

## EVOLUTION OF THE PHASE COMPOSITION OF (Nd,Pr,Dy)-Fe-B MAGNETS DURING STEPPED ANNEALING

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### Abstract

X-ray diffraction analysis and simulation of X-ray diffraction patterns are used to study the phase composition of sintered (Nd,Pr,Dy)-Fe-B magnets prepared from powder mixtures with 2 % DyH<sub>2</sub> addition. After optimum heat treatment, which includes 1 h holding at 500 °C followed by quenching in gaseous nitrogen, the magnets exhibit high magnetic properties:  $B_r = 1.29$  T,  $jH_c = 1309$  kA/m,  $H_k = 1220$  kA/m,  $(BH)_{max} = 322$  kJ/m<sup>3</sup>. The phase composition of the magnets comprises the principal hard magnetic phase based on the Nd<sub>2</sub>Fe<sub>14</sub>B compound, (Nd,Pr,Dy)-rich phase and (Nd,Pr,Dy)-O oxides. The magnets are subjected to progressive low-temperature heatings in a temperature range of 250-500 °C, annealing at 550 °C, medium-temperature annealing at 900 °C, and high-temperature annealing at 1070 °C to study the stability of hysteretic magnetic characteristics. The heat treatments are shown to lead to changes in the lattice parameters of the Nd<sub>2</sub>Fe<sub>14</sub>B-based phase and appearance of additional reflections, which can be related to the formation and dissolution of the impurity Nd<sub>1.1</sub>Fe<sub>4</sub>B<sub>4</sub> phase. Thermal magnetic analysis is used to study the possibility of existence of the phase. The obtained data demonstrate the higher thermal stability of hysteretic properties of magnets prepared from hydride-containing powder mixtures. These data are of importance for deciding the optimum heat treatment of Nd-Fe-B-based magnets and the prediction of their service stability.

**Keywords:** Permanent magnets, strip casting, thermomagnetic analysis, X-ray diffraction analysis.

### 1. INTRODUCTION

According to [1-2], the addition of heavy rare earths of Dy or Tb is effective to enhance coercivity and consequent thermal stability of the Nd-Fe-B magnets, because Dy or Tb increases the magnetic anisotropy field of the 2-14-1 Nd-Fe-B compound, but this method simultaneously results in considerable degradation of the remanence of the magnets. Recently, techniques for enhancement of coercivity of sintered Nd-Fe-B magnets by diffusing a continuous layer of Dy or Tb onto the surface of the Nd<sub>2</sub>Fe<sub>14</sub>B matrix grains without obvious reduction of the remanence have been developed by different researchers, but the detailed mechanism for the improving coercivity is unclear. Furthermore, these techniques can only be used to prepare small size magnets since the diffusion of Dy or Tb into the magnet is confined within 5 mm. In [3], the sintered Nd-Fe-B magnet with enhanced coercivity by Tb nanoparticles doping was prepared. Authors [1] report the effect on microstructure and magnetic properties of sintered Nd-Fe-B magnets with Dy nanoparticles doping.

According to [4], magnets based on Nd<sub>16</sub>Fe<sub>76</sub>B<sub>8</sub> with DyH<sub>3</sub> additions have been sintered at different temperatures and their magnetic properties, microstructure and compositions have been examined. Details of progress of Dy entering the hard matrix phase were considered and an evolution mode of the relevant sintering process was proposed. Hydrogen absorption and desorption of the magnets were examined by HDTA. The

optimum sintering temperature for these magnets has been established. Microstructural and EDX examinations have revealed that a relatively Dy-rich phase formed in the Nd-rich grain boundary phase and this slowed down the substitution of Nd by Dy in the Nd<sub>2</sub>Fe<sub>14</sub>B matrix phase, possibly enhancing local coercivity without excessive attenuation of the remanence. Hydrogen Decrepitation (HD) occurred as sintered RE-Fe-B magnets were exposed to hydrogen at room temperatures.

The effect of DyH<sub>3</sub> additions on the magnetic properties of magnets was studied in [5]. The use of DyH<sub>x</sub> powder along with DyGa, Dy<sub>3</sub>Co powders allowed the authors to increase the coercive force by 0.4-0.6 T without substantial decrease in the residual magnetization. The increase in the coercive force depends, in particular, the size of powder particles. The DyH<sub>x</sub> powder was prepared by hydrogenation of metallic Dy at 500 °C at a hydrogen pressure of 0.5 MPa. The powder was applied on the Nd-Fe-B magnet surface and annealed in a vacuum at 550 °C for 0.5 h.

This paper is aimed at structural studies of prepared magnets, which should be performed for understanding the phase composition of near-grain boundary regions and triple joints of grains.

## 2. EXPERIMENTAL

Nd-Fe-B magnets were prepared using Nd - 24, Pr - 6.5, Dy - 0.5, B - 1, Al - 0.2, Fe - 65.8 (wt.%) strip-casting alloy. The preparation procedure includes the hydrogen decrepitation of flakes in dry hydrogen (at 100 °C for 1 h) and subsequent passivation in gaseous nitrogen atmosphere. Dysprosium hydride (2 wt %) was added after cooling the powder to room temperature. The mixture was subjected to fine milling for 40 min to an average particle size of 3 μm using a vibratory mill and isopropyl alcohol medium. Samples were compacted in a magnetic field and sintered at  $t = 1070$  °C (for 2 h). The sintered blanks were subjected to the following heat treatments:

*HT-1 (optimum):* 550 °C (1 h) + quenching in gaseous nitrogen (Sample No.1);

*HT-2:* 550 °C (1 h) + quenching + 500 °C (2 h) + quenching + 500 °C + cooling for 2 h to 400 °C + 400 °C (6 h) + furnace cooling (in this case, the properties are almost unchanged, although the earlier experiments performed for similar magnets demonstrates the decrease in magnetic properties  $jH_c$  and  $H_k$ ) (Sample No. 2);

*HT-3:* 550 °C (1 h) + quenching + 500 °C (2 h) + quenching + 500 °C + cooling for 2 h to 400 °C + 400 °C (6 h) + furnace cooling + 550 °C (1 h) + quenching (properties decreases substantially) (Sample No. 3).

Earlier studies showed the partial or complete recovery of properties and even their increase for high-alloyed (with Dy, Tb, Co, Ti, Mo, V, Nb) magnets.

Magnetic properties are given in **Table 1**. The measurements were performed at room temperature using a closed circuit of hysteresis graph and samples 40 mm in diameter and 8 mm thick, which were subjected to HT-1, HT-2, and HT-3.

The X-ray diffraction analysis of "strip-casting" alloy and sintered magnets was performed using a Difrei 401 diffractometer and Cr[α] radiation. The structural studies were carried out using samples demagnetized in a vacuum at 775 K to recovery the initial state.

X-ray diffraction patterns were processed using a PowerCell software. This program allows one to simulate X-ray diffraction patterns using crystal structure parameters of a compound, crystal lattice sizes, atomic positions in the crystal lattice and X-ray wavelength.

Magnetic measurements were performed using a MicroSense vibrating-sample magnetometer. This magnetometer allows one to perform magnetization measurements in magnetic fields of to 2.5 T in a temperature range of from 78 to 1000 K. The magnetic field is produced by an electromagnet. The sample temperature changes in blowing either cooled nitrogen (for measurements below room temperature) or hot

argon (for measurements above room temperature). This allows one to rapidly reach the required temperature of sample.

The magnetization of samples of (Nd,Pr,Dy)-Fe-B magnets was measured at temperatures of 4.2-300 K using a vibrating-sample magnetometer. The measurements were performed in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland) using a superconducting solenoid (Oxford Instruments) that produces magnetic fields up to  $\mu_0 H = 15$  T. To improve the heat-exchange, before the measurements, the measuring insert was evacuated and filled with gaseous helium to a pressure of  $0.8 \cdot 10^5$  Pa.

**Table 1** Magnetic properties of sintered magnets (samples No. 1-3)

Magnetic properties	Sample No. 1	Sample No. 2	Sample No. 3
$B_R$ (T)	1.29	1.29	1.26
$H_{CM}$ (kA/m)	1309	1309	1105
$H_{CB}$ (kA/m)	981	981	895
$H_K$ (kA/m)	1262	1262	888
$(BH)_{max}$ (kJ/m <sup>3</sup> )	322	322	303

### 3. RESULTS AND DISCUSSION

#### 3.1 X-ray diffraction analysis

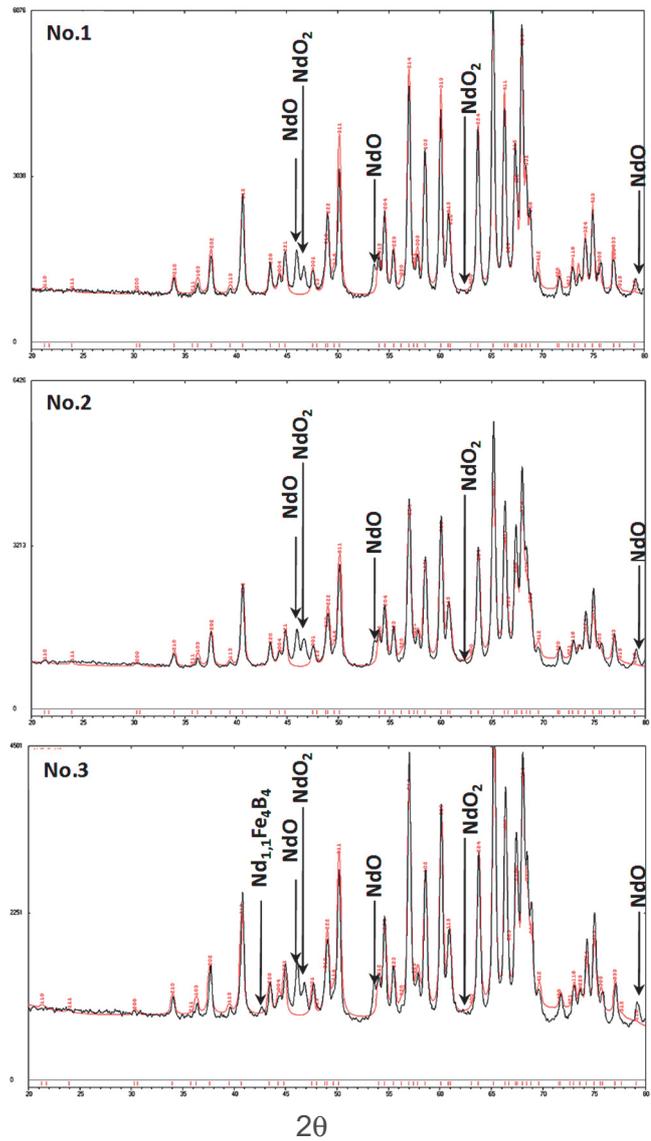
**Fig. 1** demonstrates comparison of experimental X-ray diffraction pattern (black line) and pattern simulated for the Nd<sub>2</sub>Fe<sub>14</sub>B-type structure (space group P4<sub>2</sub>/mnm) (red line). It is seen that main reflections simulated for the Nd<sub>2</sub>Fe<sub>14</sub>B coincide adequately with those in the experimental X-ray diffraction pattern; some reflections are likely to belong to other phases. These reflections are observed at 2 $\Theta$  angles of 46.01; 46.42; 53.58 and 79.13 deg. Subsequent analysis of experimental X-ray diffraction patterns was performed in detail using literature data and simulated X-ray diffraction patterns. It is known from literature that the presence of  $\alpha$ -Fe phase can affect the properties of permanent magnets [6]. However, we failed to detect the  $\alpha$ -Fe phase at the background of reflections of the Nd<sub>2</sub>Fe<sub>14</sub>B phase. The presence of the  $\alpha$ -Fe phase in all three samples was revealed by thermal magnetic analysis (Section 3.2). Based on the analysis of chemical composition and literature data [7-9], we assumed the presence of REM oxide phases in ternary junctions of samples under study. According to literature data, ternary junctions can contain different oxide phases. These are NdO with the NaCl-type structure (space group Fm-3m) [9] (the oxygen content is 50 at.%), Nd<sub>2</sub>O<sub>3</sub> with the La<sub>2</sub>O<sub>3</sub>-type structure (space group Pm-3m) (the oxygen content is 60 at.%) [7,8], and NdO<sub>2</sub> with the CaF<sub>2</sub>-type structure (space group Fm-3m) (the oxygen content is 67 at.%) [9].

Results of simulation of X-ray diffraction patterns are shown in **Fig. 1**. As is seen from these figures, patterns simulated for the structures of the NdO and Nd<sub>2</sub>O<sub>3</sub> oxides agree adequately with experimental patterns. A slight difference can be explained by the fact that the simulation was performed for the NdO and Nd<sub>2</sub>O<sub>3</sub> compounds, whereas, according to chemical analysis data, these compounds can contain Dy and Pr, i.e. can differ from the composition preset with the simulation program.

The X-ray diffraction pattern for sample No. 3 exhibits a small peak at 2 $\Theta = 42.7^\circ$  along with the other aforementioned reflections. Earlier, we assumed that this reflection corresponds to the Nd<sub>1.1</sub>Fe<sub>4</sub>B<sub>4</sub> -phase. According to literature data [10-12], the Nd<sub>1.1</sub>Fe<sub>4</sub>B<sub>4</sub> or Nd<sub>5</sub>Fe<sub>18</sub>B<sub>18</sub> phase has a structure described by space group Pccn. **Fig. 1** exhibits the X-ray diffraction pattern simulated for the structure. As is seen, the second (in

value) peak corresponds adequately to an angle  $2\Theta = 42.7^\circ$ . However, the analysis performed for the  $\text{NdO}_2$  phase with the high oxygen content (67 at.%) also exhibits the position of main reflection close to the angle  $2\Theta = 42.7^\circ$ . In the case of small changes in the lattice parameter  $a$  of the  $\text{NdO}_2$  phase, which is equal to 0.554 nm, the shift of the main reflection to the low-angle range takes place. It is likely that the shift of the reflection is related to the partial substitution of Pr and Dy atoms for Nd atoms; this leads to the decrease in the lattice parameter  $a$  since, for  $\text{PrO}_2$   $a = 0.532$  nm.

Moreover, we found the shift of reflections for samples No. 1-3 relatively to each other. This is likely to be related to the changes in the lattice parameters of the principal  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase. The calculated lattice parameters of the phase are given in **Table 2**.



**Fig.1** X-ray diffraction pattern for samples No. 1-3 ( $\lambda = 0.22909$  nm). Red line corresponds to simulated pattern for the  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type structure

**Table 2** Calculated lattice parameters of the phase with  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type structure in samples No. 1-3

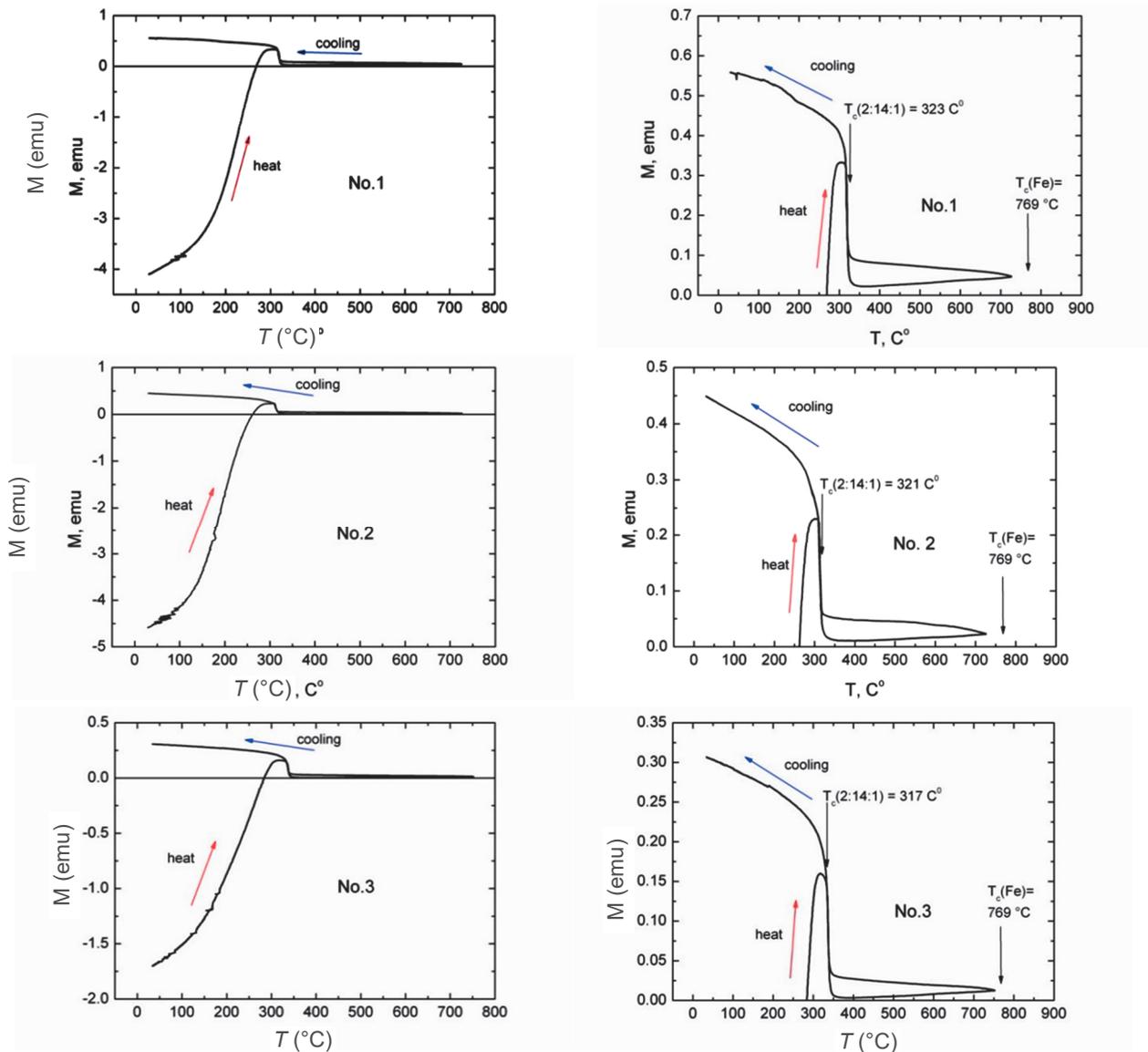
Sample	$a$ (nm)	$c$ (nm)	$c/a$
No. 1	0.8761	1.2152	1.387056
No. 2	0.8768	1.2165	1.387432
No. 3	0.876	1.2135	1.385274

## 3.2 Thermal magnetic analysis

### 3.2.1 Thermal magnetic analysis above room temperature

The thermal magnetic analysis (TMA) was performed for all samples of Nd-Fe-B-based permanent magnets (No. 1-3). Samples in the form of discs were cut from magnets; the axis of texture is in the disk plane. The measurements were performed along the texture axis. Initially, the samples were magnetized to saturation (in a field of 2 T); after that, the field was switched off. The magnetized samples were heated at a rate of 5 K/min in a magnetic field of 0.01 T. After heating to 1000 K, the samples were cooled to room temperature at the

same rate in a magnetic field of 0.01 T. **Fig. 2** shows results of measurements. As is seen from the dependences, two magnetic phases are revealed in the course of TMA. One of the phases is the main 2:14:1 hard magnetic phase with the Curie temperature close to the Nd<sub>2</sub>Fe<sub>14</sub>B compound [14]. The other phase is likely to be  $\alpha$ -Fe phase with the Curie temperature of 769 °C (the final portion of dependence demonstrates the tendency to a decrease in the magnetization). Based on the data, we cannot conclude definitely the content of  $\alpha$ -Fe phase in magnets since the  $\alpha$ -Fe and 2:14:1 phases have different magnetic permeabilities. It is likely that the  $\alpha$ -Fe phase is present at the grain surface.



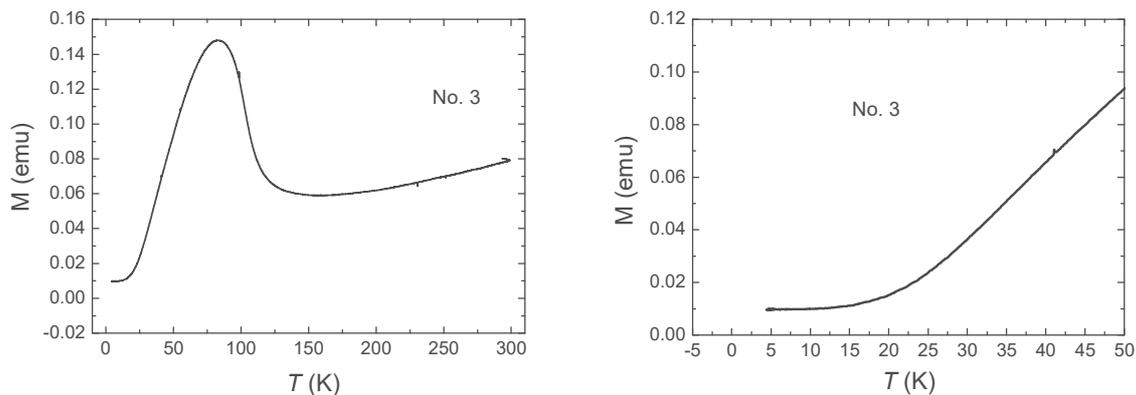
**Fig. 2** Thermal magnetic analysis of sample No.1-3 performed in a magnetic field of 0.01 T. The left dependence corresponds to heating and cooling of sample; the right dependence (given in enlarged scale) demonstrates the cooling of sample

### 3.2.2 Thermal magnetic analysis below room temperature

To detect the presence of assumed phases with Curie temperatures below room temperature, such as REM-based phases and Nd<sub>1,1</sub>Fe<sub>4</sub>B<sub>4</sub> compound with the Curie temperature of 13 K [10], we performed low-temperature measurements of magnetization. The measurements were performed in a magnetic field of 0.01 T

applied along the axis of texture in a temperature range of 4.2 - 300 K using the vibrating-sample magnetometer.

Before measurements, the sample No. 3 was completely demagnetized. **Fig. 3** shows results of measurements. As is seen from **Fig. 3**, a maximum related to the spin-reorientation transition of the main hard magnetic phase (2:14:1) took place at 84 K. The spin-reorientation transition of the Nd<sub>2</sub>Fe<sub>14</sub>B compound occurred at  $T_{SR} = 135$  K [14]. The decrease in the spin-reorientation transition is related to the substitution of other REMs (Dy, Pr) for Nd in the magnetic sublattice. As is seen from the enlarged low-temperature portion of the TMA curve, no anomaly is observed at temperatures corresponding to the Curie temperature of the Nd<sub>1.1</sub>Fe<sub>4</sub>B<sub>4</sub> phase.



**Fig. 3** TMA curve for sample No. 3 measured in a field of 0.01 T. Left curve corresponds to the heating of sample; right curve is the enlarged low-temperature portion of the curve

## CONCLUSION

Samples of high-coercivity (Nd,Pr)-Fe-B magnets were prepared using powder mixtures containing DyH<sub>2</sub>. The effect of low-temperature treatments of the magnetic properties of developed magnets was studied by X-ray diffraction analysis and thermal magnetic analysis. Conditions of the optimum low-temperature heat treatment were determined. Compositions of paramagnetic phases formed at triple junctions of 2-14-1 phase grains were determined; these phases are (Nd,Pr,Dy)-O and Nd<sub>1.1</sub>Fe<sub>4</sub>B<sub>4</sub>. Evolution of the phases during low-temperature treatments and their effect on magnetic properties, in particular, on the coercive force of magnets is discussed.

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