Microstructural studies of PrCo$_5$ magnets


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Microstructural studies were performed on two sintered Pr–Co magnets with different coercivities. The one with starting composition Pr$_{10}$Co$_{10}$ had an intrinsic coercivity $H_c = 2400$ Oe, remanent induction $B_r = 9630$ G, and energy product $(BH)_{\text{max}} = 17.5$ MGOe; the other with starting composition Pr$_{17.5}$Co$_{22.5}$ had a $H_c = 140$ Oe, a $B_r = 9010$ G and a $(BH)_{\text{max}} = 1.24$ MGOe. It was found that a hexagonal Pr oxide with lattice parameters $a = (3.85 \pm 0.1) \, \text{Å}$ and $c = (5.98 \pm 0.2) \, \text{Å}$ is the dominating impurity phase in the magnets. Quite a large number of rhombohedral Pr$_5$Co$_{17}$ grains were found in the low coercivity sample. Unlike rhombohedral Sm$_2$Co$_{17}$ precipitates which are fully coherent with the matrix in SmCo$_5$ magnet, the Pr$_5$Co$_{17}$ grew at the grain boundary forming a semicoherent interface with a neighboring PrCo$_5$ grain. The orientation relationships between 1:5H and 2:17R are identified as (1010)$_{1:5H}$ || (2110)$_{2:17R}$ and (0001)$_{1:5H}$ || (0003)$_{2:17R}$. Factors responsible for the low coercivity in PrCo$_5$ magnets were proposed from the microstructural point of view, and a comparison is made with the SmCo$_5$ system.

1. Introduction

Not long after the discovery of the extremely high magnetocrystalline anisotropy of rare-earth cobalt compounds of the RCo$_5$-type (R = Y, La, Ce, Nd, Pr and Sm) [1], SmCo$_5$ compounds were successfully fabricated into high energy permanent magnets (HEPM) with unique properties such as a high energy product and a large coercivity combined with a high Curie temperature [2,3]. So far, however, commercial applications of the RCo$_5$-type compounds have been limited only to SmCo$_5$ magnets despite similar chemical properties of other rare-earth elements. The PrCo$_5$ compound has a higher theoretical energy product (39 MGOe) than the SmCo$_5$ compound. In addition, the element Pr is more abundant in nature than Sm. The advantage of their potentially high energy product has attracted considerable interest in PrCo$_5$ magnets [4–8].

The research on PrCo$_5$ magnets was first started by Strnat et al. [4–6]. Later, active investigations were undertaken by Wallace and his co-workers [7,8]. Using commercially procured Pr, Wallace et al. fabricated a number of magnets. Their reported remanent induction $B_r$, energy product $(BH)_{\text{max}}$ and intrinsic coercivity $H_c$, ranged from 10.3 kG, 20.6 MGOe and 4.2 kOe to 10.5 kG, 22.1 MGOe and 4.6 kOe, respectively. They found that all these parameters as well as chemical stability were enhanced if ultra-pure Pr was used in the fabrication. Even though significant progress was made in comparison to the previous work, the low coercivity of PrCo$_5$ magnets has limited its applications. Recently, Ghandehari et al. reported [9] that the coercivity can be improved by adding oxide and partially substituting Pr by Sm. The energy product of their magnets is ~ 18 MGOe.

In PrCo alloys near the composition 1:5, three phases (Pr$_5$Co$_7$, Pr$_5$Co$_{19}$ and Pr$_5$Co$_{17}$), which are present as minor components, have a low magnetocrystalline anisotropy. Currently, it is commonly believed that any of the three phases other than 1:5 phase may function as inhomogeneous nucleation sites of reverse domain and it is the presence of one or more of these phases in 1:5 HEPM that leads to a low coercivity [6–8].

In contrast to the detailed microstructural investigations in SmCo$_5$ magnets [10–13], little is known about the microstructure of PrCo$_5$ mag-
nets. With the help of transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS), the present basic study is therefore undertaken to examine the microstructure of PrCo$_5$ magnets near the stoichiometric PrCo$_5$ alloy, and to correlate the microstructure with the magnetic properties. Additionally a comparison is made to the microstructure of SmCo$_5$ magnets so that a coherent picture of the low coercivity in PrCo$_5$ magnets may be understood in view of the microstructure.

2. Crystal structure

The hexagonal PrCo$_5$ compound has a space group P6/mmm and has the CaCu$_5$ structure [14]. It can be described as a layered structure perpendicular to the hexagonal c-axis, which consists of alternating close-packed cobalt layers and mixed layers of rare-earth and cobalt atoms [15]. The hexagonal Pr$_2$Co$_7$ structure (P6$_3$/mmc), the rhombohedral Pr$_5$Co$_{19}$ and the Pr$_2$Co$_{17}$ structure (R3m) may be considered as derivatives of the PrCo$_5$ structure with different sequences of 1:5 stacking unit [16,17] along the c-axis. In unit cells of the 2:7H phase, six 1:5 stacking units are superimposed in the hexagonal c-axis with the substitution of one cobalt atom by a Pr atom in every third layer. The layers 1 to 4 are also shifted by a crystallographic shear vector $\frac{1}{3}$(1010). In the unit cell of the 2:17R phase, three 1:5 stacking units are superimposed along the c-axis with one-third of the Pr atoms replaced by a pair of Co atoms. On the other hand, in 5:19R structure, twelve 1:5 stacking units are superimposed along the c-axis with one Co atom replaced by Pr in every fourth layer.

3. Experimental details

The materials used in the study are two sintered magnets of near stoichiometric PrCo$_5$ composition, that have been produced from commercial grade Pr. Magnets were chosen in such a way that the one with starting composition Pr$_{19.0}$Co$_{81.0}$ had a relatively high coercivity, and the other with starting composition Pr$_{17.3}$Co$_{82.7}$ had a low coercivity. The magnet Pr$_{19.0}$Co$_{81.0}$, with the relatively high coercivity had an intrinsic coercivity $H_{ci} = 2400$ Oe, a remanent induction $B_r = 9630$ G, and an energy product $(BH)_{max} = 17.5$ MGOe; the other magnet with a low coercivity had a $H_{ci} = 140$ Oe, a $B_r = 9010$ G and a $(BH)_{max} = 1.24$ MGOe. It should be noted that the two magnets with different compositions were fabricated through a similar process. Details of magnet fabrication have been published elsewhere [8].

The two magnets in cylindrical shape of 1 cm long and 0.42 cm in diameter were sliced both perpendicular to and parallel to the magnetization direction (c-axis). Thin specimens were prepared by ion-milling, and were then examined with a Philips 420T microscope operated at 120 kV. Structural information for the 5:19 phase was obtained from an as-cast ingot of the stoichiometric composition prepared by induction melting, and subsequently heat-treated at 1100°C for 10 days.

4. Results

4.1. Pr$_{19.0}$Co$_{81.0}$ magnet

This magnet largely consisted of 1:5 grains of about 3–10 µm in diameter with a low defect density. In the sample cut perpendicular to the magnetization direction, almost all grains were found to be well aligned with their hexagonal c-axis along the magnetization direction. Small grains (2–3 µm in diameter) were frequently observed to deviate less than 2.5° in orientation with respect to the c-axis of neighboring grains.

As shown in fig. 1a, the dominant impurity phase, in which strong Pr peaks were detected by EDS, grew both inside the 1:5 grains and in the grain boundaries. Selected area diffraction (SAD) studies (fig. 2) showed that this phase was a hexagonal phase with lattice constant $a = (3.85 \pm 0.1)$ Å and $c = (5.98 \pm 0.2)$ Å. In spite of the dominant Pr element detected in the EDS spectrum, the impurity phase is not a pure Pr α phase with space group P6$_3$/mmc because the corresponding reflection conditions (0001 : 1 = 2n;
Fig. 1. Dark field images at $g = 11\overline{2}0$ of Pr oxide distributed (a) in 1:5 matrix, (b) at the grain boundary.

hh$2\overline{h}l : 1 = 2n$) are not satisfied in SAD patterns. These Pr rich particles were found to be more easily thinned than the surrounding 1:5 matrix phase by ion-milling and showed lighter contrast than the matrix phase under microscope. This suggested the presence of light elements in the

Fig. 2. SAD patterns of the hexagonal Pr oxide at zone axes: (a) 0001, (b) 11$\overline{2}0$ and (c) 1010. The lattice parameters were measured to be $a = (3.85 \pm 0.1) \, \text{Å}$ and $c = (5.98 \pm 0.2) \, \text{Å}$. 
phase, which could not be detected in EDS spectroscopy. Considering the fact that Pr is easily oxidized, it is most likely to be hexagonal Pr$_2$O$_3$ [18]. In the EDS spectrum (fig. 3a), a small amount of Co, estimated to be 6 to 8% of Pr, was detected in the oxide. The method of estimating this will be discussed in the later part of this section. Similar (Pr,Sm)$_2$O$_3$ has been observed in (Pr,Sm)Co$_5$ magnets [19].

These oxide inclusions were dispersed non-uniformly in a 1:5 matrix, and no definite orientation relationships with the matrix were observed. The size of the oxide particles in the matrix ranged from 100 Å to 1500 Å and could be observed only

Fig. 3. EDS spectra of (a) Pr oxide; (b) heavily twinned 1:2 phase; (c) 5:19 phase; and (d) 1:5 phase.
in thin regions of the specimen. Those nucleating heterogeneously in the grain boundary were bigger than those in the matrix and some grew to 7000 Å. SAD patterns shown in fig. 2c were taken from oxide particles in the grain boundary.

A heavily twinned phase (fig. 4), always appearing dark due to twin-induced strains, was occasionally observed in the grain boundaries with a size averaging from 0.5 to 5 μm. The Pr/Co ratio of this phase obtained from the EDS spectrum (fig. 3b) was found to be much larger than that corresponding to the 5:19 phase. Since atomic diameters of rare earth atoms are substantially larger than those of transition metal atoms, the substitutional solid solubility between Pr and Co sites should be small in the 1:5 structure. Thus, the 1:5 phase was considered to be stoichiometric, and consequently could be used as a calibration to get the K factor [20] for Pr/Co in the EDS.
spectrum. In this way, the Pr/Co ratio of the twinned phase was calculated to be $0.49 \pm 0.03$ since the $K$ factor obtained from 1:5 phase was $0.82 \pm 0.03$. Therefore, this heavily twinned phase was probably PrCo$_2$. A similar (Pr,Sm)Co$_2$ phase was also observed by Ghandehari and Fidler [19]. The same method was used in the estimation of the Co content in the Pr oxide. In the magnet, no trace of the 2:17 phase was found. Because of the existence of the PrCo$_2$ phase and the absence of 2:17 phase, the magnet is believed to be slightly richer in Pr near 1:5 stoichiometry after the Pr consumed by oxygen is taken into account.

4.2. 5:19 phase

In the Pr–Co phase diagram [21], it is known that 5:19R and 2:7H phases exist in the Pr-rich side of the PrCo$_5$ alloy. Surprisingly, these phases are not observed in the Pr$_{19.6}$Co$_{81.0}$ magnet. To make sure that they would not be missed should they exist in the magnet, an alloy near the 5:19 composition was made to study the characteristic features of the 5:19 structure.

In contrast to the low defect density in the 1:5 phase, the salient feature of the 5:19 phase was the existence of strains which gave rise to a mod-

![Fig. 7. Orientation relationships between 2:17R and 1:5H phases: (a) combined patterns of 1:5H and 2:17R; (b) SAD pattern of 2:17R in the 0001 zone axis which is identical to that of the 1:5 phase in the 0001 zone axis; (c) CBED of 1:5H in the 0001 zone axis; (d) CBED of 2:17R in the 0003 zone axis. Note that the third Laue ring coincides with the first one in the 1:5 pattern because](image-url)
ulated contrast (fig. 5). From trace analysis, the modulation was perpendicular to the c-axis and stayed in the basal plane. In this paper, hexagonal coordinates in obverse setting are used to describe all rhombohedral phases. Since the modulating contrast was minimized at \( g = 0001 \) and \( g = 1120 \), from \( g \cdot R = 0 \) criterion, the contrast probably originated from planar defects in the basal plane with shear vector \( \frac{1}{2}(10\overline{1}0) \) type.

4.3. \( Pr_{7.3}Co_{92.7} \) magnet

Once again, Pr oxide was found to be a major impurity phase in the magnet. In addition to Pr oxide, quite a large number of \( Pr_2Co_{17} \) rhombohedral particles were observed in the magnet. The composition of magnet therefore appeared to be on the Co rich side of the \( PrCo_5 \) alloy if the amount of Pr element consumed by the oxide particles was taken into account.

The 2:17R particles were found to precipitate at the 1:5 grain boundary (fig. 6). A definite orientation relationship with one of neighboring 1:5 grains was observed as follows

\[
\text{(0001)}_{1:5\text{H}} \parallel \text{(0003)}_{2:17\text{R}}
\]

\[
\text{(10\overline{1}0)}_{1:5\text{H}} \parallel \text{(2\overline{1}00)}_{2:17\text{R}}.
\]

Such relationships can be determined from fig. 7. Since \( a_{2:17} \approx \sqrt{3} a_{1:5} \), the SAD patterns in the zeroth order Laue zone were identical. Higher order diffraction rings, however, looked rather different, since \( c_{2:17} \approx 3 c_{1:5} \). It can be seen that the third order ring of the 2:17R phase coincided with the first order one of the 1:5 phase. This demonstrated the layered feature of the 2:17 phase, which structurally consists of three 1:5 stacking units superimposed in the hexagonal c-direction. Of course, the difference between 2:17 and 1:5 can be most readily revealed by EDS spectra as shown in fig. 3d and fig. 8. The strain contrast was observed on the interface of the 2:17 precipitate and the neighboring 1:5 grain. Since a dislocation structure was found, the interface between the 2:17R and the neighboring 1:5 grain was semicoherent. This is different from the \( SmCo_5 \) system in which rhombohedral \( Sm_2Co_{17} \) precipitates are fully coherent with the 1:5 phase even though the same orientation relationships were identified [13]. Stacking faults in the basal plane were observed in the \( PrCo_5 \) magnet, just as they were in the 2:17 phase in the \( SmCo_5 \) magnet.

5. Discussion

A magnetized state is an energetically metastable state. It is the energy barriers to the equilibrium state that lead to hysteresis and coercivity in magnets. To a great extent, therefore, the coercivity is a measure of how well magnets can resist demagnetization processes and stay in such a metastable state. As reviewed by Livingston [22], the coercivity of the magnets depends on a number of factors, such as magnetocrystalline anisotropy, nucleation sites of reverse domains and existence of pinning mechanisms. Our discussion will be limited to the effects of grain size, impurity phases and crystal defects on coercivity.
5.1. Grain size

The critical diameter of the grains, below which a single-domain structure is of lower energy than a multi-domain structure, is given by

\[ D_c = 5.6 (JK)^{1/2} / M_s^2, \]

where \( M_s \) is the saturation magnetization, \( K \) is the magnetocrystalline anisotropy and \( J \) is the exchange constant. In the case of SmCo\(_5\) compounds, \( D_c \) is about 1 \( \mu \)m. In comparing PrCo\(_5\) compounds with SmCo\(_5\) compounds, we have:

\[ K_{\text{SmCo}_5} \approx 2.5 K_{\text{PrCo}_5} \]
\[ M_{s, \text{SmCo}_5} \approx 0.8 M_{s, \text{PrCo}_5} \]
\[ J_{\text{SmCo}_5} \approx J_{\text{PrCo}_5}, \]

therefore, \( D_c \) for the PrCo\(_5\) compounds is about half of that for the SmCo\(_5\) compounds. The actual grain size in PrCo\(_5\) magnets however was found to be the same as that in SmCo\(_5\) magnets. That is, demagnetization processes will take place more readily in the PrCo\(_5\) magnet to reach the multi-domain structure than in the SmCo\(_5\) magnets. Thus, a lower coercivity is expected in the PrCo\(_5\) magnet even when other conditions remain the same for both systems.

5.2. Oxide effect

In (Pr, Sm)Co\(_5\) magnets fabricated by Ghandehari et al. [19], the existence of Pr(Sm) oxide as a predominant precipitate is quite expected because the Cr\(_2\)O\(_3\) was intentionally added in their process. However, it is interesting to find that the Pr oxide is a major precipitate in the PrCo\(_5\) magnets used in our study even though efforts are made to reduce oxide in the magnet fabrication [7,8]. The existence of a large amount of Pr oxide in PrCo\(_5\) magnets is related to the chemical nature of the Pr element. It is known that Pr is easily oxidized and normally has to be stored in oil or an argon atmosphere. Pure Pr oxide is non-magnetic. Due to the existence of the Pr oxide, the regions of 1:5 phase near the oxide may become locally Pr depleted. Such a depletion may create appreciable lowered magnetocrystalline anisotropy \( K \). As a result, these regions may also provide nucleation sites of reverse domains for demagnetization. Our microstructural studies are consistent with results obtained by Wallace et al. [7]. They observed that the use of ultra-pure Pr material can improve the technical properties of magnets and increase the chemical stability. It appears that the role of oxides here is different from that in (Pr, Sm)Co\(_5\) magnets fabricated by Ghandehari et al.

5.3. 2:17 precipitates

The magnet with starting composition Pr\(_{17.3}\)Co\(_{82.7}\), in which Pr\(_{2}\)Co\(_{17}\) precipitated had a much lower coercivity than the magnet with starting composition Pr\(_{19.6}\)Co\(_{80.4}\) in which the Pr\(_{2}\)Co\(_{17}\) phase did not exist. Thus, the presence of Pr\(_{2}\)Co\(_{17}\) precipitates, which have planar anisotropy, is very likely to be deleterious to the magnetic coercivity. By Lorentz electron microscopy, Fidler [13] found that the Sm\(_2\)Co\(_{17}\) rhombohedral precipitates, which have uniaxial anisotropy, were responsible for the nucleation of reverse domains in the SmCo\(_5\) magnets. However, the coercivity of the SmCo\(_5\) magnet is much higher than that of the PrCo\(_5\) magnet. As mentioned earlier, the c-axis of the 1:5 grains in the PrCo\(_5\) magnets was observed to be more or less aligned in the magnetization direction. Due to the definitive orientation relationship between the 2:17 particles and the 1:5 grains, the c-axis of 2:17R particles will also be aligned in the magnetization direction. This implies that easy magnetization direction of 2:17 particles, which lies in the basal plane because of its planar anisotropy, is approximately perpendicular to the magnetization direction of the magnet. This configuration will make the demagnetization of 2:17 phase occur more readily. In addition to such an orientation effect, the Pr\(_{2}\)Co\(_{17}\) phase is magnetically much softer. This aspect, coupled with the fact that the magnetocrystalline anisotropy of PrCo\(_5\) is smaller than that of SmCo\(_5\), appear to suggest that reverse domains may nucleate more easily in Pr\(_{2}\)Co\(_{17}\) than in their counterparts in the SmCo\(_5\) magnets. These two factors explain why the PrCo\(_5\) magnet with Pr\(_{2}\)Co\(_{17}\) precipitates has a much lower coercivity than the corresponding SmCo\(_5\) magnet. In conclusion,
Pr$_2$Co$_{17}$ precipitates should be avoided in order to fabricate PrCo$_5$ magnets with an enhanced coercivity.

Unlike the Sm$_2$Co$_{17}$ precipitates which are fully coherent with the 1:5 matrix, the Pr$_2$Co$_{17}$ phase formed at the grain boundary having a semicoherent interface with one of neighboring grains. This observation is made on the basis of an examination of about 10 to 15 precipitates; in almost all these cases (except 2), we observed a grain boundary with a semicoherent interface. However, identical orientation relationships were observed between 1:5H and 2:17R. As stated earlier, the 2:17R phase can be derived from the 1:5 phase with the following relationships

$$a_{2:17} = \sqrt{3} a_{1:5}, \quad c_{2:17} = 3c_{1:5}.$$  

If a misfit in lattice parameters of the 2:17R phase is defined as

$$\Delta_a = (a_{cal} - a_{act}) / 0.5(a_{cal} + a_{act})$$

similarly,

$$\Delta_c = (c_{cal} - c_{act}) / 0.5(c_{cal} + c_{act}),$$

where the subscripts cal and act represent the lattice parameters of the 2:17R phase calculated from the lattice parameters of the 1:5 phase and the actual lattice parameters of the 2:17R phase, respectively. Based on lattice parameters compiled by Buschow [23], the misfits in PrCo systems were calculated to be $\Delta_a = 3.2\%$ and $\Delta_c = 2.6\%$, which were comparable with those obtained in the SmCo system ($\Delta_a = 3.4\%$ and $\Delta_c = 2.5\%$). This implies that the misfits in lattice parameters could not explain the absence of coherent 2:17R precipitates in the PrCo$_5$ matrix. Generally speaking, a large supercooling is required to balance the interfacial energy and misfit strain energy in order to have homogenous nucleation. Even though the sintering temperature is about 1100°C in the fabrication of both the SmCo$_5$ and PrCo$_5$ magnets, the melting point of SmCo$_5$ alloy is about 100°C higher than that of the PrCo$_5$ alloy. Thus, the smaller supercooling during sintering of the PrCo$_5$ magnet might not provide a sufficiently large driving force for the nucleation of 2:17R in the matrix. On the other hand, it is well known that the nucleation barrier at the grain boundaries is much lower than that in the matrix. This may be the reason why 2:17R was observed only at the grain boundaries in the PrCo$_5$ magnet. The same orientation relationships in both systems originated from the structural correlation between the 2:17R and 1:5 phases.

5.4. Defects in the PrCo binary phases

Structural defects in the basal plane were observed in both 5:19R and 2:17R phases, which appear to be rather common features of the layered structure in the hexagonal c-axis. In general, this type of defect renders the local atomic arrangements more likely to depart from the hexagonal structure and possibly will reduce the local magnetocrystalline anisotropy for the system with uniaxial anisotropy. Thus, such structural defects are normally not helpful in obtaining a high coercivity in magnets.

6. Conclusion

Characterization by TEM has been performed on two magnets with starting compositions Pr$_{19.0}$Co$_{81.0}$ and Pr$_{17.3}$Co$_{82.7}$ as well as an alloy near composition 5:19. It was found that hexagonal Pr oxide with lattice parameters $a = (3.85 \pm 0.1)$ Å and $c = (5.98 \pm 0.2)$ Å was the major impurity phase in both magnets. Quite a large number of Pr$_2$Co$_{17}$ precipitates was also observed in the magnet Pr$_{17.3}$Co$_{82.7}$ which had a low coercivity (140 Oe). Planar defects were found in both 5:19 and 2:17 phases. Effects on the coercivity have been discussed in terms of grain size, impurity phases and crystal defects.

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Reference