LOW-TEMPERATURE HYSTERETIC PROPERTIES OF Pr-Ho-Fe-B MAGNETS

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Abstract

Sintered permanent magnets based on the $Nd_2Fe_{14}B$ intermetallic compound are widely used in industry as a rule in a temperature range of from -60 to 150 °C. However, in recent years, there appears a need to use such magnets at cryogenic temperatures and mainly at liquid nitrogen temperature (77 K). The natural increase in B_r of Nd-Fe-B magnets with falling temperatures is well known phenomenon but it is limited to temperatures above 135 K due to the spin-reorientation in $Nd_2Fe_{14}B$-based alloys. At this temperature, the easy-axis magnetic anisotropy changes to easy-axes cone anisotropy. The $Pr_2Fe_{14}B$ compound exhibits no spin-reorientation transition up to cryogenic temperatures. Therefore, permanent magnets based on $Pr_2Fe_{14}B$ compound are of interest for investigators owing to the capability of these magnets to remain high hysteretic parameters at low and cryogenic temperatures. In this case, the natural increase in the hysteretic parameters with decreasing temperature can be adequately used. The $Pr_2Fe_{14}B$-based magnets (Pr-Fe-Ti-Al-Cu-B) were prepared by traditional powder metallurgy technology, and 3 wt.% HoH_2 was added to the main powder at the fine-milling stage. The structure of the magnets was studied in detail by scanning electron microscopy (SEM/EDX) and the formation of pronounced so-called "core-shell" structure was demonstrated. The effect of HoH_2 hydride addition on the hysteresis loop parameters of sintered Pr-Fe-Ti-Al-Cu-B magnets was studied and the marked improvement of hysteretic parameters was found. Domain structure of the magnets was studied perpendicular and parallel to the magnet texture using magnetic force microscopy. The data obtained indicate the well-formed magnetic texture. The average domain width is 1.2-1.8 μm.

Keywords: Pr-Fe-B magnets, coercive force, core-shell structure, SEM, low-temperature hysteretic properties

1. INTRODUCTION

In recent years, permanent magnets based on $(Pr,Nd)_2Fe_{14}B$ compounds are of interest for investigators owing to the possibility to use them at cryogenic temperatures (undulators, magnetic bearings, wiggler, etc.) [1-3]. $Nd_2Fe_{14}B$-based magnets with a high remanence cannot be employed for the construction of room temperature undulator because of their weak coercivity at this temperature. As the temperature decreases to cryogenic temperatures, not only the remanence but also the coercivity increase and consequently these magnets present a high resistance to demagnetization.

The natural increase in B_r of Nd-Fe-B magnets with falling temperatures is well known phenomenon but is limited to temperatures above 135 K due to the spin-reorientation in these alloys. At this temperature, the easy-axis magnetic anisotropy changes to easy-axes cone anisotropy, namely, the easy magnetization axis is tilted

from the crystallographic c-axis [001] and the spin-reorientation transition (SRT) takes place. The tilted angle increases with decreasing temperature and B_r decreases below values corresponding to the room temperature. Thus, the natural low-temperature-induced increase in hysteretic properties cannot be used adequately. The $Pr_2Fe_{14}B$-based magnets exhibit no spin-reorientation transition up to 4.2 K [4-5].

Since the majority of $Nd_2Fe_{14}B$-based magnets are operate at 200-450 K, i.e., at temperatures that are substantially higher than the liquid nitrogen temperature (77 K), previously, $Pr_2Fe_{14}B$-based magnets almost were not used. Despite of the fact that many magnetic parameters of the compound are higher than those of $Nd_2Fe_{14}B$ or comparable with them (the anisotropy field of $Pr_2Fe_{14}B$ (8.7 T) is higher than that of $Nd_2Fe_{14}B$ (6.7 T) [6]), indicating that a somewhat higher intrinsic coercivity (Hcj) could be obtained in the former; the Curie temperature of $Nd_2Fe_{14}B$ (586 K) is slightly lower than that of $Pr_2Fe_{14}B$ (569 K) [7] and the saturation magnetization of $Pr_2Fe_{14}B$ (1.56 T) is also comparable to that of $Nd_2Fe_{14}B$(1.60 T) [8]. All these factors make Pr-Fe-B magnets attractive for broad temperature range applications. However, $Pr_2Fe_{14}B$-based magnets exhibit the worse temperature and time stability. In particular, the reversible temperature coefficient of magnetic induction (α) in a temperature range of 293-373 K is ~0,015 %/K, whereas that of $Nd_2Fe_{14}B$-based magnets is 0,012 %/K [9]. The Pr-Fe-B alloys are more viscous than the Nd-Fe-B alloys; this fact determines the higher quenching rates and assumes the application of hydrogen decrepitation. However, it was shown in [10] that the presence of hydrogen changes the anisotropy nature of $Pr_{15}Fe_{79}B_6$ hydrogenated powders from uniaxial to planar in the range between 4250 and 4500 ppm of hydrogen, i.e., at room temperature, the hydrogenated $Pr_{15}Fe_{79}B_6$ composition has the planar magnetic anisotropy. This leads to the fact that, when the hydrogenated $Pr_2Fe_{14}B$ powder is compacted in a magnetic field, no texturing along the easy magnetization axis takes place, and the powder behaves similarly to an isotropic powder. In this case, the hysteretic parameters of magnets decrease abruptly. The authors of [10] suggest either to dehydrogenate the powder before compacting or to alloy the composition with dysprosium. Since, as a rule after passivation with CO, the powder is dehydrogenated by heating in a vacuum, the oxidation and carbonization of powder can occur, which affects negatively the hysteretic parameters of permanent magnets.

The aim of the present study is to investigate the effect of holmium hydride HoH_2 additions, which are subjected to fine milling together with the hydrogenated $PrFeBH_x$ alloy, on the texture formation and properties of permanent magnets over a wide temperature range (4.2 - 373 K).

2. EXPERIMENTAL

The alloy containing (wt.%) Pr-33, Ti-0.9, Al-0.3, Cu-0.15, B-1.3, Fe - balance was prepared by induction melting in an argon atmosphere and cast into a water-cooled copper mold. The alloy was subjected to hydrogen decrepitation using a bell-type furnace; the furnace chamber was preliminarily washed with nitrogen gas and flashed with hydrogen; after that, the hydrogenation was performed during heating to 200 °C for 1.5-2 h and subsequent holding at 200 °C for 1 h. After hydrogenation, the furnace chamber was washed with nitrogen gas, and the alloy was subjected to furnace cooling to room temperature. Powders of $Pr_2Fe_{14}B$-based alloy and its mixture with HoH_2 were prepared by milling in isopropyl alcohol medium using a vibratory ball mill. Magnet blanks were prepared by compacting at a compacting force of 29.4 MPa using a hydraulic press; the loading rate was no more than 10 mm/s. A texturing magnetic field of 1.6 T was applied perpendicular to the pressing force direction. The blanks were dried and sintered at 1375 K for 1 h (single-cycle technological operation) and subjected to low-temperature treatment at 775 K for 1 using vacuum resistance furnaces.

Magnetic properties of magnets were studied in a temperature range of 4.2 - 295 K in magnetic fields of to 2000 kA/m using a MH-50 hysteresis graph and a close magnetic circuit. The preliminary magnetization was realized in pulse magnetic fields of to 12 MA/m. Magnetic measurements in a temperature range of 4.2 - 295 K were performed in fields of to 7200 kA/m using a vibrating sample magnetometer.

The microstructure, phase composition, and chemical composition of the phases were studied by scanning

electron microscopy using a QUANTA 450 FEG scanning electron microscope equipped with an EDX APOLLO X analyzer. The phase composition of magnets was studied by X-ray diffraction (XRD) analysis using an Ultima IV (Rugaku, Japan) diffractometer equipped with a D/teX detector and CuK_α radiation. X-ray diffraction patterns were taken in a 2θ angular range of 3-100º at a scanning step of 0.001º. The qualitative and quantitative analyses of X-ray diffraction patterns were performed using simplified Rietveld method, PHAN and PHAN% software. The domain structure of magnets was studied perpendicular and parallel to the magnet texture by magnetic force microscopy (MFM) using Solver Pro EC (NT MDT) equipment.

3. RESULTS AND DISCUSSION

3.1. Structural Studies

Figures 1a, b show the microstructure of magnets prepared from the alloy (wt.%) Pr-33, Ti-0.9, Al-0.3, Cu-0.15, B- 1.3, Fe-balance with 3 wt.% HoH_2, which was added to the powder mixture (points of electron microprobe analysis (EMA) are indicated). According XRD data and EMA data, four structural components were found; these are the main magnetic $(Pr,Ho)_2Fe_{14}B$-based phase, $(Pr,Ho)_{rich}$ phase, $(Pr,Ho)_2O_3$ oxide phase, and Ti-containing phase (**Table 1**).

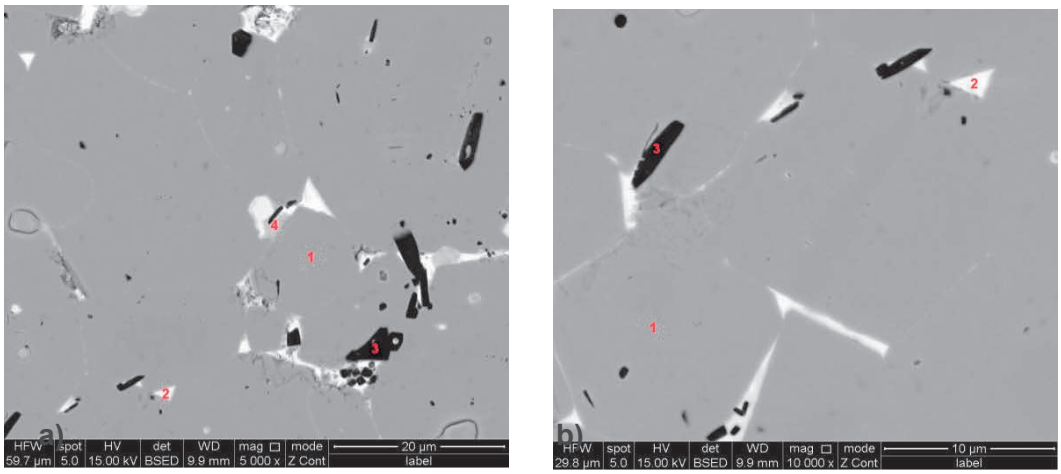

Figure 1 Microstructure (SEM, back-scattering electron mode) of the $(Pr,Ho)_2Fe_{14}B$-based magnet

Table 1 Electron microprobe analysis data (wt.%) for the Pr-Ho-Fe-B magnet (area and local analysis)

Element/phase	O	Al	Ti	Pr	Nd	Fe	Ho	Cu
Area	3.1	0.6	1.3	30.1	1.5	57.1	4.6	0.6
Phase 1	1.6	0.5	0.3	24.5	1.3	64.8	5.2	0.6
Phase 2	2.2	0.4	0.3	76.8	2.4	7.1	1.2	8.4
Phase 3	1.3	0.1	73.5	11.2	0.5	10.3	1.3	1.0
Phase 4	18.3	0.0	0.4	72.1	2.8	3.1	2.5	0.4

According to EMA data, the main magnetic phase is depleted of rare-earth metals (the content of REM (Pr+Ho+Nd) is ~32 wt.% (Nd is present as an impurity in starting praseodymium). Phase 2 corresponds to R_{rich} phase. Phases 3 and 4 are Ti-based and oxide phases, respectively. Copper mainly presents at ternary junctions of 2-14-1 grains.

The Ho distribution within the main magnetic phase grains was studied in detail (see **Figures 2a, b, c, d**). It was found that holmium demonstrates the nonuniform distribution within the 2-14-1 main magnetic phase, namely, cores of grains are Ho-depleted, whereas the edges of grains are Ho-enriched, i.e., so-called "core-

shell" structure is formed when HoH_2 hydride additions are used in powder mixture.

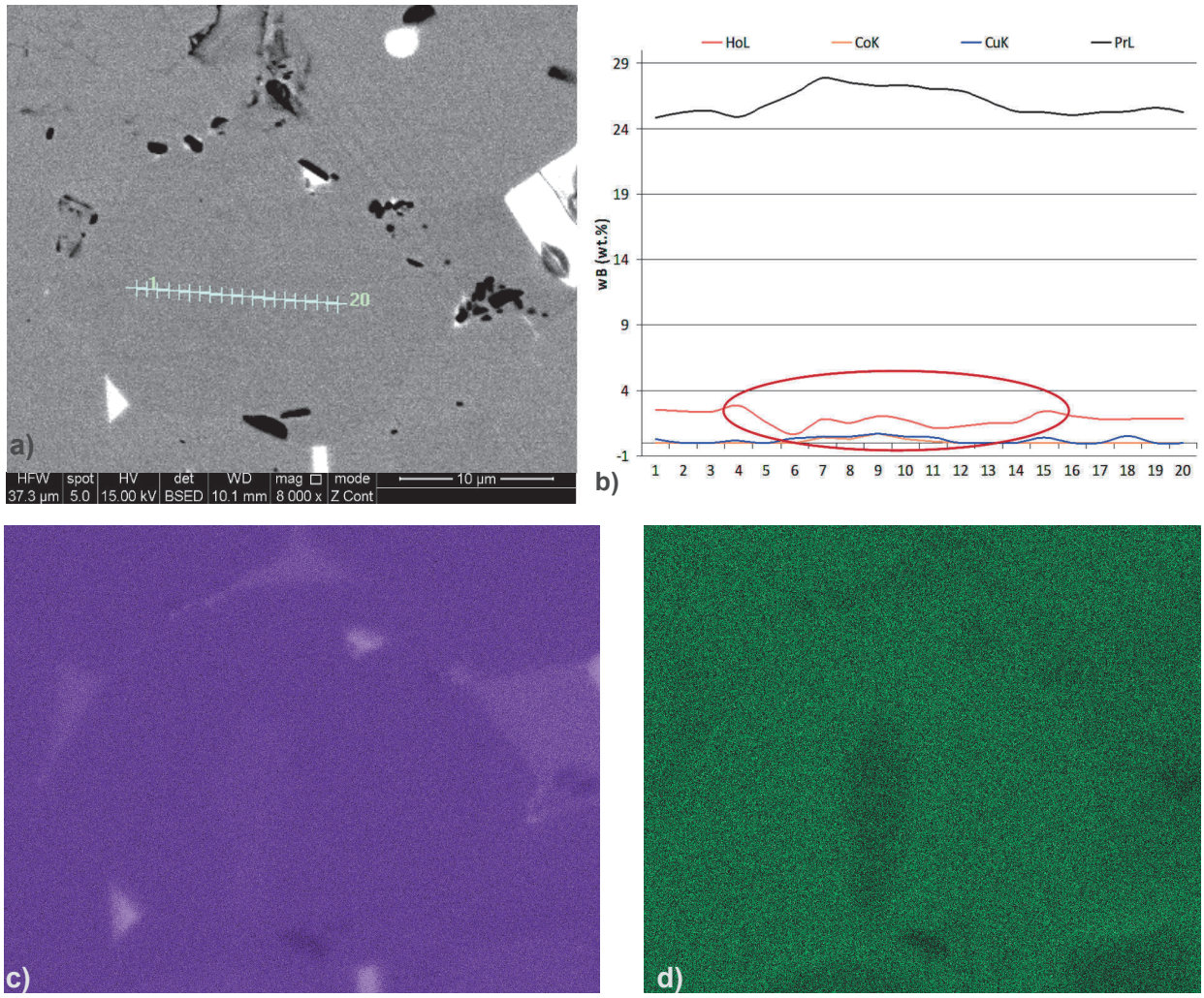

Figure 2 (a) SEM image of 2-14-1 phase grain, (b) EMA data along the scanning line in Figure 2a, (c) Ho and (d) Pr distribution maps.

3.2. Magnetic measurements

Figure 3 shows magnetization-reversal portions of hysteresis loops for the Pr-Ho-Fe-B permanent magnets measured at different temperatures. It is seen that the hysteretic properties of Ho-reached magnet are higher substantially than those of Pr-Fe-B magnet despite of the fact that Ho atoms antiferromagnetically ordered with Fe atoms. Measurements performed at low temperatures indicate the progressive increase in the magnetic induction and maximum magnetic product by 13 and 27 %, respectively. According to the magnetic measurements, no spin-reorientation transition takes place at temperatures up to 4.2 K.

The determined hydrogen content in the magnet is ~ 2500 wt. ppm. Such hydrogen content does no result in the magnetic anisotropy change for $Pr_2Fe_{14}B$ compound, which takes place at a hydrogen content of 4500 ppm [10].

The increase in the magnetic properties for the Ho-containing magnet can be related to the presence of Ho in the $Pr_2Fe_{14}B$ crystal lattice and formation of "core-shell" structure of the phase grains. Such an explanation of the increase in the coercive force is seemed to be paradoxical. It is known that the alloying of $Nd_2Fe_{14}B$-based magnets with Dy and Tb leads to the increase in the coercive force and is related to the higher anisotropy

fields of the $Dy_2Fe_{14}B$ and $Tb_2Fe_{14}B$ compounds as compared to that of $Nd_2Fe_{14}B$ (by 2 and 3 times, respectively) [7]. The analogous explanation can be applied for Nd-Fe-B-based magnets alloyed with Ho since the anisotropy field H_a of $Ho_2Fe_{14}B$ is higher, although slightly, than that of $Nd_2Fe_{14}B$ [11]. However, the anisotropy field of $Ho_2Fe_{14}B$ is equal to or slightly lower than that of $Pr_2Fe_{14}B$ [7]. Thus, the increase in the coercive force of Pr-Fe-B magnets alloyed with Ho cannot be related to the increase in the anisotropy field Ho-containing composition.

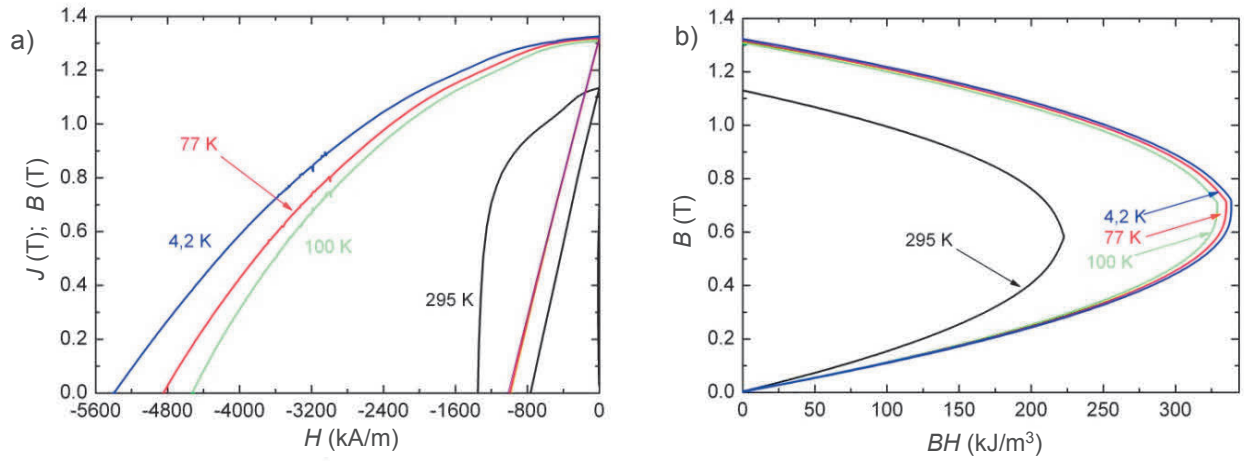

Figure 3 (a) Magnetization reversal portions of hysteresis loops (plotted with allowance for demagnetizing factor) measured at different temperatures and (b) maximum magnetic energy product for the Pr-Ho-Fe-B permanent magnet

There are calculated data in the literature [12-13], which indicate that the alloying of $Nd_2Fe_{14}B$ with heavy rare-earth metals (Dy and Tb) results in the stabilization of $Nd_2Fe_{14}B$-type structure in contrast to the effect of light rare-earth metals (La, Pr). We can assume that holmium, as the heavy rare-earth metal, also stabilizes the $Nd_2Fe_{14}B$-type structure and favors the higher resistance to the formation of crystal lattice stacking faults, which are responsible for the local decrease in the anisotropy field during operation of permanent magnets. Thus, the crystal-lattice stabilization factor can be more substantial than the averaged (over the volume or surface of 2-14-1 grain) increase in the anisotropy field. Therefore, we have the increase in the coercive force ever in the case of equal (or decreased by alloying) anisotropy field. The importance of the role of structural state of the main magnetic field was discussed by us in [14]

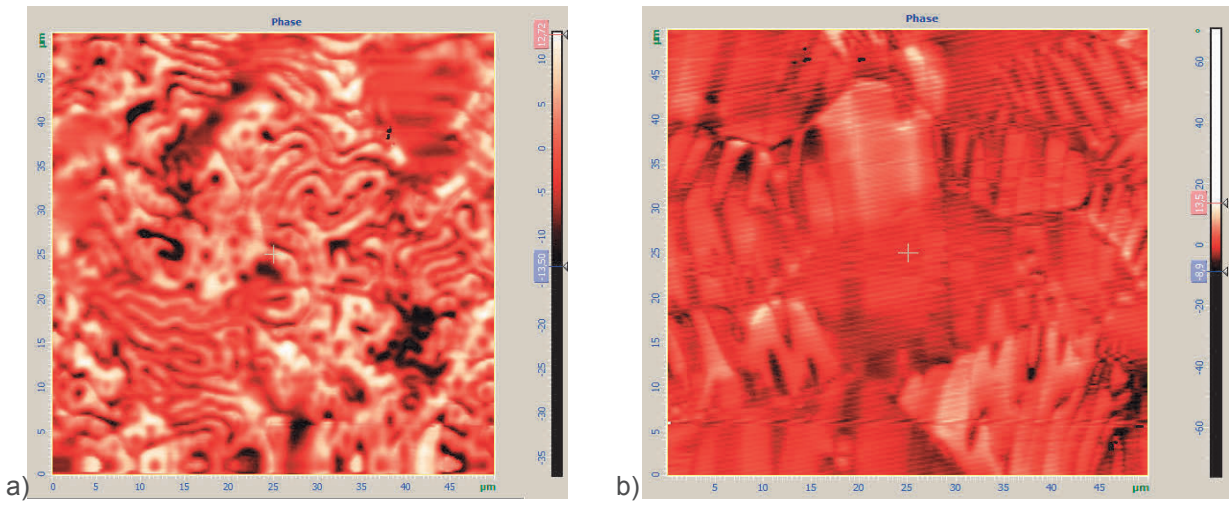

Figure 4 MFM data for the Pr-Ho-Fe-B magnet (a) perpendicular and (b) parallel to magnetic texture of the magnet

Domain structure of the Pr-Ho-Fe-B magnet is given in **Figure 4**. According to the data, the magnet has the adequate magnetic texture.

During MFM measurements of the remanent state of (Nd,Dy)-Fe-B core shell model magnets, which were prepared by co-sintering Nd-Fe-B and (Nd,Dy)-Fe-B powders [15], a magnetic contrast of core and shell within the same grain was found. Micromagnetic simulation was carried out in addition to resolve the specific nucleation site for the reversal. It was found [15] that the position of the nucleation site depends critically on the magnetocrystalline anisotropy K_{edge} in the shell edge, which is defined as the defect layer in the shell surface. Low and high K_{edge} favors the nucleation in the shell and core, respectively [15]. The analogous analysis in further should be performed for the Pr-Ho-Fe-B magnets prepared in the present study.

4. CONCLUSIONS

1) Sintered permanent magnets Pr-Ho-Fe-Ti-Al-Cu-B were prepared in using HoH_2 hydride additions; the following magnetic characteristics at room temperature were reached B_r = 1.13 T, ${}_jH_c$ = 1340 kA/m, $(BH)_{max}$ = 222 kJ/m^3. The 4.2 and 77 K the hysteretic properties are B_r = 1.33 T, ${}_jH_c$ = 5365 kA/m, $(BH)_{max}$ = 336 kJ/m^3 and B_r = 1.32 T, ${}_jH_c$ = 4815 kA/m, $(BH)_{max}$ = 333 kJ/m^3, respectively.

2) The dependence of the magnetization of the magnet on the temperature exhibits no spin-reorientation up to 4.2 K.

3) The phase composition of the magnet is characterized by the presence of 4 structural components; these are the main magnetic $(Pr,Ho)_2Fe_{14}B$, $(Pr,Ho)_{rich}$, $(Pr,Ho)_2O_3$ oxide, and TiB-based phases. The Ho content in the $(Pr,Ho)_{rich}$ phase was found to lower than that in the main magnetic 2-14-1 phase.

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