



FeCo-based soft magnetic alloys with high B_s approaching 1.75 T and good bending ductility



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ABSTRACT

Fe-rich amorphous alloys with FeCo contents above 85 at% were formed by partial replacement of Fe by Co in Fe-Si-B-P alloy system. The resulting alloys exhibit good soft magnetic properties and bending ductility after stress relief annealing. Moreover, the maximum magnetic flux density (B_s) approaches 1.75 T, which is higher than those for previous reported Fe-rich Fe-metalloid alloys. Thus, the partial substitution of Fe by Co caused both Curie temperature (T_C) and B_s exceeding those for the Fe-Si-B-P alloys. Any compositional modification so as to raise T_C was found to be effective for the further increase in the previous maximum value of B_s for the Fe-metalloid amorphous alloy system reported to date. Based on this concept, it is expected that further high B_s exceeding largely 1.75 T is obtained for Fe-based soft magnetic alloys with higher total ferromagnetic element content.

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1. Introduction

In the present eco-friendly society, it is important to develop Fe-based soft magnetic alloys with higher saturation magnetic flux density (B_s) in order to satisfy the requirement of preparing electronic devices with higher performance, smaller size and lighter weight [1]. By increasing Fe content and optimizing metalloid elements, there remains a possibility of obtaining higher B_s in Fe-metalloid alloy systems. For instance, commercialized amorphous alloy Fe_{81.5}Si₂B₁₆C_{0.5} exhibits high B_s of 1.63 T [2] exceeding that (1.53 T) of the Fe₇₈Si₉B₁₃ amorphous alloy [3]. Recently, by further increase in Fe content to 84 at%, we have succeeded in obtaining higher B_s above 1.7 T in Fe-Si-B-P-(C) alloy system. Among them, the alloy of Fe₈₄B_{8.5}Si_{4.1}P_{3.25}C_{0.15} exhibits the B_s value as high as 1.72 T, which is regarded as the highest B_s value in Fe-metalloid type soft magnetic alloys reported to date [4].

Based on the previous data on the formation of amorphous

alloys in Fe-metalloid alloy system without transition metal (TM), the highest Fe concentration is about 85 at% [5,6]. Further increase in Fe content causes the partial crystallization of the melt-spun amorphous alloy ribbons, resulting in significant degradation of soft magnetic properties [7]. Little is known about magnetic properties for amorphous alloys with higher Fe content or ferromagnetic element content above 85 at%, because no successful synthesis of such amorphous alloys has been reported to date.

In previous work, it has been reported that partial substitution of Fe by Co in Fe-metalloid alloys causes the improvement of amorphous-forming ability as well as the increase in Curie temperature [8–10]. In our present study, it has further been found that Co is effective for the formation of amorphous phase in higher Fe(Co) content range above 85 at% by the melt spinning technique, which enables the study on the structure, thermal stability and magnetic properties of the amorphous alloys with higher ferromagnetic element content.

2. Experimental procedure

With the aim of optimizing alloy compositions, we chose FeCo-

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based alloys with compositions of $(\text{Fe}_{0.8}\text{Co}_{0.2})_{83}\text{B}_9\text{Si}_5\text{P}_3$, $(\text{Fe}_{0.8}\text{Co}_{0.2})_{84}\text{B}_{8.5}\text{Si}_{4.5}\text{P}_3$, $(\text{Fe}_{0.8}\text{Co}_{0.2})_{85}\text{B}_8\text{Si}_4\text{P}_3$, $(\text{Fe}_{0.8}\text{Co}_{0.2})_{86}\text{B}_{7.5}\text{Si}_{3.5}\text{P}_3$ and $(\text{Fe}_{0.8}\text{Co}_{0.2})_{87}\text{B}_7\text{Si}_3\text{P}_3$ for the present study. These alloys are named hereafter as (FeCo)83, (FeCo)84 and etc., respectively. The alloy compositions are represented by nominal atomic percentage. Their master alloy ingots were prepared by arc melting the mixtures of pure element of Fe, Co, Si, B and Fe_3P (99.99 mass%) in an argon atmosphere. Rapidly solidified ribbons were prepared from the master alloy ingots by melt spinning with a copper wheel of 250 mm in diameter. The outer surface velocity of the wheel was about 40 m/s and the resulting alloy ribbons had a thickness of about 20 μm and a width of about 0.8–1.0 mm.

The structure was examined by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. Thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Curie temperature was measured from the initial permeability - temperature curve. The initial permeability was measured by a HP4294A impedance analyzer at $H = 0.4$ A/m and $f = 10$ kHz during successive heating process under argon atmosphere protection. The alloy ribbons were annealed under a longitudinal magnetic field (LF) of 200 Oe at the annealing temperature of $T_C - 20$ K. The B_s and coercivity (H_c) were measured with a vibrating sample magnetometer (VSM) under a field of 800 kA/m and a DC B-H loop tracer under a field of 800 A/m, respectively.

3. Results

Fig. 1 shows XRD patterns of the melt-spun FeCo-based alloy ribbons. The patterns consist of an amorphous single phase even for the alloy with high FeCo content up to 86 at% and change to amorphous plus crystalline phase for the (FeCo)87 alloy. Thus, it is notable that a single amorphous phase is formed even in the high FeCo concentration range of 83–86 at%. This result indicates that the critical maximum FeCo content for amorphous phase formation in the FeCo-based alloys lies in the vicinity of 86–87 at%. Considering the previous result [4,6] that the maximum Fe content for amorphous formation in Fe-Si-B-P alloy system is about 85 at%, it is concluded that the partial substitution of Fe by Co is effective for the extension of the maximum ferromagnetic element content to 86 at% for the amorphous single alloy.

DSC curves of the Fe-rich FeCo-based amorphous alloys (FeCo) 83–(FeCo)86 are shown in Fig. 2. The curve shows two exothermic peaks, followed by a small broad peak near 1150 K for each alloy.

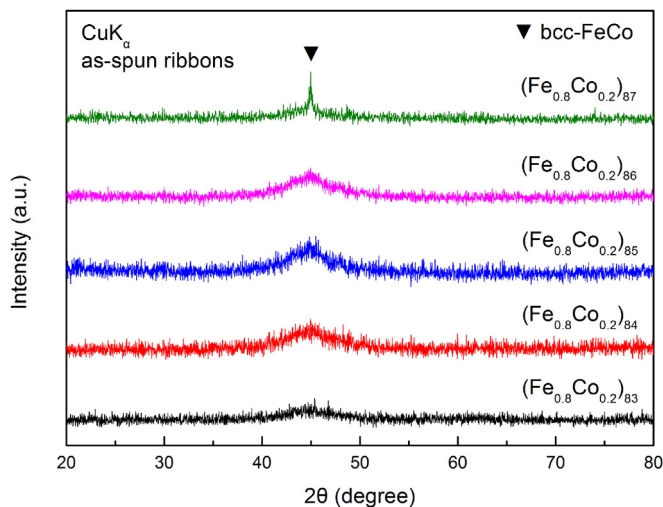


Fig. 1. X-ray diffraction patterns of the as-spun FeCoSiBP alloy ribbons.

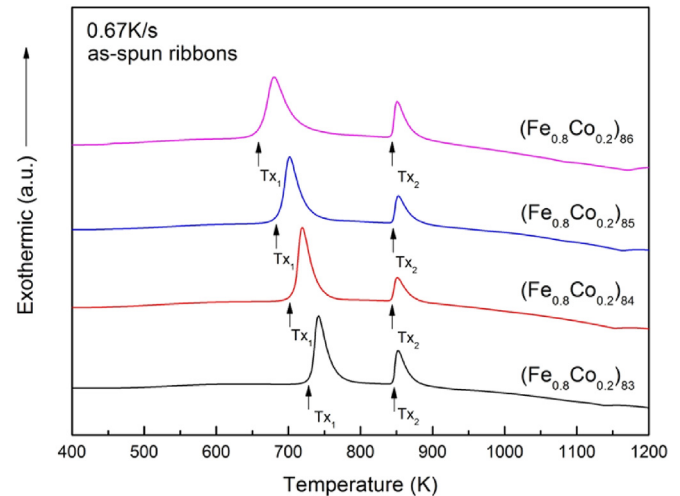


Fig. 2. DSC curves of the as-spun amorphous FeCoSiBP alloy ribbons.

The two exothermic peaks indicate that their amorphous alloys crystallize through two-stage process. The first peak at the lower temperature side is due to the precipitation of bcc-FeCo phase, while the second one at the higher temperature side is associated with the precipitations of FeCo borides from the remaining amorphous phase [11,12]. The onset temperatures of the first and second exothermic peaks (T_{x1} and T_{x2}) are summarized in Table 1. These T_{x1} values decrease with increasing FeCo content, while T_{x2} maintains nearly constant values around 840 K. As a result, the temperature interval between the two exothermic peaks ($T_{x2} - T_{x1}$) increases with increasing Fe(Co) content, in agreement with the tendency of Fe-Si-B-P amorphous alloy system [6].

In order to examine their T_C , the 85–86.5% Fe amorphous alloys were studied by the inductance analyzer under successive heating process. Fig. 3a shows the initial permeability - temperature (μ_i -T) curves revealing the change in permeability with increasing heating temperature. For each sample, μ_i remains almost unchanged in the temperature range up to near 600 K. Subsequently, a sharp decline of μ_i can be recognized, followed by the decrease of μ_i near 0 with further increasing temperature. Besides, an obvious peak before the sharp decline of μ_i can be recognized (i. e., Hopkinson peak), which is caused by the more significant decreases of effective magnetic anisotropy (K) and magnetostriction coefficient (λ_s) than M_s near the Curie point [13]. The corresponding temperature of the sharp decline of μ_i , as marked in the figure, indicates their different T_C . Fig. 3b shows the T_C values as a function of ferromagnetic element content for the present FeCo-based amorphous alloy. The data of the Fe-Si-B-P base amorphous alloys are drawn in the same plot for comparison. With increasing ferromagnetic element content, T_C shows a decrease tendency in both of the alloy systems. Moreover, one can recognize that T_C is significantly increased by partial substitution of Fe by Co from the base alloy.

Table 1

Thermal (T_{x1} , T_{x2} and T_C) and magnetic properties (B_s and H_c) of the FeCoSiBP alloys. All of the ribbons for magnetic property measurements were longitudinal field annealed at the temperature of $T_C - 20$ K for 600 s.

Alloy	T_{x1} (K)	T_{x2} (K)	T_C (K)	B_s (T)	H_c (A/m)
$(\text{Fe}_{0.8}\text{Co}_{0.2})_{83}\text{B}_9\text{Si}_5\text{P}_3$	725	844	683	1.72	3.5
$(\text{Fe}_{0.8}\text{Co}_{0.2})_{84}\text{B}_{8.5}\text{Si}_{4.5}\text{P}_3$	700	843	661	1.74	4.9
$(\text{Fe}_{0.8}\text{Co}_{0.2})_{85}\text{B}_8\text{Si}_4\text{P}_3$	679	844	645	1.76	5.8
$(\text{Fe}_{0.8}\text{Co}_{0.2})_{86}\text{B}_{7.5}\text{Si}_{3.5}\text{P}_3$	651	843	629	1.69	15.2
$(\text{Fe}_{0.8}\text{Co}_{0.2})_{87}\text{B}_7\text{Si}_3\text{P}_3$	630	843	—	1.82	26.9

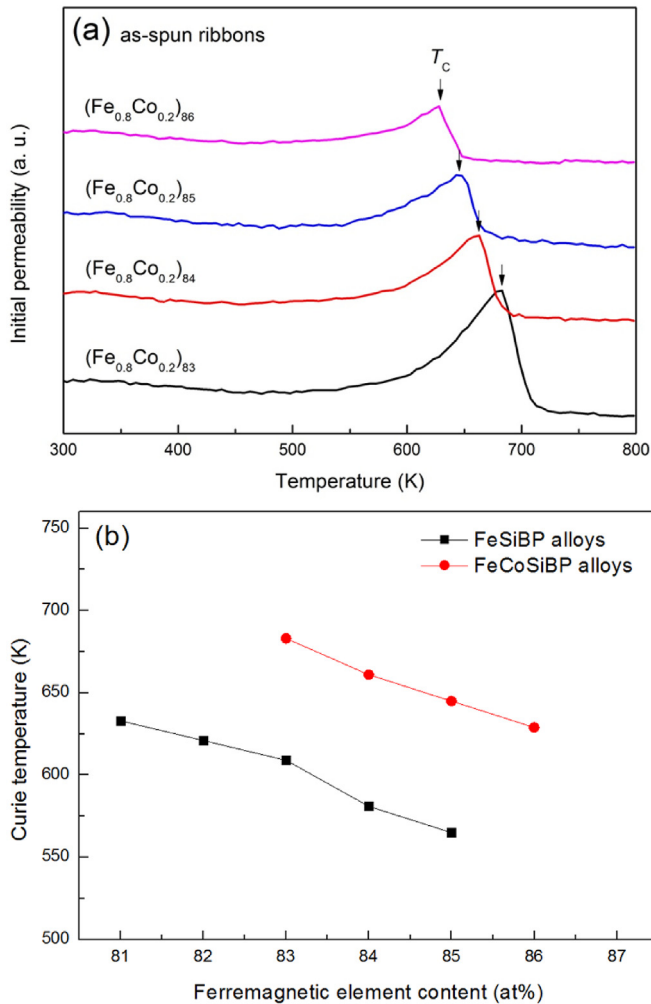


Fig. 3. (a) initial permeability-temperature curves of the FeCoSiBP alloy ribbons. (b) the plot of Curie temperature as a function of ferromagnetic element content for the FeCoSiBP and FeSiBP alloys.

Ribbon alloys were annealed at each $T_c - 20$ K for 600 s to reduce the inner stress. All the annealed ribbon samples maintain good bending ductility, which do not crack into two pieces after bending through 180° (Fig. 4a). The resulting crease marks were observed with a SEM (Fig. 4b). The surface shows a number of shear bands, which is a feature for ductile ribbon alloys. Fig. 4c shows the surface morphology of the indentation trace generated by the Vickers' hardness indenter. Several slip steps without any trace of fracture can be recognized near the indentation mark, indicating their good deformation ability against indentation. On the other hand, the resulting hardness is 846 HV, which is comparable to those of the previous Fe-Si-B-P alloys. These results indicate that the present FeCo-based amorphous alloy ribbons possess favorable combination of good ductility and wear resistance, which is important for soft magnetic materials.

4. Discussion

Generally, increasing the Fe content causes the difficulty in obtaining a single amorphous phase for the Fe-metalloid alloys. It is necessary to keep a minimum content of metalloid elements (B, Si, P, C) for the formation of amorphous phase. For instance, the minimum metalloid content is 15 at% for the formation of an

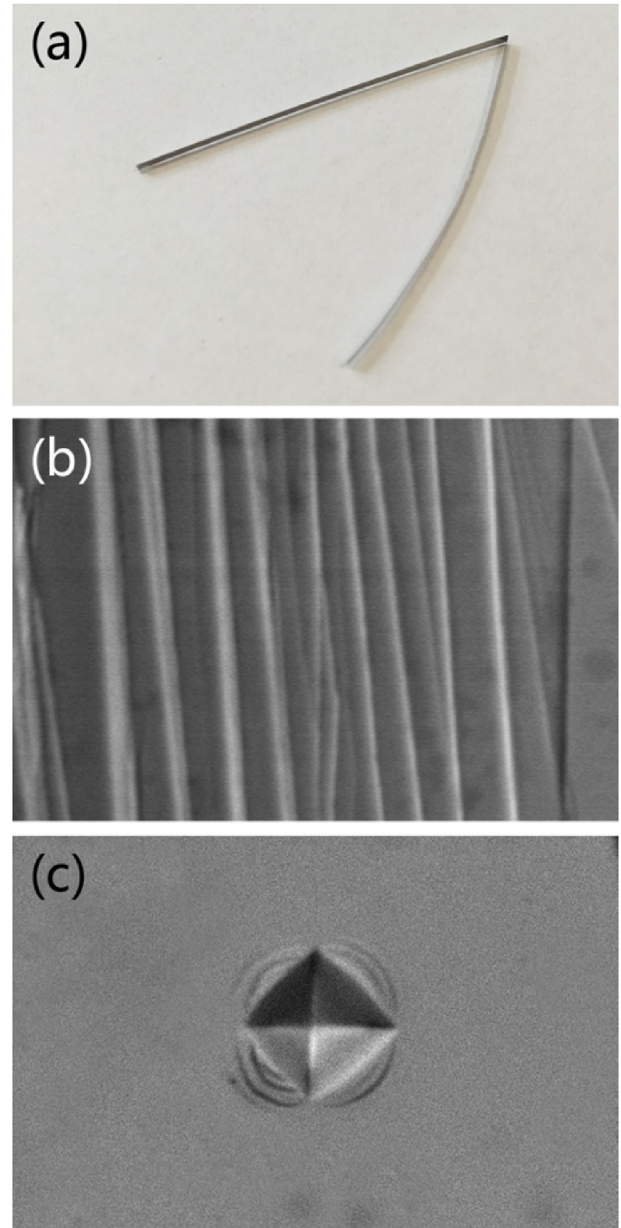


Fig. 4. (a) outer surface and (b) SEM image obtained near the crease mark of the bent alloy ribbon $(\text{Fe}_{0.8}\text{Co}_{0.2})_{85}\text{B}_8\text{Si}_4\text{P}_3$ annealed at 563 K ($T_c - 20$ K) for 600 s (c) optical microscopy image of the $(\text{Fe}_{0.8}\text{Co}_{0.2})_{85}\text{B}_8\text{Si}_4\text{P}_3$ alloy ribbon with a slip marking generated by indentation of a Vickers indenter.

amorphous phase in Fe-B binary system and Fe-Si-B-P quaternary system. In our present work, however, the partial replacement of Fe by Co enables the formation of amorphous phase with FeCo content up to 86 at%. Besides, it is reported that the addition of Co element in the Fe-based glassy alloys can also enhance their glass forming ability (GFA). For instance, the maximum diameter of glassy FeCoGaPCBSi alloy has been enlarged to 3 mm by addition of Co from 2 mm for the base FeGaPCBSi alloy [8,14]. Also, the addition of Co increased the GFA of the FeCoHfMoBY alloys in a limited composition range [15]. A partial substitution of Fe by Co has been regarded to enhance the satisfaction level of the three component rules [16] to improve the amorphous/glass-forming ability of the alloys, which is expected to synthesize amorphous and/or glassy alloys into larger size and wider composition range.

Co exhibits higher T_C of 1394 K than Fe (1043 K). A partial replacement of Fe by Co is thus expected to increase the T_C of the base alloys. To date, many researchers have succeed in obtaining high T_C Fe-base amorphous and nanocrystalline soft magnetic alloys by addition of Co element [8–11,16,17]. However, their mechanisms are different. For nanocrystalline alloys, the rise of T_C is due to the precipitates of bcc-FeCo phase, which is characterized by higher T_C than that of the amorphous matrix [18]. For amorphous alloys, the high T_C is associated with the change in short range ordered structure by addition of Co, resulting in the changes in atomic configuration. A number of researches indicate that T_C is dominated by the interaction of atomic pair for single glassy/amorphous alloys [19,20]. According to molecular theory, T_C can be expressed as:

$$T_C = \frac{S(S+1)\sum_n J_n(r)Z_n}{3k_B}$$

Here $J_n(r)$ is the distance-dependent interatomic exchange integral, Z_n is the coordination number in the n th shell, S is the atomic spin quantum number, and k_B is the Boltzmann's constant. The item of $\sum_n J_n(r)Z_n$ contains two parts: $J_d(r)Z_d$ is affected by $3d$ localization electrons which can only be interacted in one atomic distance, and the remaining part affected by s non-localization electrons can be interacted in six atomic distances [21]. By partial replacement of Fe by Co, two effects should be considered: (1) interatomic exchange integrals of Fe-Co and Co-Co are stronger than that of Fe-Fe atomic pair [22]; (2) coordination number of Co-centered clusters is larger than that of Fe-centered clusters [23]. Therefore, the addition of Co results in the increase of T_C , in agreement with the experimental data in Fe-Si-B-P and Fe-Co-Si-B-P amorphous alloy systems (Fig. 3b).

As shown in Fig. 5b, B_s increases with an increase of ferromagnetic element content up to 85 at%, and then followed by a rapid drop with further increase in FeCo content, resulting in a maximum B_s value obtained. This tendency is in consistent with the previously reported Fe-Si-B-P alloys. In order to understand this phenomenon, the change in saturation magnetization M_s as a function of temperature (T) is considered. With increasing temperature well below T_C , the relation of $M_s(T)$ vs. T can be described by the Bloch $T^{3/2}$ law:

$$M_s(T) = M_s(0) \left[1 - BT^{3/2} \right]$$

To study the increasing tendency of M_s vs. Fe content (x) at room temperature, $M_s(T)$, $M_s(0)$ as well as Bloch coefficient B are regarded as a function of x and T is constant (298 K). Therefore:

$$\frac{\partial M_s(x, 298K)}{\partial x} = \frac{\partial M_s(x, 0K)}{\partial x} \left[1 - B(x)(298K)^{3/2} \right] + M_s(x, 0K) \frac{\partial \left[1 - B(x)(298K)^{3/2} \right]}{\partial x}$$

The expression on the right side of the equal sign consists of two items. The first item describes the change of M_s vs. Fe content at 0 K, which is always positive. The second item describes the degree of decrease in M_s vs. Fe content at 298 K, which is determined by Bloch coefficient $B(x)$. The B value is proportional to the average atomic volume, which increases with increasing Fe content in the Fe-metalloid alloys. Thus the second item is always negative. As a result, it exists a certain x value (critical Fe content, x_c) which enables the algebraic sum of the two items equals to zero, resulting in a maximum value of M_s (or B_s) (This maximum B_s value is defined as $B_{s, \max}$). Further calculation proves that the x_c is determined by the combination of (1) distance-dependence interatomic exchange, and (2) coordination number and average atomic distance, i. e., by

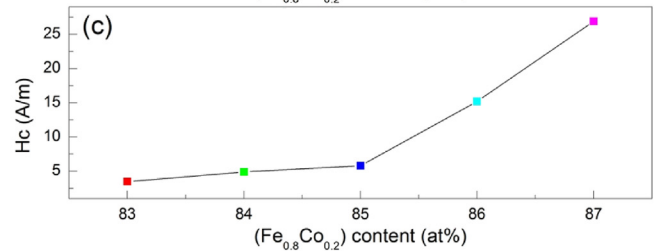
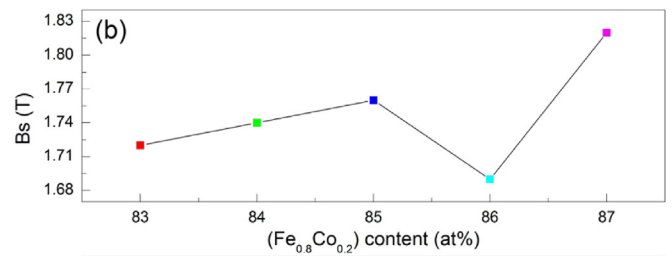
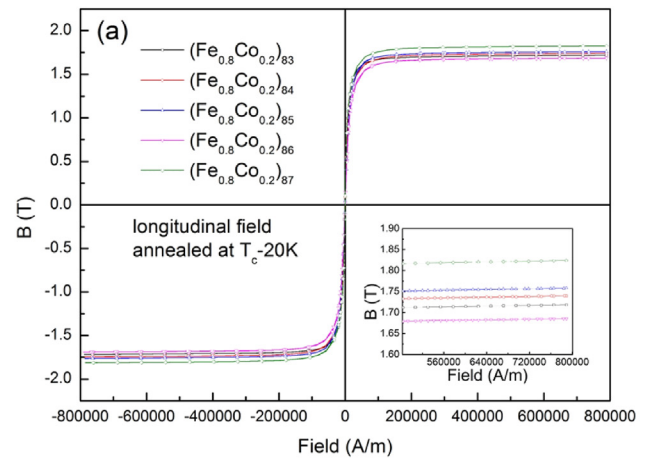


Fig. 5. (a) Hysteresis B–H loops (b) saturation magnetic flux density and (c) coercivity of the FeCoSiBP alloy ribbons after longitudinal field annealing for 600 s at temperatures of T_C-20 K.

T_C from a macroeconomic viewpoint. Besides, it is easy to demonstrate that the increase in T_C leads to the increases in x_c and $B_{s, \max}$. Fig. 6 shows the schematic diagram of the compositional

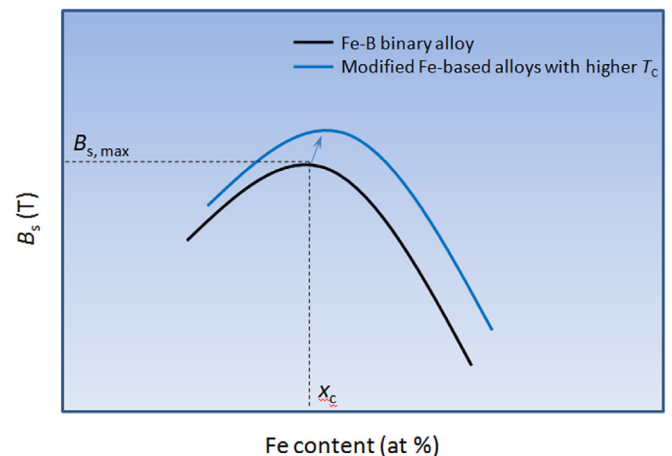


Fig. 6. Schematic diagram of the compositional modification effect on the changes in x_c and $B_{s, \max}$ in Fe-B binary amorphous alloy system.

modification effect on the changes in x_c and B_s , max. In Fe-B binary amorphous alloy system, indicated with the black line, the B_s , max (1.6 T) is obtained near 80 at% of x_c at room temperature [24]. Any compositional modification, which raises T_C caused by the changes in atomic combination configuration, leads to the increase of B_s , max, which is obtained in the alloy with higher x_c (indicated with the blue line). For instance, by partially substitution of B by carbon (C), the x_c shifted to 84 at% and the maximum B_s increased to 1.75 T [25], and ternary Fe-Si-B amorphous alloy system exhibits the x_c and maximum B_s of near 82 at% and 1.65 T [3], respectively. In addition, the highest B_s (1.7 T) is obtained near 84 at%Fe in Fe-Si-B-P-(C) amorphous alloy system [4,6]. In our present study, as discussed above, the addition of Co also causes the resulting alloy system exhibiting higher T_C , which leads to the maximum B_s obtained in the alloys with more than 84 at% Fe. Further investigation is expected to obtain higher B_s value at higher Fe (or total ferromagnetic element) content by further compositional design to increase T_C .

5. Conclusion

In the present work, we succeed in synthesizing an amorphous phase in Fe-rich FeCo-based alloys with ferromagnetic element concentration range from 83 to 86 at%. The results obtained are summarized as follows:

- (1) Co is effective for the formation of amorphous phase in the higher Fe(Co)-content range above 85 at%, which is higher than that of the highest ferromagnetic element content obtained to date in Fe-metalloid alloy system.
- (2) Partial substitution of Fe by Co causes further increase in Curie temperature of the Fe-Si-B-P amorphous alloys.
- (3) The present Fe-Co-Si-B-P amorphous alloys exhibit high B_s up to 1.75 T in conjunction with good soft magnetic properties as well as good bending ductility.
- (4) Based on the theoretical analysis, it is expected to obtain higher B_s value at higher Fe (or total ferromagnetic element) content by further optimum compositional design so as to increase T_C .

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