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 (Hc) 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 Jc of about 1.67 T than that of the typical Fe-based amorphous alloy and show the low coercivity (Hc) 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 (Jc) 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 Jc.12–15

In order to obtain high Jc, 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 Jc.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 Jc.

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 µm in thickness. The structure of the as-quenched ribbons was identified by X-ray diffraction (XRD) with Cu-Kα 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 (Hc) under a maximum applied field of 10 kA/m−1 was measured by a dc B-H loop tracer with the accuracy of 0.1 Am−1. The Jc under a maximum applied field of 800 kA/m−1 were measured by vibrating sample magnetometer (VSM). The density of the as-quenched ribbons was measured by Archimedeans 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 Fe81.7Si8P2Cu0.3, Fe83.1Si6B7P2Cu0.7, Fe84.3Si6B6P3Cu0.7 and Fe85.3Si2B0.7P2Cu0.7 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 Fe$_{82}$B$_{18}$Si$_{6}$, Fe$_{81,7}$B$_{18}$Si$_{6}$P$_{2}$Cu$_{0,3}$, Fe$_{83,3}$Si$_{6}$B$_{12}$P$_{2}$Cu$_{0,7}$, Fe$_{84,3}$Si$_{6}$B$_{12}$P$_{2}$Cu$_{0,7}$, and Fe$_{85,3}$Si$_{2}$B$_{10}$P$_{2}$Cu$_{0,7}$ ribbons.

Fig. 2 Compositional dependence of $H_c$ on P and Cu contents for as-quenched Fe$_{82-x}$Si$_{6}$B$_{18}$P$_{2}$Cu$_{y}$ (x = 0−6, y = 0−0.4) 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 $\alpha$-Fe crystals as evidenced form 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 3−4% P and 0.3% Cu. Since the proper amount of P and Cu additions dramatically decrease the $H_c$ of as-spun Fe$_{82-x}$Si$_{6}$B$_{18}$P$_{2}$Cu$_{y}$ alloys, one may expect the formation of amorphous or hetero-amorphous FeSiB alloys with both low $H_c$ and high $J_c$ (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 compositional 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 Fe$_{85,3}$Si$_{2}$B$_{10}$P$_{2}$Cu$_{0,7}$ alloy exhibit a much lower $H_c$ of 4 Am$^{-1}$ than that of Fe$_{82}$B$_{18}$Si$_{6}$.

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 Fe$_{81,7}$B$_{18}$Si$_{6}$P$_{2}$Cu$_{0,3}$ and Fe$_{85,3}$Si$_{2}$-B$_{10}$P$_{2}$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 Fe$_{82}$B$_{18}$Si$_{6}$P$_{2}$Cu$_{0,3}$ and Fe$_{85,3}$Si$_{2}$B$_{10}$P$_{2}$Cu$_{0,7}$ alloys. The HRTEM images further confirm the formation of homogeneously dispersed $\alpha$-Fe crystals. Due to the small size (about 3 nm), these $\alpha$-Fe nanocrystals cannot be identified by XRD. These results indicate that the simultaneous additions of P and Cu play an important role in refining the $\alpha$-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 negative mixing enthalpy (13 kJ/mol) between them. On the other hand, an attractive interaction exists between Cu and P atoms due to the positive 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 $\alpha$-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 $J_c$. Consequently the $J_c$ of the as-spun FeSiBPCu ribbons were measured. Figure 6 presents the $J$−$H$ curves of the as-quenched Fe$_{84,3}$Si$_{6}$B$_{12}$P$_{2}$Cu$_{0,7}$, Fe$_{85,3}$Si$_{2}$B$_{10}$P$_{2}$Cu$_{0,7}$, and Fe$_{78}$Si$_{9}$B$_{13}$ ribbons, from where the $J_c$ 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 $J_c$.

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(FCu) 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 Fe$_{81.7}$B$_7$Si$_6$P$_2$Cu$_{0.3}$ ribbon.

Fig. 5 HRTEM image and SAED pattern of the as-quenched Fe$_{85.3}$Si$_2$B$_{10}$P$_2$Cu$_{0.7}$ ribbon.
The simultaneous additions of P and Cu decrease the grain size of the $\alpha$-Fe in the as-quenched FeSiB alloys from 93 to about 3 nm.

The $H_c$ of as-quenched FeSiBCu alloy decreases from 45 to 4 Am$^{-1}$ which is resulted from the refinement of $\alpha$-Fe phase in the as-quenched alloys.

The FeSiBCu alloy with an extremely high Fe content of 84.3 at% exhibits high $J_s$ value of 1.67 T.

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

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