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Magnetic properties of low rare-earth composition Pr–Fe–Co–Ti–Nb–B system exchange-spring magnets

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Abstract

Amorphous melt-spun ribbons of $Pr_6Fe_{94-w-x-y-z}Co_wTi_xNb_yB_z$ (w = 7.0–9.0, x = 1.0–2.0, y = 0–1.5, z = 6.0–8.0) alloys were prepared by the single roller liquid rapid-quenching method, and the effects of composition, substrate surface velocity and annealing condition on the magnetic properties were studied. The optimum preparing condition and some properties were as follows: composition, $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$; substrate surface velocity, 20.0 m/s; annealing condition, 625 °C for 5 min; heating rate, 625 °C/min in Ar atmosphere; magnetic properties, J_r = 1.15 T, H_{cJ} = 416.6 kA/m, H_{cB} = 339.8 kA/m, $(BH)_{max}$ = 128.0 kJ/m^3, $H_k/H_{cJ} \times 100$ = 27.7% recoil ratio = 64.2%, T_c = 398.0%, $\alpha(J_r)$ = −0.03%/°C, and $\alpha(H_{cJ})$ = −0.44 %/°C. From TEM observation, the average particle size of this ribbon was found to be about 23 nm. The value of $(BH)_{max}$ for the compression molding isotropic bonded magnets prepared by using the $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ ribbons (annealing condition: 625 °C for 5 min, heating rate: 625 °C/min) was 69.7 kJ/m^3 (8.7 MGOe), and the density was 6.1 Mg/m^3.

Keywords: Pr–Fe–Co–Ti–Nb–B alloys; Melt-spun ribbons; Magnetic properties; Temperature coefficient; Bonded magnet

1. Introduction

Since the principle of nanocomposite permanent magnets of exchange coupling between soft and hard magnetic phases have been shown by Kneller and Hawing [1], these magnets were prospective as the next generation magnets. Recently, these high quality melt-spun Nd(Pr)–Fe–B system exchange coupled permanent magnets have been reported [2–13]. It is known that the magnetic anisotropy constant (K_A) of $Pr_2Fe_{14}B$ compound is larger than that of $Nd_2Fe_{14}B$ compound. However the saturation magnetization of $Pr_2Fe_{14}B$ compound is smaller than that of $Nd_2Fe_{14}B$ compound [14]. This experiment carried out to investigate the effect of Co, Ti and Nb substitution for Fe in melt-spun ribbons of low rare-earth Pr–Fe–Co–Ti–Nb–B system alloys on the magnetic properties. And the magnetic properties of the compression molding Pr–Fe–Co–Ti–Nb–B isotropic bonded magnets made of the optimum composition ribbons were examined.

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2. Experimental procedure

The raw materials used in this experiment are metallic Pr, Fe, Co, Ti, Nb and metalloid B. The composition were chosen with the following formula: $Pr_6Fe_{94-w-x-y-z}Co_wTi_xNb_yB_z$, as a proposal: where w = 7.0–9.0, x = 1.0–2.0, y = 0–1.5, z = 6.0–8.0 in at.%. The master alloys of these compositions were prepared in a rod shape by a vacuum-suction method after melting in Ar gas atmosphere in high-frequency induction furnace. The melt-spun ribbons were prepared by using the single roller liquid rapid quenching method in which a molten material was injected onto a roller surface. The substrate surface velocity was varied between 15.0 and 30.0 m/s, and the roller-diameter was 0.3 m. The amorphous ribbons were annealed at various temperatures between 625 and 675 °C and annealing time from 3 to 7 min with heating rate 125–625 °C/min. The compression molding isotropic bonded magnets were made by using melt-spun Pr–Fe–Co–Ti–Nb–B powder crushed under 150 μm (using 2.5 wt.% epoxy resin as a binder). After 4.5 MA/m pulsed magnetization, the magnetic properties, Curie temperature and temperature coefficient of H_{cJ} and J_r for ribbons were measured by a VSM.

The crystallization temperature of as-quenched ribbons was measured by a DTA device. The crystal structure was examined by X-ray diffraction method on the powder samples with Cu Kα radiation. The microstructure of ribbons was observed by a TEM.

3. Results and discussion

Fig. 1 shows the effect of Co substitution in melt-spun $Pr_6Fe_{84.5-w}Co_wTi_{1.5}Nb_1B_7$ (w = 7.0–9.0) system ribbons prepared at the substrate surface velocity 20.0 m/s, annealed at 625 °C for 5 min (heating rate: 625 °C/min). From this figure, it was found that the values of $(BH)_{max}$, H_{cJ} and H_{cB} increased with increasing the w value from 7.0 to 8.0, then decreased, while the value of J_r increased with increasing the w value. From this result, the optimum w value was 8.0 at.% in this experiment.

Fig. 2 shows the magnetic properties of melt-spun $Pr_6Fe_{78-x}Co_8Ti_xNb_1B_7$ (x = 1.0–2.0) system ribbons prepared at the substrate surface velocity 20.0 m/s, annealed at 625 °C for 5 min (heating rate: 625 °C/min). From this figure, the values of $(BH)_{max}$, H_{cJ} and H_{cB} increased with increasing the x value from 1.0 to 1.5, then decreased, while J_r showed almost constant. As this result, the optimum x value was 1.5 at.%.

Next, the amount of Nb was changed. Fig. 3 shows the magnetic properties of melt-spun $Pr_6Fe_{77.5-y}Co_8Ti_{1.5}Nb_yB_7$ (y = 0–1.5) system ribbons. Preparing conditions are the same as the case where the above-mentioned amount of Co or Ti is changed. From this figure, the value of $(BH)_{max}$, H_{cJ} and H_{cB} increased with increasing the y value from 0 to 1.0, then decreased.

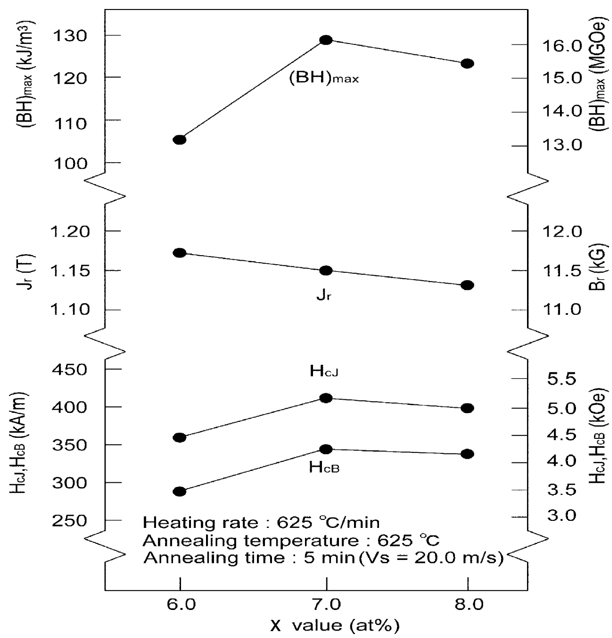

Fig. 2. Magnetic properties of melt-spun $Pr_6Fe_{78-x}Co_8Ti_xNb_1B_7$ alloy ribbons.

Additionally, the value of J_r decreased a little with increasing the y value. From this result, the optimum y value was 1.0 at.%.

Fig. 4 shows the magnetic properties of melt-spun $Pr_6Fe_{83.5-z}Co_8Ti_{1.5}Nb_1B_z$ (z = 6.0–8.0) system ribbons. Preparing conditions are the same as that of Fig. 3. From

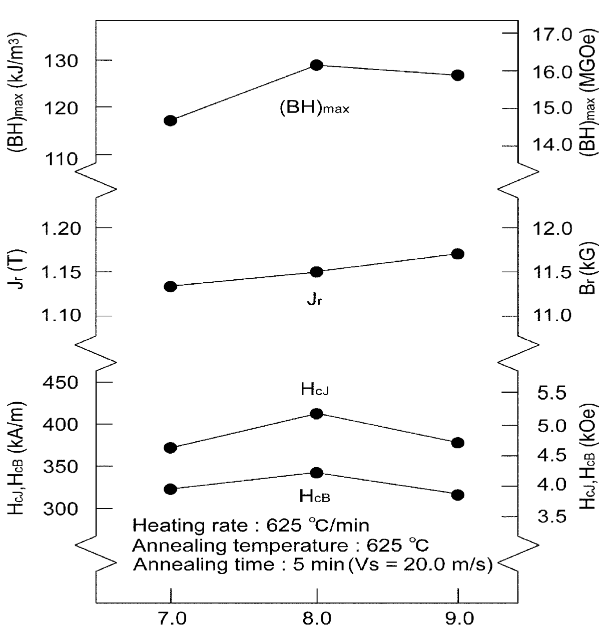

Fig. 1. Magnetic properties of melt-spun $Pr_6Fe_{84.5-w}Co_wTi_{1.5}Nb_1B_7$ alloy ribbons.

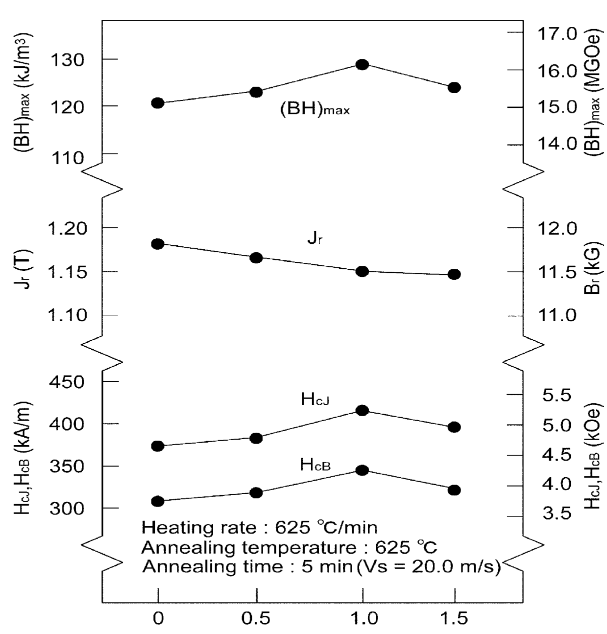

Fig. 3. Magnetic properties of melt-spun $Pr_6Fe_{77.5-y}Co_8Ti_{1.5}Nb_yB_7$ alloy ribbons.

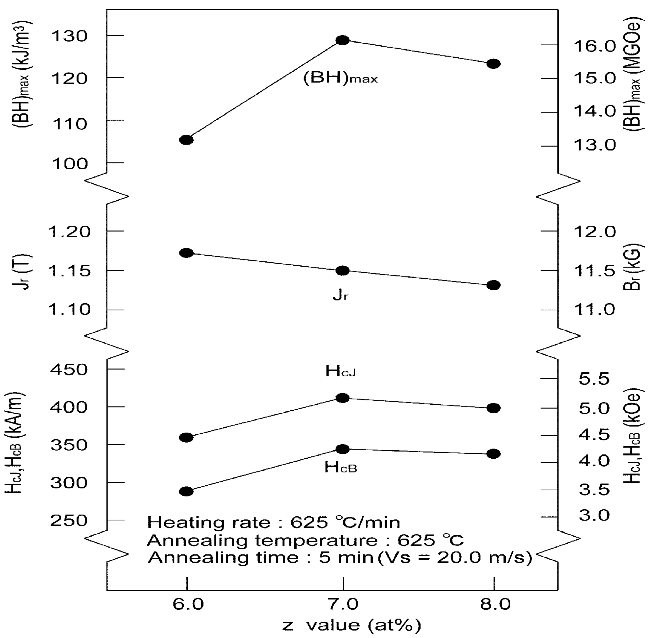

Fig. 4. Magnetic properties of melt-spun $Pr_6Fe_{83.5-z}Co_8Ti_{1.5}Nb_1B_z$ alloy ribbons.

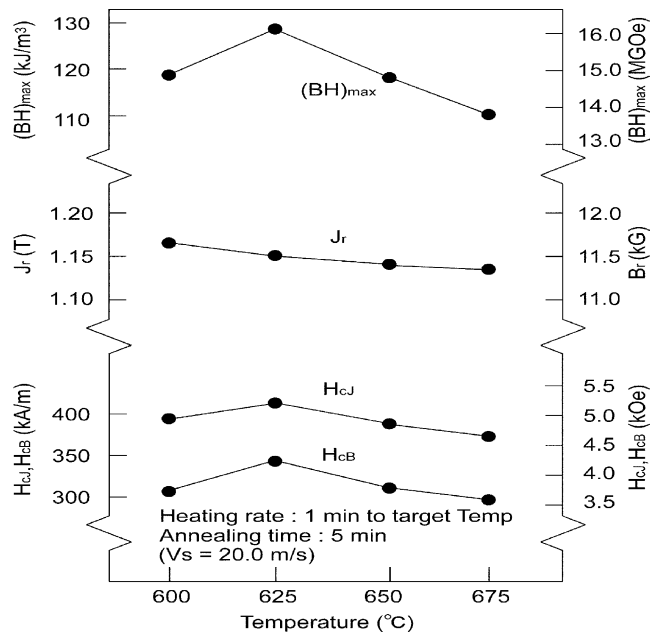

Fig. 5. Effect of annealing temperature on magnetic properties of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons.

this figure, it was found that the values of $(BH)_{max}$, H_{cJ} and H_{cB} increased with increasing the z value from 6.0 to 7.0, then decreased. Additionally, the value of J_r decreased a little with increasing the z value. The very high coercivity $H_{cJ} = 416.6$ kA/m ($J_r = 1.15$ T, $(BH)_{max} = 128.0$ kJ/m^3) was shown at $z = 7.0$ in low rare-earth composition. From these results, it was found that the optimum composition was $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ in this experiment.

Next, the effect of the substrate surface velocity (15.0–30.0 m/s) on magnetic properties of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons annealed at 625 °C for 5 min were examined. From this result, the optimum substrate surface velocity was 20.0 m/s.

Fig. 5 shows the effect of annealing temperature on the magnetic properties of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons prepared at the substrate surface velocity 20.0 m/s. Before heat-treatment, the DTA curve of this sample was examined. It was shown that three exothermal peaks (α-Fe, $Pr_2Fe_{14}B$ and Fe_3B type structure from X-ray diffraction patterns) were appeared. From the DTA curve, the crystallization temperature of these ribbons was determined about 580 °C, so the annealing treatment was done over 600 °C in this experiment. In this heat treatment, the heating rate was 625 °C/min, and the sample was heated up until the annealing temperature, and then it was held 5 min. Finally, it was rapidly quenched. From this figure, the values of $(BH)_{max}$, H_{cJ} and H_{cB} increased with increasing the annealing temperature from 600 to 625 °C, and then decreased. The value of J_r decreased a little with increasing the annealing temperature. From this result, the optimum annealing temperature was 625 °C. Next, the effect of annealing time (3–7 min) on the magnetic properties of these ribbons were investigated. From this result, it was found that the optimum annealing time was 5 min in this composition.

Fig. 6 shows the X-ray diffraction patterns of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons. As shown in this figure, it was found that $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ ribbons consisted of two phases $Pr_2Fe_{14}B$ type and α-Fe type structure. And Fe_3B type phase observed in the DTA curve was decomposed by the heat-treatment and seemed to diffuse.

When the above results were summarized, the optimum preparing condition was as follows: composition, $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$; substrate surface velocity,

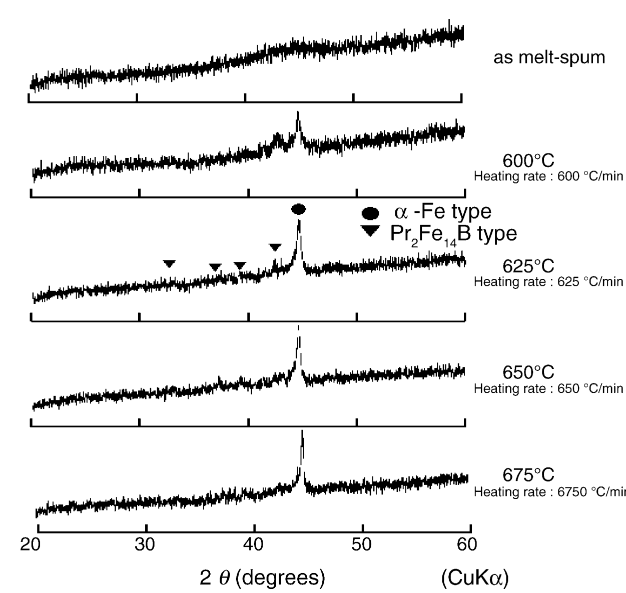

Fig. 6. X-ray diffraction patterns of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons.

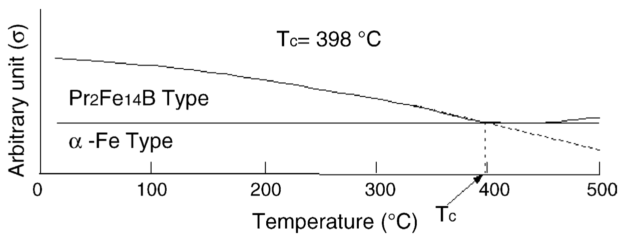

Fig. 7. Temperature dependence of magnetization for melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons.

20.0 m/s; annealing condition, 625 °C for 5 min; heating rate, 625 °C/min.

Fig. 7 shows the σ–T curve for melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbon prepared at the optimum condition. From the σ–T curve, the Curie temperature was 398 °C, this alloy ribbon consisted of two phases of $Pr_2Fe_{14}B$ type and α-Fe type structure. Further more the roughly volume percentage of each phase was 56% $Pr_2Fe_{14}B$ type and 44% α-Fe type phase, respectively.

Fig. 8 shows the TEM micrograph and the electron diffraction pattern of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons annealed at 625 °C for 5 min. It is shown that the average particle size was about 23 nm. And fine grain is distributed from spotty ring of electron diffraction, so this sample was the isotropic one.

The demagnetization curve of these ribbons is single phase. From X-ray diffraction patterns, TEM, and σ–T, it was found these samples were the exchange spring magnet.

Fig. 9 shows the temperature dependence of J_r and H_{cJ} of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbon annealed at the optimum condition. From this result, the temperature coefficient of J_r was $\alpha(J_r) = -0.03\%/°C$ (reversible). The curve of H_{cJ} corresponds to the irreversible one. The temperature coefficient of H_{cJ} in the range from 25 to 100 °C obtained by a linear extrapolation was $\alpha(H_{cJ}) = -0.44\,\%/°C$.

Fig. 10 shows the demagnetization curve for the compression molding $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ isotropic bonded

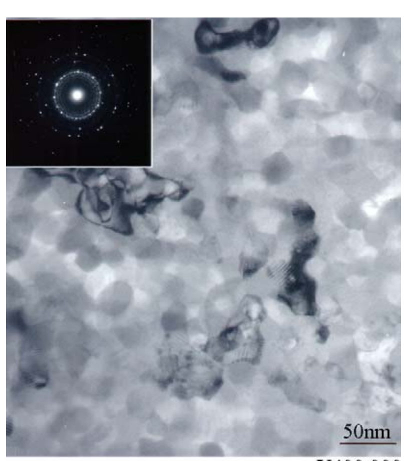

Fig. 8. TEM photograph of melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons.

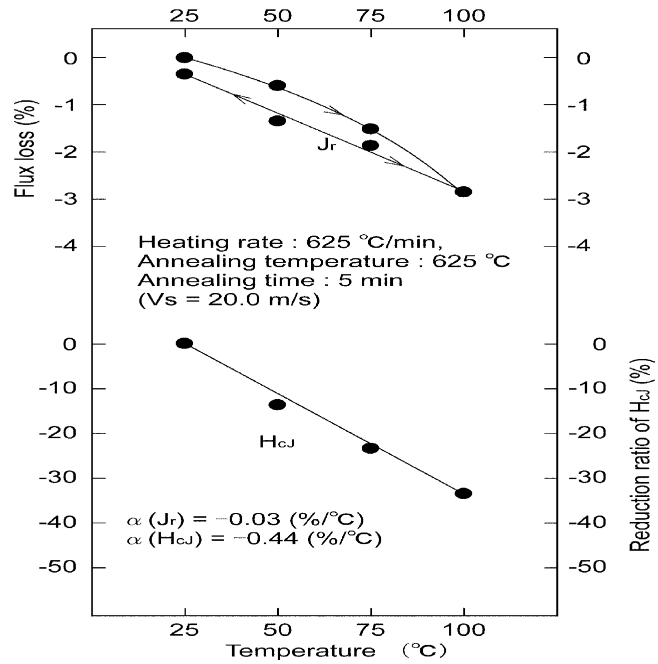

Fig. 9. Temperature dependence of J_r and H_{cJ} in melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbons.

magnet prepared by using the ribbons annealed at optimum condition. Bonded magnets were made by crushing the ribbons into a powder under 150 μm, and the compression molding the powder under the pressure of 980 MPa. As the binder, epoxy resin was added to make up 2.5 wt.% The den-

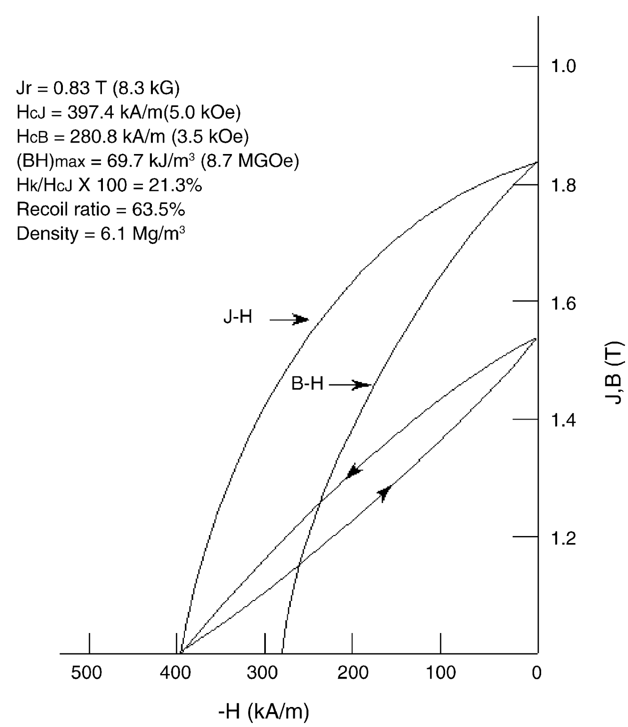

Fig. 10. Demagnetization curves and recoil loop for a bonded magnet prepared by melt-spun $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbon. Annealing condition: 625 °C for 5 min.

sity of this magnet is 6.1 Mg/m^3. The magnetic properties of a typical bonded magnet are J_r = 0.83 T, H_{cJ} = 397.4 kA/m, H_{cB} = 280.8 kA/m and $(BH)_{max}$ = 69.7 kJ/m^3.

4. Conclusion

The result obtained in the experiment is summarized.

In $Pr_6Fe_{76.5}Co_8Ti_{1.5}Nb_1B_7$ alloy ribbon, when the substrate surface velocity is 20.0 m/s, annealing temperature is 625 °C for 5 min, and heating rate is 625 °C/min, the best magnetic properties are obtained. Magnetic properties of ribbon are J_r = 1.15 T, H_{cJ} = 416.6 kA/m, H_{cB} = 339.8 kA/m, $(BH)_{max}$ = 128.0 kJ/m^3, $H_k/H_{cJ} \times 100$ = 27.7 °C, recoil ratio = 64.2%, T_c = 398.0 °C, $\alpha(J_r) = -0.03$%/°C, and $\alpha(H_{cJ}) = -0.44$%/°C. In low rare-earth content, especially the value of H_{cJ} was obtained for the first time over 416.6 kA/m. The value of $(BH)_{max}$ for the isotropic bonded magnet prepared by using these ribbons is 69.7 kJ/m^3.

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