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Ferromagnetic phases in Pr–Nd–Fe

Augusto C. Neiva
Instituto de Física, Universidade de São Paulo, CP 20516, São Paulo, S.P. (Brazil)

Fernando J. G. Landgraf
Instituto de Pesquisas Tecnológicas do Estado de São Paulo, CP 7141, São Paulo, S.P. (Brazil)

Frank P. Missell
Instituto de Física, Universidade de São Paulo, CP 20516, São Paulo, S.P. (Brazil)

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Abstract

Ferromagnetic phases in Pr–Fe and Pr–Nd–Fe were investigated by energy-dispersive X-ray analysis, optical metallography and magnetic measurements. The Pr–Fe phase analogous to Nd_5Fe_{17} was not obtained. In Pr–Nd–Fe alloys, samples with higher Pr:Nd ratios have slower formation rates for $(Pr,Nd)_5Fe_{17}$.

1. Introduction

As-cast Pr–Fe samples are known to show high coercivities. High coercivities are also reported for PrFeB magnets. Since these systems are closely related to Nd–Fe and Nd–Fe–B, the recent discovery of Nd_5Fe_{17} and the metastable A_1 phases in Nd–Fe [1–8] and of the important role played by A_1 in NdFeB magnets [3, 4] has stimulated interest in the study of new phases in Pr–Fe and Pr–Fe–B. Furthermore, the production of praseodymium or (Nd,Pr)-based magnets by hot pressing [9], hot rolling [10] or die upsetting [11] has shown the importance of minority phases in determining the coercivity.

For Nd–Fe a revised phase diagram was recently presented with the new Nd_5Fe_{17} phase, formed peritectically between 770 and 795 °C [5], with hexagonal symmetry $P6_3/mcm$ [6]. This phase, with Curie temperature $T_C = 230$ °C, previously referred to as A_2 by Schneider and coworkers [5–7], is formed from the metastable A_1 phase after relatively short anneals and from Nd_2Fe_{17} after long anneals.

The Pr–Fe system was first studied by Ray [12], who proposed the existence of two intermetallic compounds: Pr_2Fe_{17} and another peritectic phase tentatively described as $PrFe_2$. Two metastable phases were reported by Cabral and coworkers [2, 8]. The first, herein called A_1, with $T_C = 222$ °C, is observed in as-cast samples. The second, with $T_C = 240$ °C, was reported to be found in as-cast [2] materials and in samples annealed for short times at 600 °C [2, 8]. Two phases were also observed by Sánchez *et al.* [13] in as-cast samples. The first one, A_1, was found to have $T_C = 225$ °C in samples with 15–40 at.% Fe and lower T_C values down to 182 °C in samples with 2.5 at.% Fe. The second one, observed in binary samples with 22.5–27.5 at.% Fe, was reported to have $T_C = 200$ °C.

In the present work Pr–Fe and Pr–Nd–Fe magnetic and microstructure results are analysed and compared with previous data on Pr–Fe and Nd–Fe.

2. Experiment

Binary Pr–Fe samples with 2.5–40 at.% Fe and ternary Pr–Nd–Fe samples were arc melted under pure argon from 99.9% Pr, 99.9% Nd and 99.98% Fe. Annealing treatments were performed in quartz ampoules filled with pure argon, and finalized by water quenching. Magnetic measurements were performed with a vibrating sample magnetometer. The Curie temperatures T_C were obtained by the "kink point method". Their values were taken at the minima of numerically calculated dM/dT *vs.* T curves [3]. The quoted uncertainties correspond to the width of the dM/dT *vs.* T curves at half the minimum value. The coercive fields H_c were taken at the maxima of numerically calculated dM/dH *vs.* H (irreversible susceptibility) curves. The samples were also analysed by energy-dispersive X-ray analysis (EDXA) in a Cambridge Stereoscan 240 scanning electron microscope and by optical metallography.

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3. Results and discussion

3.1. As-cast Pr–Fe

Previously [14] we found for the metastable A_1 phase in the Pr–Fe as-cast materials a Curie temperature $T_C = 227 \pm 10$ °C and a coercive field $H_c = 4.7 \pm 1.1$ kOe for all compositions with less than 35 at.% Fe. A_1 forms a very fine fibrous eutectic with α-Pr which is responsible for the high coercivity observed and which is similar to the fibrous A_1 + Nd eutectic observed in Nd–Fe [5], Nd–Fe–B [3] and other systems. An additional magnetic transition, associated with Curie temperatures in the range 169–198 °C, was also observed in these Pr–Fe samples for compositions with 25–30 at.% Fe. This transition was associated with a second eutectic morphology, the feathery lamellar, which was referred to as A_1'. The name was also used to describe the feathery lamellar eutectic in as-cast Nd–Fe samples. The term was extended to include the coarser feathery lamellar phase observed in differential thermal analysis (DTA) solidified samples and to the metastable platelet phase observed in samples annealed for short times. Recently, however, Mössbauer experiments have revealed very similar iron subspectra for A_1 and the platelet A_1' [15], strongly suggesting that they are the same phase.

3.2. As-cast and annealed Pr–Nd–Fe

3.2.1. Metastable fibrous eutectic and feathery lamellar eutectic

To examine the hypothesis advanced in ref. 14 that the feathery lamellar A_1' phase observed in both Pr–Fe and Nd–Fe as-cast samples is different from the fibrous eutectic A_1 phase, we prepared samples with compositions $(70-x)$Pr–xNd–30at.%Fe (x = 17.5, 35 and 52.5) in the arc furnace. We expected to find, in addition to the higher T_C transitions of A_1, the lower T_C transitions of A_1', whose values should be closer to those of A_1 as the Nd:Pr ratio increases. Only the T_C and H_c transitions of A_1 were observed, however.

The microstructures of these samples showed some feathery lamellar eutectic, but only a very small fraction compared with the Pr–Fe samples of ref 14. Two possibilities then arise: (a) in these samples the volume fraction of A_1' is too small to be observed in the magnetic measurements; (b) the iron-rich phase of the feathery lamellar eutectic is A_1 or has the same T_C and the second Curie transition observed in the Pr–Fe samples is not associated with this phase. In both cases another question arises: what is the reason for the different volume fractions of the feathery lamellar eutectic in these samples? This may, for example, be due to different cooling rates in the arc furnace or to different oxygen pick-ups in the samples. In any case we have not discovered how to reproducibly produce the feathery lamellar eutectic in arc-melted samples and this makes its study rather difficult.

3.2.2. The 5:17 phase

An attempt was made to produce the phase analogous to Nd_5Fe_{17} in the Pr–Fe system. As mentioned in Section 1, Nd_5Fe_{17} is formed from A_1 after relatively short anneals and from Nd_2Fe_{17} after long anneals [3–5, 7]. In the Nd–Fe system it shows low coercivity owing to planar anisotropy and therefore is not of interest for permanent magnets. A phase with the same structure, however, is observed in sputtered Sm–Fe–Ti samples, with coercivities up to 50 kOe at room temperature [16, 17].

Since long anneals are necessary to form Nd_5Fe_{17} from Nd_2Fe_{17}, we first tried to produce Pr_5Fe_{17} by annealing Pr–78.8at.%Fe for 75 days at 600 °C. However, only α-Pr and Pr_2Fe_{17} were observed. Considering then the possibility that in Pr–Fe the 5:17 phase might be stable only at lower temperatures, another sample (Pr–20at.%Fe) was annealed at 450 °C for 30 days. For the low temperature anneal we chose this 2:17-free composition in order to increase the kinetics of Pr_5Fe_{17} formation – as observed in Nd–Fe [5]. This sample also showed only α-Pr and Pr_2Fe_{17} after the anneal. These results are in good agreement with those of Cabral and Gama [8], who did not detect any other phase after 24 and 730 h anneals at 600 °C.

We then prepared two series of Pr–Nd–Fe samples in order to determine the upper solubility limit for praseodymium in Nd_5Fe_{17} and the magnetic properties of this phase. The first series, $(80-x)$Pr–xNd–20at.%Fe (x = 10, 30, 50 and 70), consisted of A_1 + (Pr,Nd) in the as-cast condition, with increasing T_C for increasing Nd:Pr ratio, as expected. Figure 1(a) presents these values; a typical dM/dT *vs.* T curve is shown in Fig. 2, curve (a). Figure 1(b) presents the corresponding H_c values, which remain constant over the composition range.

These samples were annealed for 24 h – time enough to produce Nd_5Fe_{17} in samples with this iron content. Only the neodymium-rich sample (Pr–70at.%Nd–20at.%Fe) (Fig. 2, curve (b)) showed the 5:17 phase in addition to the 2:17 and (Pr,Nd) phases which were present in all samples. Longer anneals (2 and 6 weeks, 600 °C) of these samples, however, showed the 2:17 phase to be metastable for the Pr–70at.%Nd–20at.%Fe composition: the relative amount is smaller after 2 weeks and the phase has disappeared after 6 weeks (Fig. 2, curves (c) and (d)).

The second series, $(30-x)$Pr–xNd–70at.%Fe (x = 7.5, 15 and 22.5), consisted of 2:17 + A_1 + (Pr,Nd) in the as-cast condition. The samples were annealed at 600 °C for 4 and 8 weeks. The corresponding dM/dT *vs.* T curves are shown in Figs. 3 and 4 respectively. After

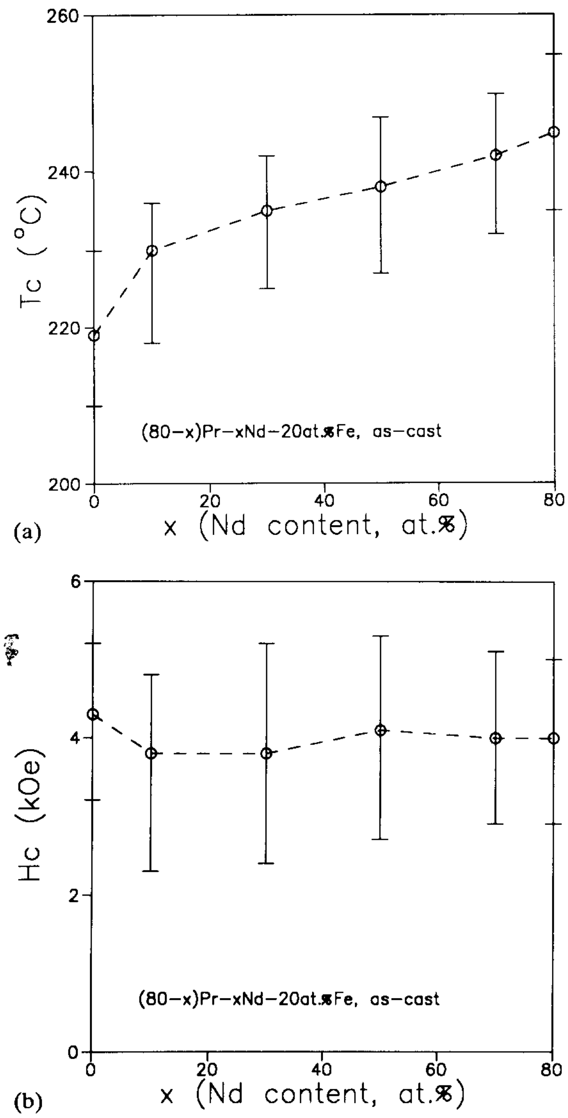

Fig. 1. (a) T_C for $(80-x)$Pr–xNd–20at.%Fe ($x=10$, 30, 50 and 70). (b) H_c for the same samples.

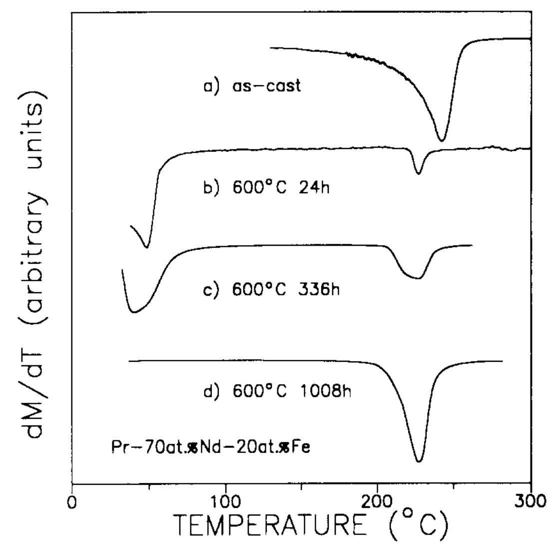

Fig. 2. dM/dT *vs.* T for Pr–70at.%Nd–20at.%Fe (a) as cast, (b) annealed at 600 °C for 24 h; (c) annealed at 600 °C for 2 weeks and (d) annealed at 600 °C for 6 weeks.

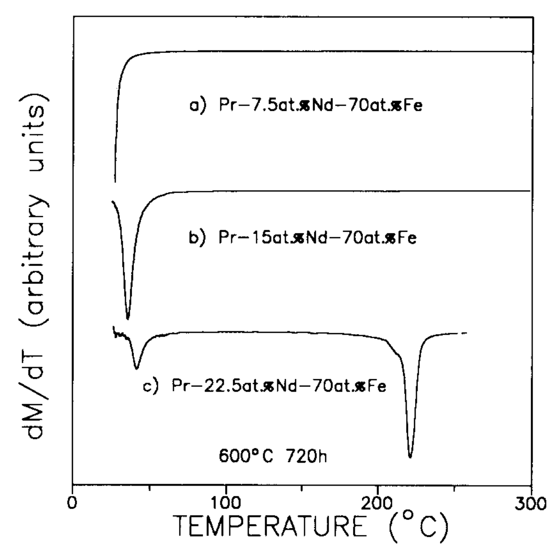

Fig. 3. dM/dT *vs.* T for $(30-x)$Pr–xNd–70at.%Fe ($x=7.5$, 15 and 22.5) annealed at 600 °C for 4 weeks.

4 weeks, only the neodymium-rich sample showed the 5:17 phase, with $T_C=223\pm4$ °C, in addition to the 2:17 and (Pr,Nd) phases (Fig. 3, curve (c)). The 5:17 and 2:17 compositions in this sample were determined by EDXA to be $Pr_{4.7}Nd_{18.2}Fe_{77.1}$ and $Pr_{1.8}Nd_{8.8}Fe_{89.4}$, respectively. The (Pr,Nd) phase is present with a very fine morphology, less than 1 μm. Therefore, even for the low acceleration voltages used for these analyses (12 keV), the X-ray resolution (about 1 μm) was not sharp enough to avoid stray X-ray emission from the surrounding 2:17 phase. This contribution was estimated and subtracted from the measured results: a Pr:Nd ratio of 0.41 ± 0.01 was determined for any assumed iron content in (Pr,Nd).

This configuration revealed itself to be metastable, however. After 8 weeks the 2:17 phase has disappeared from this sample and the Curie temperature of 5:17 has increased to 230 ± 3 °C (Fig. 4, curve (c)), suggesting that the Nd:Pr ratio of this 5:17 is higher than that of the 4 week annealed sample. After 8 weeks the Pr–15at.%Nd–70at.%Fe sample – two phase after 4 weeks (Fig. 3, curve (b)) – is three phase: a slight T_C transition corresponding to 5:17 can be observed at 224 °C in addition to that of 2:17 at 27 °C (Fig. 4, curve (b)).

If this 8 week annealed Pr–15at.%Nd–70at.%Fe sample is stably three phase, then praseodymium should have nearly reached its solubility limit in $(Pr,Nd)_5Fe_{17}$. The praseodymium content of 5:17 in this sample was not measured, because its volume fraction was very small. However, it can be estimated to be near 4.7

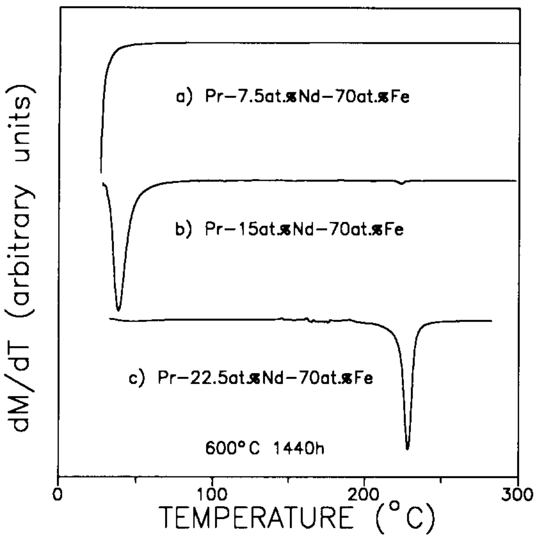

Fig. 4. dM/dT *vs.* T for $(30-x)$Pr–xNd–70at.%Fe (x = 7.5, 15 and 22.5) annealed at 600 °C for 8 weeks.

at.% — the praseodymium content of 5:17 in the 4 week annealed Pt–22.5at.%Nd–70at.%Fe sample — in as much as the T_C values of 5:17 in both samples are similar. We believe, however, that the Pr–15at.%Nd–70at.%Fe and praseodymium-rich samples are not stable, since we have observed, for both the 20 and 70 at.% Fe series, that the formation of 5:17 is much slower for higher Pr:Nd ratios.

Long-term anneals are therefore under way in order to verify if 2:17 is also metastable in Pr–15at.%Nd–70at.%Fe and if 5:17 is formed at higher praseodymium contents.

4. Conclusions

Compared with Nd–Fe, some remarkable differences arise in the Pr–Fe system. First, no stable intermetallic phase corresponding to Nd_5Fe_{17} was obtained in Pr–Fe. In Pr–Nd–Fe, alloys with higher Pr:Nd ratios have slower formation rates for $(Pr,Nd)_5Fe_{17}$. Secondly, an additional Curie temperature, at 169–198 °C, and an additional H_c transition are observed in Pr–Fe as-cast samples which show the feathery lamellar eutectic morphology (besides the $A_1+\alpha$-Pr fibrous eutectic morphology). The Pr–Fe A_1 phase was observed by Sánchez *et al.* [13] in the same composition range, but, in contrast to these authors, who observed a sharp decrease in the T_C value of A_1 below 15 at.% Fe, we observed a constant value over the entire composition range. Our results for samples annealed for long times, where the only intermetallic phase found is Pr_2Fe_{17}, agree with those of Cabral and coworkers [2, 8]. No such agreement is found, however, for shorter anneals. We investigated the 600 °C annealing behaviour of binary samples with 20 at.% Fe. As reported by Cabral and coworkers [2, 8], A_1 proved to be metastable, since it disappeared after both 2 and 24 h anneals. The only magnetic phase observed in the annealed samples, however, ws Pr_2Fe_{17}. The magnetically hard, metastable phase with $T_C = 240$ °C reported by Cabral and coworkers [2, 8] in samples annealed for short times was not observed by metallography or magnetic analysis.

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