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Effect of quench rate on nanostructure and magnetic properties of PrCo5

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The effect of quench rate on nanostructure and magnetic properties of PrCo5 alloy has been investigated. The increase of quench rate through wheel speed in melt spinning suppresses the formation of the secondary Pr2Co17 and Pr5Co19 phases with low magnetocrystalline anisotropy field and refines the nanostructure. This significantly improves the coercivity, remanence, and energy product. For example, increasing the wheel speed from 30 m/s to 70 m/s increases the coercivity and energy product from 3.2 kOe and 4.0 MGOe to 10.3 kOe and 13.7 MGOe, respectively. The magnetic hardening mechanism appears to be a mixture of reversed-domain-nucleation and domain-wall-pinning. The temperature coefficient of coercivity for the 70 m/s sample is $-0.16%/K$ from 300 to 700 K, which is better than that of sintered SmCo5 magnets. Low temperature coefficients of coercivity and remanence indicate that rapidly quenched PrCo5 ribbons may be suitable for bonded magnets with high operation temperature.

I. INTRODUCTION

Hexagonal PrCo5 has attractive properties among the RCo5 compounds because of its large theoretical energy product (36 MGOe), moderately high Curie temperature (900 K), and high magnetocrystalline anisotropy field (170 kOe).1–3 The coercivity of PrCo5 materials is rather low in comparison with the anisotropy field. This mainly arises from the existence of impurity Pr2Co17 and Pr5Co19 phases with low anisotropy field, which are generated by the eutectoid reaction at 1119 K shown in Fig. 1.4 The low coercivity hinders the development of energy product. Carbon addition retards the formation of impurity phases and thus significantly improves coercivity, but decreases remanence.5 The increase of quench rate was found to improve coercivity,6 but the effect of quench rate on nanostructure is unclear. The reason for the coercivity enhancement has not been investigated. Up until now, the coercivity of the binary Pr-Co alloys is still rather low (<5 kOe). In this work, we study the influence of quench rate on nanostructure and magnetic properties of nanocrystalline PrCo5, analyze the nanostructure-magnetic property relationship, and clarify the origin of magnetic property enhancement.

II. EXPERIMENT METHODS

Ingots of PrCo5 were arc melted from high-purity elements in an argon atmosphere. A 3% weight loss was accounted for. The ribbons were made by ejecting molten alloys in a quartz tube onto the surface of a copper wheel with speeds of 30–70 m/s. The ribbons are about 2 mm wide and 50 μm thick. The phase components were examined by Rigaku D/MAX-B X-ray diffraction (XRD) with Co Kα radiation. The nanostructure was observed by a Tecnai Osiris Transmission Electron Microscope (TEM). The energy dispersive X-ray (EDX) analysis results show that the composition of the sample is PrCo5.05. The hysteresis loops were measured by a superconducting quantum interference device (SQUID) magnetometer at fields up to 7 T and physical property measurement system (PPMS) vibration sample magnetometer (VSM). The applied field is parallel to the long direction of the ribbon.

III. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of nanocrystalline PrCo5 at various wheel speeds. The ribbons consist of PrCo5 and a small amount of impurity Pr2Co17 and Pr5Co19 phases. The relative intensities of the diffraction peaks for the impurity

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phases decrease with the increase of wheel speed. This indicates that the increase of wheel speed suppresses the formation of impurity phases. For the fastest velocity, \( v = 70 \text{ m/s} \), the sample is composed of single-phase PrCo\(_5\). The full width at half maximum of the diffraction peaks for PrCo\(_5\) decreases with the increase of wheel speed, indicating that the mean grain size of PrCo\(_5\) is decreased by increasing wheel speed.

Figure 3 shows TEM images of the 30 m/s and 70 m/s samples and corresponding statistical grain size distribution. Two characteristic maxima are observed in the grain-size distribution of Fig. 3(c). The first maximum may represent impurity phase grains and the second maximum may originate from PrCo\(_5\) grains. The grain size of PrCo\(_5\) is distributed in the range of 170–450 nm. The average grain size for PrCo\(_5\) and impurity phase is 290 and 110 nm, respectively.

One maximum is seen in Fig. 3(d), which implies that the 70 m/s sample consists of PrCo\(_5\). The grain size is distributed in the range of 12–28 nm with a mean grain size of 19 nm. The above results indicate that the large increase of wheel speed fully impedes the formation of impurity phases and refines the nanostructure, which is in good agreement with the XRD results.

Figure 4 shows hysteresis loops of nanocrystalline PrCo\(_5\) at different wheel speeds. The increase of wheel speed increases the volume fraction of the hard magnetic phase PrCo\(_5\), refines the nanostructure as shown in Fig. 3, and promotes the effective exchange coupling of the soft magnetic phases. Therefore, the remanence ratio, coercivity, and the rectangular of the demagnetization curves are significantly improved due to the increase of wheel speed. The energy product increases almost two times. The best magnetic properties: \( H_c = 10.3 \text{ kOe} \) and \( (BH)_{\text{max}} = 13.7 \text{ MGOe} \), which is
the highest among the isotropic PrCo5-based ribbons, were obtained for the 70 m/s sample. Here, the value of coercivity is close to that of nanocrystalline Pr2Fe14B. Simultaneously, the energy product is lower than that of nanocrystalline Pr2Fe14B due to smaller Js of PrCo5. However, PrCo5 has much higher Tc than that of Pr2Fe14B. Melt-spun PrCo5 may be a good candidate for high temperature application.

Figure 5 shows hysteresis loops at various temperature of nanocrystalline PrCo5 at 70 m/s and deduced temperature dependence of magnetic property. The coercivity of the sample decreases with the temperature increasing because of the decrease of the magnetocrystalline anisotropy field. The temperature coefficients of remanence $\alpha$, coercivity $\beta$, and energy product $\gamma$ are defined as: $\alpha = \frac{\{J_r(T_0) - J_r(T_1)\}/\{J_r(T_0) - J_r(T_1)\} \times (T_0 - T_1)\}}{100\%}$; $\beta = \frac{\{H_c(T_0) - H_c(T_1)\}/\{H_c(T_0) - H_c(T_1)\} \times (T_0 - T_1)\}}{100\%}$; and $\gamma = \frac{\{(BH)_{max}(T_0) - (BH)_{max}(T_1)\}/\{(BH)_{max}(T_0) \times (T_0 - T_1)\}\}}{100\%}$. $\alpha$ is $-0.06%/K$ within 300–700 K, which is close to that of sintered SmCo5 magnets. $\beta$ is $0.16%/K$, which is much lower than that ($0.30%/K$) of sintered SmCo5 magnets, and $\gamma$ is $-0.16%/K$. The above results suggest that melt-spun PrCo5 is a good candidate for high temperature application. The inset of Fig. 5(a) presents the applied-field dependence of coercivity. The coercivity increases linearly for $H < 16$ kOe. It approaches saturation at the high field of 35 kOe, which is much larger than the saturated coercivity. This indicated that domain walls move neither easily nor freely. The magnetically hardening mechanism may be a mixture of the nucleation of reverse domains and the pinning of domain walls.

IV. CONCLUSIONS

High-performance nanocrystalline PrCo5 has been produced by adjusting the quench rate. By increasing wheel speeds, the volume fraction of the hard magnetic phase was increased and nanostructure was refined. This leads to the significant increase of remanence, coercivity, and energy product. The energy product of 13.7 MGOe, which is the record value so far among the isotropic PrCo5 ribbons, is achieved for $v = 70$ m/s. The temperature coefficient of coercivity for the 70 m/s ribbon is superior to that of sintered SmCo5 magnets. This indicates that nanocrystalline PrCo5 ribbons have favorable properties for high-temperature applications. The coercivity mechanism of nanocrystalline PrCo5 is a mixture of reverse-domain-nucleation and domain-wall-pinning.

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