Fe-Rich Soft Magnetic FeSiBPCu Hetero-Amorphous Alloys with High Saturation Magnetization

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Magnetic properties are perhaps the most remarkable and unique properties of Fe-based amorphous alloys. To obtain high saturation magnetization, high Fe content is preferred. However, there is a strict upper limit of Fe content for the formation of a single amorphous structure with good magnetic softness. Fe-based amorphous alloys with high Fe content over the limit have an as-quenched structure consisting of coarse α -Fe grains in an amorphous matrix, which inevitably results in inferior magnetic softness. We have studied the effect of P and/or Cu additions on the microstructure of Fe-based amorphous alloys with high Fe content. The α -Fe grain size and the coercivity (H_c) decrease by the simultaneously adding P and Cu. The Fe-rich FeSiBPCu alloys with the optimized composition have an extremely small α -Fe-like phase of about 3 nm or smaller in a diameter, exhibits the higher J_s of about 1.67 T than that of the typical Fe-based amorphous alloy and show the low coercivity (H_c) of about 4 Am⁻¹ in an as-quenched state. [doi:10.2320/matertrans.ME200831]

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1. Introduction

The silicon steel (Fe-3.5 mass% Si crystalline alloy)¹⁾ has occupied the largest market share in the soft magnetic material field due to the high saturation magnetization (J_s) of about 2 T and the low material cost. However, the silicon steel exhibits inferior magnetic softness which is resulted from the large magnetocrystalline anisotropy. The Fe-based amorphous and hetero-amorphous alloys²⁻⁸⁾ shows low intrinsic magnetocrystalline anisotropy and therefore are regarded as substitutes for the silicon steel in the future applications. Consequently great efforts have been devoted to develop Fe-based amorphous and hetero-amorphous alloys with lower material cost, higher productivity,⁹⁻¹¹⁾ better soft magnetic properties and higher J_s .¹²⁻¹⁵⁾

In order to obtain high J_s , high Fe content is required for the Fe-based amorphous and hetero-amorphous alloys. However, there is a strict upper limit of the Fe content for forming amorphous phase with good magnetic softness. The alloys with a Fe content exceeding 80 at% have an as-quenched structure consisting of coarse α -Fe grains and amorphous matrix. These coarse α -Fe grains inevitably result in inferior magnetic softness. It has been reported that the additions of P and Cu can refine the coarse α -Fe grains and enable the formation of amorphous FeNbBPCu alloy with good magnetic softness and high J_s .^{12,16)} In this paper we further studied the effect of P and Cu additions on the structure and properties of FeSiBPCu. The new FeSiBPCu hetero-amorphous alloys with optimized P and Cu additions exhibit a unique combination of good soft magnetic property and high J_s .

2. Experimental Procedure

Alloy ingots were prepared by arc-melting of Fe (99.98 mass%), Si (99.98 mass%), B (99.5 mass%), Cu (99.99 mass%) and pre-alloyed Fe-P (99.9 mass%) in a purified argon atmosphere. Rapidly solidified ribbons were produced by a single-roller melt-spinning method in air. The prepared ribbons were about 2 mm in width and 20 μ m in thickness. The structure of the as-quenched ribbons was identified by X-ray diffraction (XRD) with Cu-K α radiation and transmission electron microscopy (TEM). The coarse α -Fe grain size was estimated by Scherrer equation from the full width at half maximum of the bcc {110} reflection peak from α -Fe phase. The coercivity (H_c) under a maximum applied field of 10 kAm⁻¹ was measured by a dc B-H loop tracer with the accuracy of 0.1 Am⁻¹. The J_s under a maximum applied field of 800 kAm⁻¹ were measured by vibrating sample magnetometer (VSM). The density of the as-quenched ribbons was measured by Archimedeian method with n-tridecane. All the property measurements were carried out at room temperature.

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-quenched FeSiBPCu ribbons. The alloy without P and Cu additions exhibit a broad diffraction hump consisted with a sharp peak corresponding to α -Fe. According to the Scherrer equation, the mean grain size of the α -Fe phase is determined to be about 93 nm. The diffraction peak disappears with the simultaneous additions of P and Cu in Fe_{81.7}B₇Si₉P₂Cu_{0.3}, Fe_{83.3}Si₄B₈P₄Cu_{0.7}, Fe_{84.3}Si₄B₈P₃Cu_{0.7} and Fe_{85.3}Si₂B₁₀-P₂Cu_{0.7} alloys. It can be seen that the simultaneous additions of P and Cu play an important role on the structure improvement. Amorphous structure (in XRD scale) can be obtained in the FeSiBPCu alloys even with a Fe content exceeding the upper limit of 80 at%.

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Fig. 1 XRD diffraction pattern for the as-quenched $\text{Fe}_{82}\text{B}_9\text{Si}_9$, $\text{Fe}_{81.7}\text{B}_7\text{Si}_9\text{P}_2\text{Cu}_{0.3}$, $\text{Fe}_{83.3}\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_{0.7}$, $\text{Fe}_{84.3}\text{Si}_4\text{B}_8\text{P}_3\text{Cu}_{0.7}$ and $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ ribbons.

Fig. 2 Compositional dependence of H_c on P and Cu contents for as-quenched $\text{Fe}_{82-y}\text{Si}_9\text{B}_{9-x}\text{P}_x\text{Cu}_y$ ($x = 0\sim 6$, $y = 0\sim 0.4$) ribbons.

Figure 2 presents the composition dependence of H_c on P and Cu for the as-quenched $\text{Fe}_{82-y}\text{Si}_9\text{B}_{9-x}\text{P}_x\text{Cu}_y$ ($x = 0\sim 6$, $y = 0\sim 0.4$) alloys. The alloy without P and Cu additions shows the largest H_c value of 45 Am^{-1} , which is due to the existence of the coarse α -Fe crystals as evidenced from the XRD pattern in Fig. 1. The H_c decreases with the additions of P and Cu. The minimum H_c value of 7 Am^{-1} appears at the composition vicinity with $3\sim 4\%$ P and 0.3% Cu. Since the proper amount of P and Cu additions dramatically decrease the H_c of as-spun $\text{Fe}_{82-y}\text{Si}_9\text{B}_{9-x}\text{P}_x\text{Cu}_y$ alloys, one may expect the formation of amorphous or hetero-amorphous FeSiB alloys with both low H_c and high J_s (high Fe content) by P and Cu additions. Therefore the simultaneous additions of P and Cu were performed on the alloys with higher Fe content. Figure 3 shows the composition dependence of H_c on the Fe content. It is clearly that the P and Cu additions are also effective to decrease the H_c for the alloys with extremely high Fe content. Even the as-quenched $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ alloy exhibit a much lower H_c of 4 Am^{-1} than that of $\text{Fe}_{82}\text{B}_9\text{Si}_9$.

To exhaust the reason that why the simultaneous additions of P and Cu lead to the dramatic decrease in H_c , the local structure of the as-spun $\text{Fe}_{81.7}\text{B}_7\text{Si}_9\text{P}_2\text{Cu}_{0.3}$ and $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$

Fig. 3 Compositional dependence of H_c on Fe content for as-quenched $\text{Fe}_{82}\text{B}_9\text{Si}_9$, $\text{Fe}_{81.7}\text{B}_7\text{Si}_9\text{P}_2\text{Cu}_{0.3}$, $\text{Fe}_{83.3}\text{Si}_4\text{B}_8\text{P}_4\text{Cu}_{0.7}$, $\text{Fe}_{84.3}\text{Si}_4\text{B}_8\text{P}_3\text{Cu}_{0.7}$ and $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ ribbons.

$\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ alloys were investigated by TEM. The HRTEM images and the selected area electron diffraction (SAED) patterns of the two alloys are shown in Fig. 4 and Fig. 5, respectively. The rather sharp SAED patterns suggest the existence of nanocrystals in the as-quenched $\text{Fe}_{81.7}\text{B}_7\text{Si}_9\text{P}_2\text{Cu}_{0.3}$ and $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ alloys. The HRTEM images further confirm the formation of homogeneously dispersed α -Fe crystals. Due to the small size (about 3 nm), these α -Fe nanocrystals cannot be identified by XRD. These results indicate that the simultaneous additions of P and Cu play an important role on refining the α -Fe crystals for the FeSiB alloys. The significant effect of the refining may be related to the mixing enthalpy between the constituent elements. A repulsive interaction exists between Fe and Cu atoms due to the positive mixing enthalpy (13 kJ/mol) between them. On the other hand, an attractive interaction exists between Cu and P atoms due to the negative mixing enthalpy (-9 kJ/mol). Once these adverse interactions between these elements form, P-rich and Cu-rich regions can be dispersed in the FeSiB amorphous matrix and form nucleation sites for α -Fe during cooling. Thus the P and Cu additions can improve the microstructure of the as-quenched FeSiB alloys and therefore lead to lower H_c . Such similar effect has also been found in FeNbB alloys.¹³⁾

As described above, by the simultaneous additions of P and Cu, hetero-amorphous FeSiB alloys with extremely high Fe content can be developed, which provides the possibility to produce Fe-based alloys with both low H_c and high J_s . Consequently the J_s of the as-spun FeSiBPCu ribbons were measured. Figure 6 presents the J - H curves of the as-quenched $\text{Fe}_{84.3}\text{Si}_4\text{B}_8\text{P}_3\text{Cu}_{0.7}$, $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ and $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ ribbons, from where the J_s of the three alloys are determined to be 1.67 T, 1.58 T, and 1.49 T, respectively. It is clear that the FeSiBPCu alloys with higher Fe content has a lower J_s .

4. Conclusions

The effects of the simultaneous additions of P and Cu on the microstructure and magnetic properties were investigated for the as-quenched FeSiB(PCu) alloys with high Fe content exceeding the limit for the formation of a single amorphous phase.

Fig. 4 HRTEM image (a) and SAED pattern (b) of the as-quenched $\text{Fe}_{81.7}\text{B}_7\text{Si}_9\text{P}_2\text{Cu}_{0.3}$ ribbon.

Fig. 5 HRTEM image and SAED pattern of the as-quenched $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ ribbon.

Fig. 6 J - H curve of as quenched $\text{Fe}_{84.3}\text{Si}_4\text{B}_8\text{P}_3\text{Cu}_{0.7}$, $\text{Fe}_{85.3}\text{Si}_2\text{B}_{10}\text{P}_2\text{Cu}_{0.7}$ and $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ ribbons.

- (1) The simultaneous additions of P and Cu decrease the grain size of the α -Fe in the as-quenched FeSiB alloys from 93 to about 3 nm.
- (2) The H_c of as-quenched FeSiBPCu alloy decreases from 45 to 4 Am^{-1} which is resulted from the refinement of α -Fe phase in the as-quenched alloys.
- (3) The FeSiBPCu alloy with an extremely high Fe content of 84.3 at% exhibits high J_s value of 1.67 T.

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