Soft Magnetic Properties of (Fe, Co)-RE-B Amorphous Alloys with a Large Supercooled Liquid Region

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Fe-based amorphous alloys with high B concentrations in (Fe, Co)-RE-B system were found to exhibit a large supercooled liquid region (ΔT_x) in a composition range 22.5–30 at%B, 0–30 at%Co and 2.5–6 at%RE. The ΔT_x values exceeding 50 K were obtained for a series of Fe₆₂Co_{9.5}RE_{3.5}B₂₅ (RE = Pr, Nd, Sm, Gd, Tb, Dy, Er) amorphous alloys. The Fe₆₂Co_{9.5}RE_{3.5}B₂₅ amorphous alloys exhibit good soft magnetic properties of 1.35 to 1.43 T for saturation magnetization, 1.0 to 3.8 A/m for coercive force, and 8300 to 12500 for permeability at 1 kHz in the annealed state for 600 s at 773 K. The synthesis of the (Fe, Co)-RE-B amorphous alloys exhibiting a large supercooled liquid region and good soft magnetic properties with a high saturation magnetization is promising for future development as a new type of soft magnetic material.

(Received March 19, 2001; Accepted May 8, 2001)

Keywords: iron-based amorphous alloy, iron-cobalt-rare earth-boron system, high boron concentration, supercooled liquid region, soft magnetic properties

1. Introduction

Since the finding of a melt-spun amorphous Fe-P-C alloy with ferromagnetism in 1967,¹⁾ Fe-based magnetic amorphous alloys have attracted increasing interest. Subsequently, (Fe, Co)-P-B and (Fe, Co)-B-Si alloys were reported to exhibit good soft magnetic properties in 1974,²⁻⁴⁾ followed by (Fe, Co)-(Cr, Mo, W)-C,⁵⁾ (Fe, Co)-(Zr, Hf),^{6,7)} and then (Fe, Co)-(Zr, Hf, Nb)-B⁸⁾ alloys in the early 1980 s. Among these, the melt-spun (Fe, Co)-B-Si amorphous alloys have been practically used as soft magnetic materials in pole and switching transformers.⁹⁾ However, these amorphous alloys does not have high glass-formation ability (GFA) and have been produced at high cooling rates of over 10⁵ K/s by melt spinning. The resulting ribbon thickness has been usually limited to less than about 70 μ m.

Since 1988, it has been reported that a number of non-ferrous metal-based amorphous alloys in multicomponent Mg-,¹⁰⁾ RE-,¹¹⁾ Zr-^{12,13)} and Pd-¹⁴⁾ based alloy systems (RE = rare earth elements) exhibit a large supercooled liquid region with a temperature interval exceeding 50 K and can be made into a bulk form. The high GFA is attributed to the high thermal stability of the supercooled liquid against crystallization. In addition, the large deformation and easy working due to its low viscosity and ideal Newtonian flow have been reported to be obtained in the supercooled liquid region.¹⁵⁾ These amorphous alloys always satisfy the following three empirical rules,^{16,17)} i.e., (1) multicomponent systems consisting of more than three elements, (2) significant difference in atomic size above about 12% among the main three constituent elements, and (3) large negative heats of mixing among the elements. Recently, based on the three empirical rules, we have succeeded in forming ferrous metal-based amorphous alloys with a large supercooled liquid region and reported that Fe-based amorphous alloys with a large supercooled liquid region above 50 K as well as a high GFA in the Fe-(Al, Ga)-(P, C, B, Si)¹⁸⁾ and Fe-

(Co, Ni)-(Zr, Hf, Nb)-B¹⁹⁾ systems exhibit good soft magnetic properties. However, high solute concentrations lead to a low saturation magnetization value less than 1.2 T. More recently, we have also searched for a new Fe-based amorphous alloy in (Fe, Co)-RE-B system, which exhibits a large supercooled liquid region reaching 63 K and good soft magnetic properties with a high saturation magnetization. This letter intends to present the alloy compositions, thermal stability of the supercooled liquid and soft magnetic properties of the Fe-based amorphous alloys.

2. Experimental Procedure

Alloy ingots with different compositions in (Fe, Co)-RE-B system were prepared by arc melting the mixture of pure metals and B crystal in an argon atmosphere. The ingots were crushed into small pieces, in order to place them into a quartz crucible for melt spinning. The nozzle size of the crucible is about 0.5 mm in diameter. Ribbons were produced at a circumferential velocity of 35 m/s in an argon atmosphere. The structure of the samples was examined by X-ray diffraction (Cu K α). Thermal stability was examined by differential scanning calorimetry (DSC) and differential thermal analysis (DTA) under an argon atmosphere at a heating rate of 0.67 K/s and 0.033 K/s, respectively. The saturation magnetization was measured at room temperature with a vibrating sample magnetometer (VSM) under a maximum applied magnetic field of 670 kA/m. The density of the ribbons were determined as 7.38–7.57 Mg/m³ for of Fe₆₂Co_{9.5}RE_{3.5}B₂₅ (RE = Pr, Nd, Sm, Gd, Tb, Dy, Er) amorphous alloys. The coercive force was measured with a B-H loop tracer. Permeability was evaluated at 1 kHz with an impedance analyzer. The saturated magnetostriction was measured by a capacitance method in a field of 240 kA/m.

Fig. 1 DSC curves of melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 17.5$ to 35 at%) amorphous alloys.

3. Results and Discussion

The X-ray diffraction patterns indicated that the melt-spun ribbons in the composition range of 0 to 80%Co, 0 to 10%RE and 16 to 40 at.%B were composed of an amorphous single phase. Figure 1 shows the DSC curves of the $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 17.5$ to 35 at%) amorphous alloys. As marked with the glass transition temperature (T_g) and crystallization temperature (T_x), it is noticed that the glass transition and supercooled liquid region ($\Delta T_x = T_x - T_g$) are seen in the B concentration range of 20 to 35 at%. Based on the DSC curves, T_x , T_g and ΔT_x values are plotted as a function of B content in Fig. 2. The T_g and T_x values increase from 801 to 888 K and 846 to 933 K, respectively, with increasing B content from 20 to 30 at%. The ΔT_x increases from 45 to 57 K with increasing B content from 20 to 27.5 at% and then decreases to 36 K with a further increase in B content to 35 at%. The larger ΔT_x values of 56 K and 57 K are obtained at 25 and 27.5 at%B, respectively. We further measured the melting point (T_m) by DTA. The reduced glass transition temperature (T_g/T_m) is determined to be 0.58–0.59 for the $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 25$ to 30 at%) glassy alloys. The wide ΔT_x and higher T_g/T_m indicate the possibility that the high glass-forming ability is obtained for the alloys containing 25 to 27.5 at%B.^{16,17)}

The previous data show that the maximum B content for formation of an amorphous phase in the Fe–B binary alloys is about 25 at% and no glass transition is observed for the binary alloys.^{20,21)} The addition of the rare earth and Co elements is useful for the extensions of the amorphous formation range as well as the supercooled liquid range. The reason for the effectiveness of the additional rare earth and Co elements is thought to result from the satisfaction of the three empirical rules for the increase in the thermal stability of the supercooled liquid against crystallization. That is, the addition

Fig. 2 T_g , T_x and $\Delta T_x = T_x - T_g$ as a function of B content for melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 17.5$ to 35 at%) amorphous alloys.

of these elements causes the sequent change in atomic size in the order of $\text{RE} \gg \text{Fe} > \text{Co} \gg \text{B}$, as well as the generation of new atomic pairs with relatively large negative heats of mixing. In the supercooled liquid in which the three empirical rules are satisfied at a high level, the topological and chemical short-range orderings are enhanced, leading to the formation of a dense random packed structure with low diffusivity. This concept can be applied to the present (Fe, Co)-RE-B amorphous alloys. In addition, the larger supercooled liquid region for the (Fe, Co)-RE-B amorphous alloys containing 25–27.5 at%B is presumed to result from the formation of a higher degree of dense random packed structure at these B concentrations.

The saturation magnetization (I_s) and Curie point (T_c) values of the melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 20$ to 30 at%) amorphous alloys decrease gradually from 1.53 to 1.26 T and 678 to 638 K, respectively, with increasing B content from 20 to 30 at%. The coercive force (H_c) and saturated magnetostriction (λ_s) values also decrease gradually from 10.4 to 3.2 A/m and 21.6×10^{-6} to 15.7×10^{-6} with increasing B content from 20 to 27.5 at%. The I_s , H_c , λ_s and T_c values are 1.37 T, 4.6 A/m, 17.9×10^{-6} and 663 K, respectively, for 25 at%B alloy. From the compositional dependence of ΔT_x , H_c , I_s , λ_s , and T_c , it is concluded that the $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ amorphous alloy has a good combination of higher thermal stability of the supercooled liquid and better soft magnetic properties with high T_c .

Considering that rare earth elements have very alike chemical properties, we further investigate thermal stability of the supercooled liquid properties and soft magnetic properties of the (Fe, Co)-RE-B (RE = Pr, Sm, Gd, Tb, Dy, Er) amorphous alloys with high B concentrations. Figure 3 shows the DSC curves of the $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ (RE = Pr, Sm, Gd, Tb, Dy, Er) amorphous alloys. It is seen that a glass transition and a large supercooled liquid range are ob-

Table 1 Thermal stability and magnetic properties of $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ amorphous alloys.

Composition (at%)	Thermal stability			Magnetic properties			
	T_g (K)	T_x (K)	ΔT_x (K)	I_s (T)	H_c (Am^{-1})	λ_s (10^{-6})	μ_e (at 1 kHz)
$\text{Fe}_{62}\text{Co}_{9.5}\text{Pr}_{3.5}\text{B}_{25}$	833	884	51	1.36	3.7	22	10600
$\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_{3.5}\text{B}_{25}$	844	900	56	1.41	2.6	24	12000
$\text{Fe}_{62}\text{Co}_{9.5}\text{Sm}_{3.5}\text{B}_{25}$	841	893	52	1.35	3.8	23	11700
$\text{Fe}_{62}\text{Co}_{9.5}\text{Gd}_{3.5}\text{B}_{25}$	844	907	63	1.41	1.9	24	11000
$\text{Fe}_{62}\text{Co}_{9.5}\text{Dy}_{3.5}\text{B}_{25}$	856	914	58	1.43	3.0	19	8300
$\text{Fe}_{62}\text{Co}_{9.5}\text{Tb}_{3.5}\text{B}_{25}$	842	903	61	1.36	3.1	27	12500
$\text{Fe}_{62}\text{Co}_{9.5}\text{Er}_{3.5}\text{B}_{25}$	830	884	54	1.38	1.0	32	8900

served distinctly for all the alloys. The supercooled liquid range ΔT_x exceeds 50 K, and the largest ΔT_x is 63 K for $\text{Fe}_{62}\text{Co}_{9.5}\text{Gd}_{3.5}\text{B}_{25}$ alloy. The $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ amorphous alloys with a large supercooled liquid range exhibit good soft magnetic properties. Figure 4 shows the hysteresis B-H loops of the $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ (RE = Pr, Gd, Dy, Er) amorphous alloys in the state annealed for 600 s at 773 K. It is seen that the amorphous alloys exhibit higher saturation magnetization (I_s) and low coercive force (H_c). The I_s , H_c , magnetostriction (λ_s) and the permeability (μ_e) at 1 kHz values are in the range 1.35–1.43 T, 1.0–3.8 A/m, $19\text{--}32 \times 10^{-6}$ and 8300–12500, respectively.

Table 1 summarizes the thermal stability of the supercooled liquid (T_g , T_x and ΔT_x) and the magnetic properties (I_s , H_c , λ_s , μ_e) of the $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ amorphous alloys in the state annealed for 600 s at 773 K. The features of the present Fe-Co-RE-B amorphous alloys are summarized as follows: (1) high thermal stability which is evidenced from the higher T_x and the larger ΔT_x greater than 50 K, (2) higher I_s exceeding 1.35 T, which is higher than those for the other Fe-based amorphous alloy with a large supercooled liquid range,²²⁾ and (3) low H_c and high μ_e comparable to those for the other Fe-based amorphous alloys.²²⁾

Fig. 3 DSC curves of melt-spun $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ (RE = Pr, Sm, Gd, Tb, Dy, Er) amorphous alloys.

4. Summary

Ferromagnetic amorphous alloys with a large supercooled liquid region were formed in (Fe, Co)-RE-B alloys with high boron concentrations of 22.5 to 30 at%. The ΔT_x of the $\text{Fe}_{100-x-y-z}\text{Co}_x\text{RE}_y\text{B}_z$ amorphous alloys exceeds 50 K in the range 0–30 at% Co, 2.5–6 at% RE, 22.5–30 at% B. The $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ (RE = Pr, Nd, Sm, Gd, Tb, Dy, Er) amorphous alloys exhibit good soft magnetic properties, e.g., high I_s of 1.35–1.43 T, low H_c of 1.0–3.8 A/m, and high μ_e at 1 kHz of 8300–12500. The new Fe-based amorphous alloys are expected to be developed as a new soft magnetic material with high saturation magnetization and large glass-forming ability.

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Fig. 4 Hysteresis B-H loops of $\text{Fe}_{62}\text{Co}_{9.5}\text{RE}_{3.5}\text{B}_{25}$ (RE = Pr, Gd, Dy, Er) amorphous alloys in the state annealed for 600 s at 773 K.

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