

SINTERED PERMANENT MAGNETS PREPARED FROM HYDROGENATED (Nd-Fe-B STRIP-CAST ALLOY + Pr₃(Co,Cu) COMPOUND) MIXTURE

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Abstract

The application of powder blending procedure shows promise in manufacturing Nd-Fe-B magnets; in this case, hydrides, oxides, intermetallic compounds, etc. are used as one of the mixture components. The application of these additions allows one to increase the hysteretic characteristics of Nd-Fe-B magnets at the expense of realized grain-boundary diffusion and grain-boundary structuring processes since these characteristics of the magnets are highly sensitive to their microstructure, composition of phases, and distribution of alloy components as well. This study is focused on the possibility of using the Pr₃Co_{0.6}Cu_{0.4}H_x composition as the addition to the powder mixture for manufacturing Nd-Fe-B magnets and on the processes occurred during hydrogen treatment of the addition. The base alloy having the composition Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Fe-balance was prepared by strip-casting and subjected to hydrogen decrepitation at 270 °C for 1 h. The Pr₃Co_{0.6}Cu_{0.4} alloy was prepared by arc melting in an argon atmosphere and subjected to homogenizing annealing at 600 °C for 90 h and subsequent hydrogenation under the conditions used for the strip-cast alloy. The phase composition of Pr₃Co_{0.6}Cu_{0.4}H_x was studied by X-ray diffraction analysis, DTA, scanning electron microscopy, and electron microprobe analysis. The Pr₃Co_{0.6}Cu_{0.4}H_x composition was shown to undergo the hydrogenolysis with the formation of PrH_x hydride (or hydrogen solid solution in Pr), Co+Cu fine mixture, and PrCu compound. The behavior of the additions in manufacturing sintered permanent magnets is analyzed from the viewpoint of the grain-boundary structuring effect of the addition. The sintered magnet prepared from the hydrogenated mixture Nd-Fe-B strip-cast alloy + Pr₃(Co,Cu) compound exhibits the following hysteretic parameters: $B_r = 1.35$ T, $j_{Hc} = 1008$ kA/m, and $(BH)_{max} = 349$ kJ/m³.

Keywords: Nd-Fe-B magnets, blending procedure, intermetallic compound, coercive force, grain boundary

1. INTRODUCTION

Sintered Nd-Fe-B permanent magnets are used in many electronic devices, such as hybrid engines, medical equipment, wind generators, etc. A wide variety of applications of Nd-Fe-B magnets stimulates the development of approaches allowing the phase composition and microstructure of magnets to be optimized and the hysteretic characteristics to be increased. One of the effective approaches to improving the hysteresis properties is the use of binary mixture technology with the implementation of grain boundary diffusion and grain boundary restructuring processes [1-5]. A number of studies are focused on the possibility of increasing the hysteretic characteristics of sintered Nd-Fe-B permanent magnets in using Pr-Cu system alloys as

additives for the implementation of diffusion processes and structuring grain boundaries. In [6], the $\text{Pr}_{68}\text{Cu}_{32}$ and $\text{Pr}_{35}\text{Dy}_{35}\text{Cu}_{30}$ alloys in the form of foils were used. The coercivity enhancement of the diffused magnets by $\text{Pr}_{68}\text{Cu}_{32}$ alloy was mainly resulted from relatively continuous and thin intergranular layers isolating $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based grains, which were achieved only by post-diffusion annealing. It was observed that the grain boundary phases of the $\text{Pr}_{68}\text{Cu}_{32}$ -diffused Nd-Fe-B magnets became more continuous and clear because Pr and Cu dissolved and diffused into the intergranular phase adjacent to $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. In work [7], the mixed hydride (Pr, Dy, Cu)-H_x was used as the additive. It was shown that in using the 2 wt% (Pr, Dy, Cu)-H_x addition, the significant increase in the coercive force from 1200 to 1456 kA/m is observed. In [8], the $\text{Pr}_{83}\text{Cu}_{17}$ (wt%) eutectic alloy was used as an additive; the dependence of the coercive force on the content of the additive is shown. The coercivity of the prepared alloy is shown to be highly sensitive to the annealing temperature. After optimal heat treatment, the coercive force increases from 680 to 1024 and to 1176 kA/m with additive contents of 0-5 and 10 wt%. Pr-Cu addition slightly enlarges grain sizes and introduces new boundary phase constitutions: Cu-higher phase (h- RE_2O_3) and Cu lower phase (fcc REO_2).

Fangming Wan et al. [9] have studied the Pr-Cu alloy diffused into Nd-Fe-B sintered magnets and reported that the coercivity increased from 1120 (original magnet) to 1680 kA/m (diffusion-treated magnet). This result was attributed to the grain size of the magnets, which decreased from 6.5 to 4.5 μm and the thickness of grain boundary phases approximately increased from 4 to 20 nm. Thus, it was indicated that the pre-diffusion process could suppress the formation of coarse grain regions due to Pr-Cu alloy addition but the low melting point Pr-Cu alloys could not diffuse uniformly.

In [10], the effect of Pr-Co additives on the coercive force and thermal stability was investigated. It is shown that the increase in the content of the additive to 15 wt% leads to the sharp decrease in the intrinsic coercivity from about 14.8 to 320 kA/m. According to the authors' opinion, this is associated with the formation of new ferromagnetic phases, in particular, the soft magnetic $(\text{NdPr})(\text{FeCo})_2$ phases. However, the further increase in the additive content from 15 to 20%, results in a sharp increase in the coercive force, which is associated with the formation of the nonmagnetic phase $(\text{NdPr})_3(\text{FeCo})$ and the transformation of the phase $(\text{NdPr})(\text{FeCo})_2$ from soft ferromagnet into the non-magnetic phase. Thus, the use of Pr-Cu and Pr-Co systems as additives in manufacturing the Nd-Fe-B permanent magnets allows one to modify the phase composition and properties of them.

The aim of this work is to study the possibility of using the hydrogenated $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}$ compound as an additive in manufacturing Nd-Fe-B permanent magnets by powder blending procedure.

2. EXPERIMENTAL

The base alloy (wt%) Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Fe-balance was prepared by strip-casting technique and subjected to hydrogen decrepitation during heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h dwell at this temperature. The $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}$ alloy was prepared by arc melting of starting components (Pr-99.5 at%, electrolytic Co K-1 grade, and oxygen-free copper) in an argon atmosphere using a water-cooled copper mould and a nonconsumable tungsten electrode. The ingot was subjected to homogenizing annealing at 600°C for 90 h followed by rapid cooling (20°C/min). The ingot was subjected to hydrogenation under conditions used for the strip-casting alloy, namely, during heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h holding at this temperature.

The structure of the hydrogenated composition was studied on QUANTA 450 FEG scanning electron microscope equipped with an EDX APOLLO X microanalyzer; the back-scattered electron mode image was used. The phase composition of $\text{Pr}_3(\text{Co,Cu})\text{H}_x$ was studied by X-ray diffraction (XRD) analysis using an Ultima IV (Rigaku», Japan) diffractometer equipped with a "D/teX" detector and $\text{CuK}\alpha$ radiation; the scanning step is 0.001°. The differential thermal analysis of the hydrogenated $\text{Pr}_3(\text{Co,Cu})\text{H}_x$ composition was carried out in an argon atmosphere at a heating rate of 15°C/min using a Setaram Setsys -1750 installation.

The mixture of the $\text{Pr}_3(\text{Co,Cu})\text{H}_x$ and hydrogen-decrepitated strip-casting alloy was subjected to fine milling for 40 min to an average particle size of 3 μm using a vibratory mill and isopropyl alcohol medium. After wet compaction of the pulp in a transverse magnetic field of 1500 kA/m, blanks of magnets were sintered at $T = 1080\text{ }^\circ\text{C}$ for 2 h and subjected to post-sintering annealing at 500 $^\circ\text{C}$ for 2 h. The hysteretic properties were measured using a hysteresisgraph.

3. RESULTS AND DISCUSSION

3.1. Study of the structure and phase composition of $\text{Pr}_3(\text{Co}_{0.6}\text{Cu}_{0.4})\text{H}_x$

To study the usefulness of application of the $\text{Pr}_3(\text{Co,Cu})\text{H}_x$ addition in manufacturing sintered Nd-Fe-B magnets, its phase composition was investigated in detail.

The microstructure (SEM) of hydrogenated $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}\text{H}_x$ composition is shown in **Figure 1**. Results of electron microprobe analysis (EMA) of the found phases are given in **Table 1**.

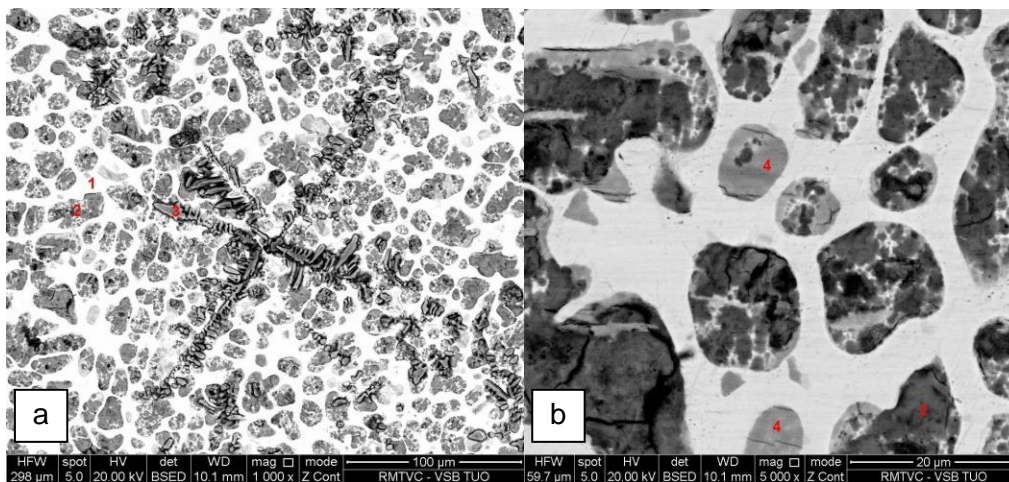


Figure 1 Microstructure (SEM, BSE mode) of the hydrogenated $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}\text{H}_x$ composition; points of electron microprobe analysis are shown

According to the data, the hydrogenated composition is characterized by multi-phase structure. Regular rounded and dendritic inclusions are observed in the matrix phase (**Figure 1a**, point 1), the phase composition of which is complex and is based on Pr-rich phases. Taking into account the fact that data on the mutual solubility of components in the found phases are absent, we have calculated the phase composition of phase 1 using stoichiometry of the phases and EMA data. The assumed phase composition of the matrix phase includes (mole fractions) Pr_3Co (0.29), PrCu (0.43), Pr (0.28). It is likely that PrCu and Pr form the eutectic. Inclusions (points 2, 3, 4) observed in the matrix show the presence of Pr with small contents of cobalt and copper. It should be noted that observed dendritic inclusions (**Figure 1a**) also corresponds to Pr .

According to DTA data (**Figure 2**) for the hydrogenated $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}\text{H}_x$ composition, several thermal effects are observed. It should be noted that the phase composition of $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}\text{H}_x$ is due to the partial hydrogenolysis of $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}$. In accordance to the Pr-Cu and Pr-Co phase diagrams [11], the thermal effect at $\sim 734^\circ\text{C}$ is related to the solidus for the two-phase region Pr crystallites + $(\text{PrCu} + \text{Pr})$ eutectic. The onset of the thermal effect corresponding to $\sim 420^\circ\text{C}$ can indicate the allotropic transformation of Co (cubic to hexagonal). The late effect is overlapped with the thermal effect related to the $\text{L} \rightarrow \text{PrCu} + \text{Pr}$ eutectic reaction. Thus, the multiphase composition added to the powder mixture in manufacturing sintered permanent magnet contains mainly Pr (PrH_x) and PrCu .

Table 1 Results of electron microprobe analysis (at. %) of the Pr₃Co_{0.6}Cu_{0.4}H_x addition

Elements	Pr	Co	Cu
Phase_1_1	7.7	7.1	22.2
Phase_1_2	70.9	7.5	21.6
Phase_1_3	71.3	7.1	21.6
Phase_1_averaged	71.0	7.2	21.8
Phase_2_1	98.7	0.3	1.0
Phase_2_2	99.7	0.0	0.3
Phase_2_3	99.1	0.2	0.7
Phase_2_averaged	99.2	0.2	0.6
Phase_3_1	99.4	0.0	0.6
Phase_3_2	99.6	0.0	0.4
Phase_3_3	99.7	0.0	0.3
Phase_3_averaged	99.6	0.0	0.4
Phase_4_1	99.3	0.0	0.7
Phase_4_2	99.5	0.0	0.5
Phase_4_3	97.8	0.2	2.0
Phase_4_averaged	98.9	0.0	1.1

These results were confirmed by X-ray diffraction data. The X-ray diffraction data are given in **Figure 3** and **Table 2**. The formation of the Co₃PrH_x is unlike; however, the thermal effect at ~1050 °C (related to the peritectic reaction of the Co₃Pr phase) is observed. The total content of Pr and PrH_x phase is estimated to be ~50%. Among the alloy components, only Co can diffuse into the Nd₂Fe₁₄B-based phase grains (the reflection of Co is observed in the X-ray diffraction pattern in Fig. 2). Cobalt cannot be observed in the alloy structure by SEM since, as it was shown in [12, 13], the hydrogenolysis of the R₃Co compounds (with R = Tb, Dy) leads to their decomposition with the formation of fine Co and Cu particles. The other components will improve the grain boundary structure via enhanced wettability between the Nd₂Fe₁₄B-based grains and the Nd-rich phase and decreasing exchange coupling between Nd₂Fe₁₄B-based grains [14, 15]. According to [12], cobalt, in using Tb₃Co_{0.6}Cu_{0.4}H_x addition, forms core/shell microstructure, which favors the improved thermal stability of coercive force [16].

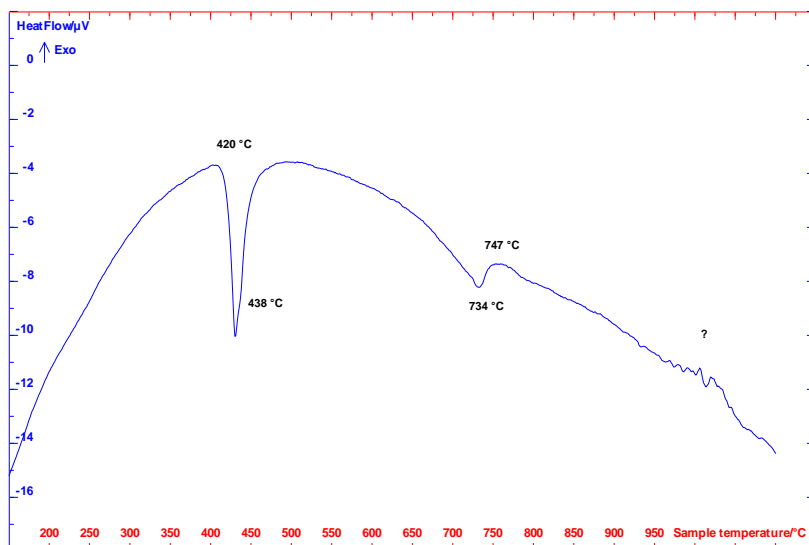


Figure 2 DTA curve of the Pr₃Co_{0.6}Cu_{0.4}H_x composition measured during heating at a rate of 15 °C/min (Al₂O₃ crucible, heating 20 – 1150 °C, inert dynamic atmosphere Ar (6N), *m* = 67 mg)

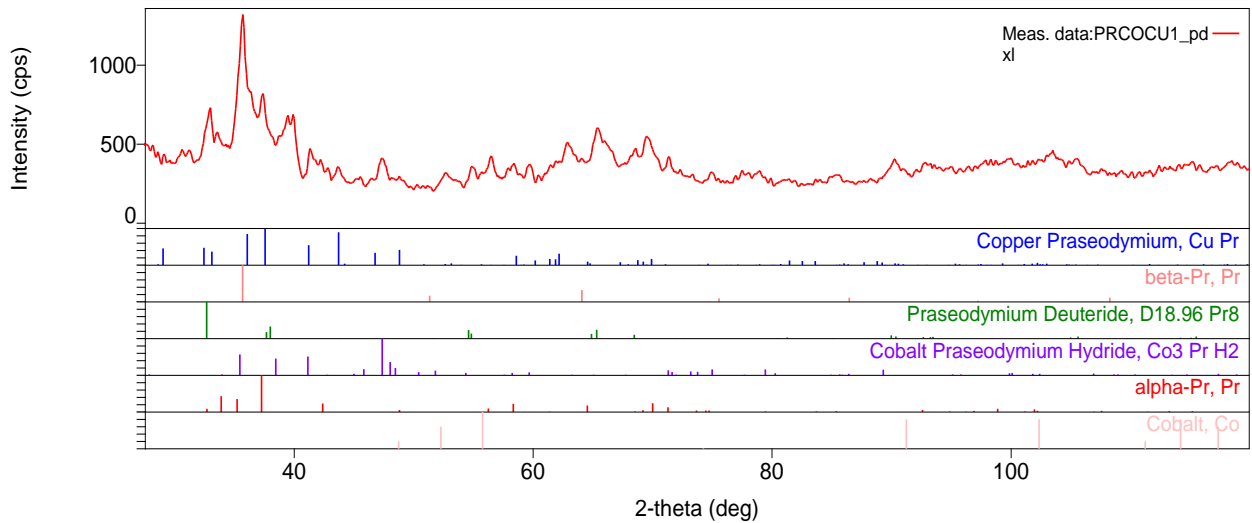


Figure 3 X-ray diffraction pattern of the $\text{Pr}_3(\text{Co,Cu})\text{H}_x$ composition

Table 2 Results of quantitative X-ray phase analysis

Phase	CuPr	β -Pr	PrH_2	Co_3PrH_2	α -Pr	Co
Content (wt%)	22.0	28	8.0	12.0	23.2	7.0

3.2. Magnetic properties of sintered magnet

The sintered magnets were prepared using strip-casting alloy subjected to hydrogen decrepitation and either 2 % $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}$ composition undergone the hydrogenolysis or 2% PrH_x . The magnets in the form of disk 48 mm in diameter and 8 mm in height were sintered at 1080 °C and subsequently subjected to post-sintering annealing at 500 °C for 2 h. The density of the magnet prepared with 2 % $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}\text{H}_x$ is 7.52 g/cm³. The magnetic hysteresis properties of the magnet are given in **Figure 4** and **Table 3**. As the reference magnet, we use the sintered magnet prepared in using the strip-casting alloy and 2 % PrH_x as the addition.

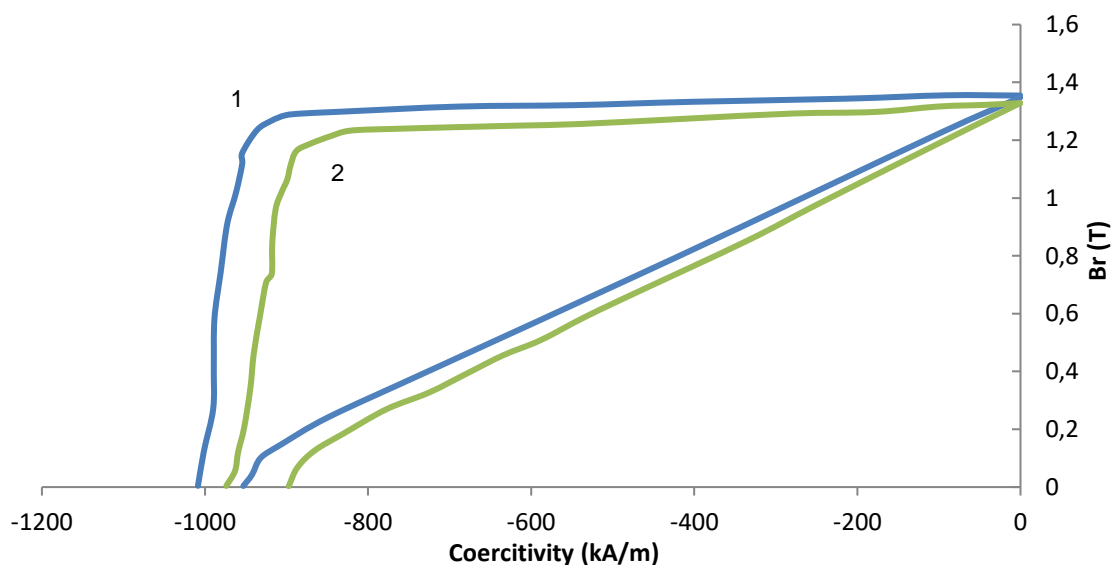


Figure 4 Magnetization reversal curves of sintered magnets prepared by powder blending procedure in using (1) $\text{Pr}_3\text{Co}_{0.6}\text{Cu}_{0.4}\text{H}_x$ and (2) PrH_x additions.

Table 3 Magnetic hysteretic characteristics of sintered magnets prepared by powder blending procedure in using Pr₃Co_{0.6}Cu_{0.4}H_x and PrH_x additions

Addition	B_r (T)	jH_c (kA/m)	H_k (kA/m)	$(BH)_{max}$ (kJ/m ³)
2 wt% Pr ₃ Co _{0.6} Cu _{0.4} H _x	1.35	1004	943	349
2 wt% PrH _x	1.33	973	874	317

As is seen, in using the Pr₃Co_{0.6}Cu_{0.4} addition, both the remanence and coercive force of sintered magnet increase as compared to those of the magnet prepared with PrH_x hydride. Moreover, the maximum energy product increases and squareness of the hysteresis loop improves.

The higher magnetic hysteresis characteristics of the magnet prepared with the Pr₃Co_{0.6}Cu_{0.4}H_x addition are related to the structuring of grain boundaries, namely, the improvement of their both wetting at the expense of low-melting copper-containing composition and magnetic isolation.

4. CONCLUSIONS

- The phase composition of the hydrogenated Pr₃Co_{0.6}Cu_{0.4} addition was studied by SEM, EMA, and X-ray diffraction. The Pr₃Co_{0.6}Cu_{0.4}H_x composition is undergone the hydrogenolysis and is shown to be multiphase and include Pr-rich components, such as Pr, PrH_x, and PrCu and Co phases. All these components are known to exhibit different diffusion behavior in the course of manufacturing the sintered magnet.
- The Pr, PrH_x, and PrCu components modify the grain boundaries of sintered magnet and improve the wetting between Nd₂Fe₁₄B-based grains and Nd(Pr)-rich intergranular phase. Fine Co particles can diffuse into the Nd₂Fe₁₄B-based grains to form Nd₂Fe₁₄B-core/Nd₂(Fe,Co)₁₄B-shell microstructure, which improves thermal stability of the coercive force.
- The hysteretic properties of the sintered magnet prepared from the strip-casting alloy in using the hydrogenated Pr₃Co_{0.6}Cu_{0.4}H_x addition are shown can be improved as compared to those reached in the case of application of PrH_x hydride in the powder mixture.

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