrm{W \cdot kg^{-1}}$ within the Bm range of 1.7 T.

Conclusions

1. The crystallization process of Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys follows a diffusion-controlled three-dimensional growth mechanism with varying nucleation rates. Tx1 and Tp1 decrease gradually with increasing Fe content, while Tx2 and Tp2 remain essentially unchanged, resulting in reduced apparent activation energy for crystallization.
2. The precipitate types during crystallization are consistent across Fex(SiB)96-xP3Cu1 (x = 75, 78, 80, 83, and 85) alloys. Increasing Fe content reduces grain size and improves uniformity after annealing. The annealed Fe75Si8B13P3Cu1 alloy exhibits grain sizes ranging from 5–50 nm with substantial residual amorphous phase, while the annealed Fe85Si3B8P3Cu1 alloy shows uniform ~10 nm grains with minimal

amorphous phase.

3. Higher Fe content in FeSiBPCu alloys yields superior soft magnetic properties. The annealed Fe85Si3B8P3Cu1 alloy demonstrates excellent performance with Js = 1.87 T, Hc < 12 A · m^{-1}, and W < 1.0 W · kg^{-1} at Bm up to 1.7 T.

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