ELECTRICAL AND MAGNETIC PROPERTIES

Magnetics Hysteresis Properties and Microstructure of High-Energy (Nd,Dy)—Fe—B Magnets with Low Oxygen Content

D. Yu. Vasilenko^a, A. V. Shitov^{a,b,*}, D. Yu. Bratushev^a, K. I. Podkorytov^a, V. S. Gaviko^{b,c},
O. A. Golovnya^{b,c,**}, and A. G. Popov^{b,c}

^a *Urals Electromechanical Plant, Joint-Stock Company, Ekaterinburg, 620137 Russia*

^b *M.N. Miheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Ekaterinburg, 620108 Russia*

^c *Ural Federal University, Ekaterinburg, 620002 Russia*

**e-mail: shitov@uemz.ru*

***e-mail: golovnya@imp.uran.ru*

Received July 2, 2021; revised August 2, 2021; accepted August 4, 2021

Abstract—Magnetic properties and microstructure of high-energy (Nd,Dy)—Fe—B magnets with Dy of no more than 1 wt % prepared via a low-oxygen routine are studied. Oxygen content in magnets does not exceed 0.20 wt %. 0.5 wt %—Dy addition reliably stabilizes the coercivity MH_c higher than 13 kOe; in this case, the maximum energy density product $(BH)_{\max}$ of magnets is 48.5–49.5 MG Oe. High magnetic hysteresis properties are gained via optimization of chemical and phase compositions of magnets, as well as their microstructure. The grain size of the main $Nd_2Fe_{14}B$ phase is approximately 3.5 μm ; and according to X-ray analysis, the weight fraction of additional Nd-rich phases (NdO_x and Nd_2O_3) does not exceed 2.5%. Scanning electron microscopy study has demonstrated that in triple junctions of $Nd_2Fe_{14}B$ grains there are two types of inclusions (B and C) of the NdO_x phase, which significantly differ by their chemical composition. C-phase inclusions with low oxygen content ($x \approx 0.03$) are enriched in Fe (40–50 wt %); whereas, B-phase with high oxygen content ($x \approx 0.70$) contains 3–5 times less Fe. The angular dependences of coercivity of (Nd,Dy)—Fe—B magnets are presented.

Keywords: Nd—Fe—B, permanent magnet, microstructure

DOI: 10.1134/S0031918X21120127

INTRODUCTION

Sintered Nd—Fe—B magnets are successfully applied in a wide range of efficient technical devices. Among all permanent magnets, these magnets possess the highest maximum energy density product $(BH)_{\max} \geq 50$ MG Oe at room temperature. The high hysteresis properties of these magnets are provided by a favorable combination of the intrinsic magnetic properties of $Nd_2Fe_{14}B$ (the saturation magnetization, Curie temperature, anisotropy constant) and Nd—Fe—B phase equilibrium which allows liquid-phase sintering of powders [1–6]. Multiphase microstructure of sintered Nd—Fe—B magnets consists of the $Nd_2Fe_{14}B$ grains, inclusions of phases localized at triple junctions of the $Nd_2Fe_{14}B$ grains, and thin layers of the phase developed at the boundaries of grains. Nd-rich phases at triple junctions can be the double hexagonal close-packed Nd (dhcp Nd), face-centered cubic NdO_x (fcc NdO_x), and hexagonal close-packed Nd_2O_3 (hcp Nd_2O_3) structures [7–18]. Volume fractions of oxides are controlled by oxygen content in magnets. The higher the oxygen concentration in

magnets, the higher volume fraction of paramagnetic oxides (NdO_x and Nd_2O_3) which are detrimental for the remanence B_r and $(BH)_{\max}$. In addition, the oxidation of excess Nd impedes the development of continuous thin layers of the Nd-rich phase, which provide magnetic isolation of the $Nd_2Fe_{14}B$ grains. As a result, numerous regions of nucleation emerge and significantly decrease the coercivity H_c of magnets. Thus, the low oxygen content and optimized microstructure of sintered magnets are key factors for high magnetic hysteresis properties.

Recently, researchers from Japan have studied in detail the chemical composition and structure of Nd-rich phases [11, 12, 14–17]. They have established that thin layers that separate the $Nd_2Fe_{14}B$ grains have amorphous structure [9] and do not contain oxygen; however, they are ferromagnetic, because of their high Fe content [12, 19]. The nucleation of reverse magnetization domains can proceed easily at such boundaries. This result overturned the theory of nucleation mechanism of magnetization reversal in sintered Nd—Fe—B magnets [20], which dominated in science since

Table 1. Chemical composition and formula of alloys used for magnet preparation

No.	Content, wt %								Formula, at %
	Nd	Dy	Fe	Co	Cu	Ga	B	O	
Alloys of high-energy magnets									
1	29.1	—	68.59	1.0	0.1	0.1	1.1	0.010	Nd _{13.00} Fe _{79.12} Co _{1.09} Cu _{0.10} Ga _{0.09} B _{6.56} O _{0.04}
2	29.3	—	68.57	1.00	0.11	0.10	0.9	0.019	Nd _{13.24} Fe _{80.03} Co _{1.11} Cu _{0.11} Ga _{0.09} B _{5.42} O _{0.08}
3	29.4	—	67.58	1.0	0.1	0.1	0.9	0.016	Nd _{13.28} Fe _{79.99} Co _{1.11} Cu _{0.10} Ga _{0.09} B _{5.43} O _{0.07}
4	29.7	—	68.00	1.0	0.19	0.19	0.9	0.019	Nd _{13.45} Fe _{79.62} Co _{1.11} Cu _{0.20} Ga _{0.18} B _{5.44} O _{0.08}
5	29.7	0.06	68.04	1.0	0.1	0.1	1.0	*	Nd _{13.40} Dy _{0.02} Fe _{79.27} Co _{1.10} Cu _{0.10} Ga _{0.09} B _{6.02}
6	29.0	0.5	68.37	1.0	0.11	0.10	0.9	0.020	Nd _{13.11} Dy _{0.20} Fe _{79.95} Co _{1.11} Cu _{0.11} Ga _{0.09} B _{5.43} O _{0.12}
7	29.1	0.5	68.31	0.95	0.11	0.10	0.9	0.029	Nd _{13.16} Dy _{0.20} Fe _{79.96} Co _{1.05} Cu _{0.11} Ga _{0.09} B _{5.43} O _{0.12}
8	29.5	0.55	67.82	1.0	0.11	0.10	0.9	0.021	Nd _{13.39} Dy _{0.22} Fe _{79.63} Co _{1.11} Cu _{0.11} Ga _{0.09} B _{5.45} O _{0.13}
9	29.0	1.0	67.56	1.2	0.17	0.09	0.95	0.032	Nd _{13.14} Dy _{0.40} Fe _{79.14} Co _{1.33} Cu _{0.17} Ga _{0.08} B _{5.74} O _{0.07}
10	29.1	1.0	67.67	1.0	0.1	0.1	1.0	0.033	Nd _{13.16} Dy _{0.40} Fe _{79.09} Co _{1.11} Cu _{0.10} Ga _{0.09} B _{6.04} O _{0.13}
11	29.9	1	66.97	1.0	0.12	0.1	0.9	0.014	Nd _{13.67} Dy _{0.41} Fe _{79.10} Co _{1.12} Cu _{0.12} Ga _{0.09} B _{5.49} O _{0.06}

* Oxygen content was not determined in alloy 5.

the development of these magnets [21]. Presently, active discussion of the origin of magnetic hysteresis of high-energy sintered Nd–Fe–B magnets favors the pinning-controlled coercivity mechanism rather than nucleation [19, 22].

Russia considerably falls behind the world leaders, namely, Japan and China, in both quality and amount of production of Nd–Fe–B magnets. Up to the end of the first decade of the XXI century, $(BH)_{\max}$ of domestically produced Nd–Fe–B magnets hardly exceeded 40 MG Oe [23–29]. A noticeable break-through was made by specialists of the Ural school of magnetism. The Urals Electromechanical Plant, Joint-Stock Company implemented the low-oxygen technology, thus, increasing $(BH)_{\max}$ of sintered magnets up to 50 MG Oe [30]; however, the existing magnet production capacity can provide only 1 ton per year. Demands of domestic industry are mainly satisfied by Chinese magnets, which contradicts the strategy of Russia's technological safety. Development of the complete cycle of production of high-quality Nd–Fe–B permanent magnets by domestic companies is an urgent task.

This article presents the study of magnetic hysteresis properties and microstructure of a wide range of high-quality (Nd,Dy)–Fe–B magnets produced by Urals Electromechanical Plant, Joint-Stock Company via the low-oxygen routine. The high-energy (Nd,Dy)–Fe–B magnets, in which Dy substitutes for Nd by no more than 1 wt %, are considered. Such magnets possess $(BH)_{\max} = 48–50$ MG Oe, preserving moderate coercivity.

EXPERIMENTAL

Alloys for high-energy (Nd,Dy)–Fe–B magnets were prepared by strip casting, which had been devel-

oped by Showa Denko company [31, 32]. The linear velocity of a water-cooled copper wheel was 1 m/s. The plates produced were 0.30 to 0.45 mm thick and approximately 3 cm-in-width, their microstructure was similar to the one described in [33]. Alloy compositions are listed in Table 1. From each alloy, magnets were prepared via the low-oxygen routine. To make the alloys more brittle, their plates were preliminarily subjected to the hydrogen decrepitation. The coarse powders were milled in a jet mill in nitrogen atmosphere. The average size of powder particles D_{av} was determined by Fisher subsieve method and fell in the range of 2.7–3.2 μm . The powder was transported between stages (from jet milling to sintering) in a hermetic steel container filled with inert gas with the oxygen content less than 10 ppm. The powder was magnetically aligned and pressed in a press combined with an electromagnet and placed in a glovebox with nitrogen atmosphere. The strength of the dc magnetic field was 16 kOe. The pressing was carried out perpendicular to the magnetic field direction. The result was green compacts with the dimensions $22 \times 27 \times 60$ mm³ and alignment axis along the 22-mm side. The green compacts were sintered in vacuum at 1040–1055°C for 2 hours with the consequent quenching in argon to room temperature; the 7.57–7.62 g/cm³ density was obtained. To increase H_c , the sintered magnets were subjected to the two-stage heat treatment at $T_1 = 880^\circ\text{C}$, 1 h and $T_2 = 480–550^\circ\text{C}$, 1–2 h.

Magnetization reversal curves of the heat-treated samples were measured with Permagraph L. Angular dependences of coercivity were obtained on spherical samples with a Lakeshore 7407 vibrating-sample magnetometer. Oxygen content in magnets was deter-

Fig. 1. Magnetic hysteresis properties of magnets vs. rare-earth element content in initial alloy.

mined by the restoring method with a gas analyzer Leco ONH-836. The microstructure and chemical composition of magnets was studied in back scattered electrons (BSE) mode with a microscope TESCAN MIRA3. Prior to microanalysis, the polished surfaces of samples were covered by a carbon layer with a Quorum Q150R. X-ray diffraction was performed with a diffractometer Empyrean (PANalytical) in $\text{CuK}\alpha$ irradiation.

RESULTS AND DISCUSSION

1. Magnetic Properties of Nd–Fe–B Magnets

Figure 1 shows the dependence of magnetic hysteresis properties of magnets on the total rare-earth element (R) content in initial alloys. A Dy-free magnet has the lowest Nd content of 29.2 wt %, which results in the highest B_r and $(BH)_{max}$, and the lowest coercivity. With increasing Nd content, the coercivity MH_c increases up to 12–13 kOe; however, B_r and $(BH)_{max}$ monotonously decrease. To stabilize the coercivity of magnets, 0.5 and 1.0 wt % Dy were added to alloys. This Dy addition stabilizes MH_c at a value no less than 13 kOe for $R = \text{Nd} + \text{Dy} > 29.6$ wt %. In this case, $(BH)_{max}$ of magnets with 0.5 wt % Dy and 29.6–30.1 wt % R is in the range of 48.5–49.5 MG Oe, and that of magnets with 1.0 wt % Dy decreases down to 47 MG Oe. The magnetization reversal curves of magnets with various Dy contents are shown in Fig. 2.

Thus, in the alloys with 30 wt % R, the 0.5 wt % Dy addition is a convenient way to stabilize high hysteresis properties of high-energy magnets.

The total chemical composition, phase composition, and microstructure significantly affect structure-sensitive hysteresis properties of Nd–Fe–B magnets. In the course of sintering, oxygen adsorbed by powder upon preparation with a considerable part of excess Nd forms oxides between $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Figure 3 shows the effects of oxygen concentration in magnets on their properties. Similarly, B_r , H_c , and $(BH)_{max}$ tend to decrease in the Dy-free and 0.5/1.0 wt % Dy-containing magnets. On the one hand, this trend is caused by an increase in the R content of magnets (Fig. 1); on the other hand, this result indicates that the higher R content, the higher oxygen content in magnets.

2. Phase Composition and Microstructure of Magnets vs. Dy and O Contents

As is well known, the Nd-rich phases localized between $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains have various crystal structures and have different oxygen contents [10]. In order to find a correlation between magnetic properties, phase composition of the magnets, and their oxygen content, some magnets were studied by X-ray analysis and electron microscopy. Figure 4 shows diffraction patterns of the magnets prepared from alloys 3 (Dy 0%), 6 (Dy 0.5%), and 11 (Dy 1.0%). The phase composi-

Fig. 2. Magnetization reversal curves of high-energy Nd–Fe–B and (Nd, Dy)–Fe–B magnets with 0.5 and 1.0 wt % Dy.

Fig. 3. Magnetic hysteresis properties of magnets vs. oxygen content.

Fig. 4. X-ray powder diffraction patterns of magnets prepared from alloy 3 (Dy 0%) (a); 6 (Dy 0.5%) (b), and 11 (Dy 1%) (c).

tions of these magnets are listed in Table 2. In addition to the main $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, all magnets contain NdO_x with the fcc structure of NaCl (Space group $Fm\bar{3}m$).

Additionally, in magnets prepared from alloys 6 and 11, the stable Nd_2O_3 oxide has been found; however, its quantity is too small for X-ray determination. Despite the fact that the amount of oxides is determined with insufficient accuracy, it qualitatively shows that their weight fraction grows with oxygen content in magnets.

The microstructure of magnets whose phase composition was studied by X-ray diffraction analysis (XRD) was investigated. For instance, Fig. 5 demonstrates the microstructure of an unetched polished and etched surfaces of the magnet prepared from alloy 6.

In the microstructure study, the plane of surfaces was parallel to the alignment axis which is vertical in the figure. The microphotograph of the etched surface (Fig. 5a) has clear boundaries between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, which allows correct estimation of grain sizes. In the magnets under consideration with 0, 0.5, and 1.0 wt % Dy, the average grain size D_{av} of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase weakly depends on the Dy content and falls into the range of 3.5–3.8 μm . The electron-microscopy micrographs of the unetched surfaces (Fig. 5b) contain several phases different by the image contrast. The grains of the main $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (A) have uniform dark-grey contrast. In the triple junctions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, there are Nd-rich phases. The largest volume of triple junctions is occupied by bright-light inclusions (B). According to the XRD, inclusions

Table 2. Results of X-ray phase analysis

No. alloy	Dy wt %	O wt %	Phase (Space group)	a , Å	c , Å	Weight fraction, %
3	0	0.13	$\text{Nd}_2\text{Fe}_{14}\text{B}$ ($P42/mnm$)	8.802	12.196	99.5
			NdO_x ($Fm\bar{3}m$)	5.098	—	0.5
6	0.5	0.17	$\text{Nd}_2\text{Fe}_{14}\text{B}$ ($P42/mnm$)	8.801	12.191	98.3
			NdO_x ($Fm\bar{3}m$)	5.096	—	1.7
11	1.1	0.20	$\text{Nd}_2\text{Fe}_{14}\text{B}$ ($P42/mnm$)	8.807	12.199	97.6
			NdO_x ($Fm\bar{3}m$)	5.105	—	2.4

Fig. 5. Micrographs of microstructure of sintered magnet prepared from alloy 6 with 0.5% Dy: (a) etched polished surface; (b) unetched polished surface. A, B, C designate corresponding phases; IGB, intergranular boundaries.

(B) are the NdO_x phase with a fcc structure. It can be persistently found that, in the vicinity of sharp edges of the triple junctions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, phase (B) changes to light-gray phase (C). The crystal structure determination of this phase requires additional investigation. Rarely, the Nd_2O_3 phase in the shape of dark-gray circular inclusions (D) (absent in Fig. 5b) can be found in the micrographs. The phase contrast of the observed regions depends on the content of main elements and oxygen. The results of phase microanalysis of magnets prepared from alloys 2 (Dy 0%), 6 (Dy 0.5%), and 11 (Dy 1%) are listed in Table 3. According to the microanalysis (M/A), in phases, the oxygen content is overestimated by 0.8–1.0 wt %. This conclusion derives from the fact that, first, there is no oxygen in the $(\text{Nd}, \text{Dy})_2\text{Fe}_{14}\text{B}$ grains, and, second, the M/A data on the oxygen content determined on a large surface area are an order greater than the results of chemical analysis (C/A) of the same magnets. Such discrepancy can be caused by oxidation of the polished surfaces which are employed for microanalysis. Taking into account this discrepancy, the composition formula was corrected to decrease oxygen concentration in each phase by a value equal to the erroneously determined oxygen in the $(\text{Nd}, \text{Dy})_2\text{Fe}_{14}\text{B}$ grains of each magnet.

For phase (B) (NdO_x) with the fcc structure, the ratio $x = \text{O}/\text{Nd}$ is approximately ~ 0.7 . In addition to Nd and O, this phase contains up to 10 wt % Fe, as well as negligible amount of doping elements M , i.e., Co, Cu, Ga; therefore, in Table 3, phase (B) is designated by the generalized composition formula $(\text{Nd}, \text{Fe}, M)\text{O}_x$. Let us note that Li et al. [34] showed by the 3D atom-probe tomography (3DAP) that the NdO_x phase had a large Fe content. According to their results, the composition of NdO_x corresponds to $\text{Nd}_{30.8}\text{Fe}_{45}\text{Cu}_{1.9}\text{B}_{2.8}\text{O}_{19.5}$.

In phase (C) (in Table 3, its composition is designated by the generalized formula $(\text{Nd}, \text{Fe}, M)\text{O}_x$), the oxygen content is negligible ($x \leq 0.05$). However, Fe content of this phase is high; the ratio $r = \text{Fe}/(\text{Nd} + \text{Dy})$ can reach ~ 3 . Besides, Cu and/or Ga are primarily localized in phase (C); generally, their contents in this phase exceed their total concentrations in a magnet. Phase (C) localized in the triple junctions is connected through its acute angles with thin light-gray Nd-rich intergranular boundaries (IGB), which separate the grains and are clearly visible in Fig. 5b. In the course of additional annealing of sintered Nd–Fe–B–M ($M = \text{Cu}, \text{Ga}, \text{Co}$) magnets at 520–600°C, phase (C) acts as a source for the liquid-phase diffusion of elements M , which spread over the IGB due to capillary effects [18, 35, 36]. It is worth noting the anisotropy of the microstructure morphology. Nd-rich inclusions are mainly localized at the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain faces perpendicular to the c axis of easy magnetization (alignment axis is vertical in the figure plane); whereas, the IGBs separate the grain faces which form small angles with the c axis. Structural and chemical compositions of the IGBs were studied in detail by the high-resolution transmission electron microscopy and 3DAP in a series of works performed in Japan [9, 11, 12, 15, 16, 37, 38]. In these works, it was shown that after annealing at 520–600°C, the width of the IGBs is around 3 nm. The IGBs with planes mainly perpendicular to the c axis of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are crystalline and enriched in Nd; whereas, boundaries parallel to the c axis are amorphous and enriched in Fe [15]. The chemical composition of amorphous IGBs determined by the 3DAP was $\text{Nd}_{30}\text{Fe}_{66}\text{B}_3\text{Cu}_1$ [12, 39]. There is no oxygen in this phase. Copper and gallium introduced into the initial alloy in content of around 0.1% are mainly localized in this phase in the shape of segregations at the IGB interface with the $\text{Nd}_2\text{Fe}_{14}\text{B}$

Table 3. Microanalysis of Nd–Fe–B magnets

Element content, wt %									Composition formula
Magnet/phase	Nd	Dy	Fe	Co	Cu	Ga	O	B	
Magnet Dy 0%, O—0.13%									
C/A	29.30	0.00	69.37	1.00	0.10	0.10	0.13	0.90	Nd _{2.44} (Fe _{0.97} M _{0.03}) ₁₄ B ₁ O _{0.10}
M/A	30.15	0.13	67.19	1.15	0.17	0.00	1.21	—	Nd _{2.40} (Fe _{0.98} M _{0.02}) ₁₄ B ₁ O _{0.86}
phase (A)	27.66	0.16	70.01	1.27	0.13	0.00	0.77	—	Nd _{2.11} (Fe _{0.98} M _{0.02}) ₁₄ B ₁
phase (B)	80.68	0.13	9.57	0.19	0.37	0.00	9.06	—	(Nd _{0.74} Fe _{0.25} M _{0.01})O _{0.69}
phase (C)	54.05	0.00	39.21	3.60	1.77	0.00	1.37	—	(Nd _{0.32} Fe _{0.61} M _{0.06})O _{0.03}
Magnet Dy 0.5%, O—0.17%									
C/A	29.50	0.50	68.63	1.00	0.10	0.10	0.17	0.90	(Nd _{0.99} Dy _{0.01}) _{2.49} (Fe _{0.98} M _{0.02}) ₁₄ B ₁ O _{0.13}
M/A	29.84	0.51	66.85	1.50	0.10	0.13	1.07	—	(Nd _{0.99} Dy _{0.01}) _{2.40} (Fe _{0.98} M _{0.02}) ₁₄ B ₁ O _{0.76}
phase (A)	27.52	0.53	69.82	1.30	0.00	0.00	0.83	—	(Nd _{0.98} Dy _{0.02}) _{2.14} (Fe _{0.98} M _{0.02}) ₁₄ B ₁
phase (B)	80.79	1.83	7.73	0.01	0.04	0.13	9.47	—	(Nd _{0.77} Dy _{0.02} Fe _{0.19} M _{0.03})O _{0.74}
phase (C)	46.90	0.80	47.42	0.87	0.11	2.11	1.79	—	(Nd _{0.26} Fe _{0.70} M _{0.04})O _{0.05}
phase (D)	76.64	1.54	6.18	0.00	0.03	0.00	15.62	—	(Nd _{0.82} Dy _{0.01} Fe _{0.17}) ₂ O _{2.84}
Magnet Dy 1.0%, O—0.20%									
C/A	29.7	1.10	67.63	1.10	0.16	0.11	0.20	0.90	(Nd _{0.97} Dy _{0.03}) _{2.55} (Fe _{0.98} M _{0.02}) ₁₄ B ₁ O _{0.15}
M/A	29.35	1.06	67.08	1.27	0.09	0.00	1.15	—	(Nd _{0.97} Dy _{0.03}) _{2.40} (Fe _{0.98} M _{0.02}) ₁₄ B ₁ O _{0.82}
phase (A)	26.62	1.19	69.99	1.38	0.00	0.00	0.83	—	(Nd _{0.96} Dy _{0.04}) _{2.10} (Fe _{0.98} M _{0.02}) ₁₄ B ₁
phase (B)	82.91	2.26	6.04	0.00	0.24	0.00	8.56	—	(Nd _{0.80} Dy _{0.02} Fe _{0.17} M _{0.01})O _{0.68}
phase (C)	45.35	1.08	48.35	0.75	2.01	1.32	1.14	—	(Nd _{0.25} Dy _{0.01} Fe _{0.69} M _{0.05})O _{0.02}

grains. It was revealed by special methods, i.e., spin-polarized scanning electron microscopy [40] and X-ray magnetic dichroism [19] that this phase is ferromagnetic at room temperature with the saturation magnetization around 80 G cm³/g. As could be expected from the amorphous structure, this phase is soft magnetic. The nucleation of the reverse magnetization can occur in this amorphous IGB phase. However, the magnetization reversal does not proceed easily in these interfaces, because the Nd₂Fe₁₄B grains and soft magnetic IGB layers are exchange-coupled. Due to the great difference in magnetic anisotropy constants of the Nd₂Fe₁₄B and IGB phases, domain walls of the emerging reverse nuclei will be pinned at the interfaces with the high gradient of domain wall energy, until the strength of the demagnetizing magnetic field reaches the values close to the coercivity, which is followed by the avalanche-like growth of the reverse nuclei and complete magnetization reversal of the magnet [22, 41]. Thus, it has been concluded that the main mechanism of magnetization reversal of the sintered Nd–Fe–B magnets with the ferromagnetic IGBs is pinning, rather than nucleation. Such view on magnetization reversal of the sintered Nd–Fe–B magnets agrees with the angular dependence of coercivity of these magnets, which has been studied by Matsuura et al. [42, 43].

3. Angular Dependence of Coercivity

The angular dependence of coercivity is an important tool to identify processes controlling magnetization reversal in hard magnetic materials. In order to determine the main processes of magnetization reversal of the magnets under consideration, we measured angular dependence of H_c for spherical samples cut out of magnets with 0.5 and 1.0 wt % Dy. Prior to measurement, samples were magnetized along the alignment direction in the pulsed magnetic field of a amplitude of 70 kOe. After placing a sample into a vibrating sample magnetometer, the alignment axis of the sample was turned by the angle ϕ off the direction of the applied field; then, the magnetization reversal was recorded. Figure 6 shows angular dependences of the relative coercivity $h = H_c(\phi)/H_c(0)$, where $H_c(\phi)$ designates values measured at the angle ϕ between the alignment axis and applied field; $H_c(0)$, along the alignment axis.

Experimental dependences are compared with two theoretical models of angular dependence of coercivity. The Stoner–Wohlfarth model (S–W) considers coherent rotation of magnetization vectors. According to the S–W model, the critical field is equal to:

$$H_c^{SW}(\phi) = H_A(\cos^{2/3}\phi + \sin^{2/3}\phi)^{-3/2}, \quad (1)$$

Fig. 6. Angular dependences of reduced coercivity $H_c(\phi)/H_c(0)$ of magnets with 0.5 and 1.0 wt % Dy.

where $H_A = 2K_1/\mu_0 M_s$ is the anisotropy field, K_1 is the constant of uniaxial magnetic anisotropy, and M_s is the saturation magnetization. This model is used to qualitatively estimate a contribution from nucleation to the magnetization reversal. The Kondorsky model described by the following expression:

$$H_c^K(\phi) = H_p / \cos \phi \quad (2)$$

was initially developed to consider the pinning of domain walls (DW) at internal defects. Here, H_p is the pinning field required to move the DW from defects ($H_p \ll H_A$) upon the magnetization reversal along the easy axis of magnetization. Figure 6 shows that none of these theoretical models adequately describes the experimental results. The inset in the figure shows that for small angles $\phi < 30^\circ$, $h < 1$; i.e., the magnetization reversal is mainly controlled by the nucleation. Contrary, at $30^\circ < \phi < 70^\circ$, $h > 1$, but they are considerably lower than the $1/\cos\phi$ dependence. This evidences that together with the main pinning mechanism of magnetization reversal, the hysteresis is also controlled by the nucleation. The curve $h(\phi)$ of the magnet with 1 wt % Dy has a maximum at $\phi = 60^\circ$; it appears because at $\phi > 60^\circ$ the projection of the applied field on the alignment axis is not sufficient to demagnetize a considerable volume of the magnet. The higher $H_c(0)$, the smaller angles ϕ at which the maximum is observed.

Thus, the angular dependences of H_c of the high-energy sintered Nd–Fe–B magnets show that their magnetization reversal is controlled by both the nucleation and pinning. Similar deviations of the angular dependences of H_c from the Stoner–Wohlfarth and

Kondorsky models were studied in detail by Bance et al. [44] by finite-element micromagnetic calculations. It has been shown that this deviation is caused by a number of reasons, including presence of soft magnetic defects at the grain surface and width of the IGBs.

CONCLUSIONS

The Urals Electromechanical Plant, Joint-Stock Company prepared high-energy Nd–Fe–B magnets doped with dysprosium of no more than 1 wt %, which had $(BH)_{\max} = 48\text{--}50$ MG Oe and $M H_c = 12\text{--}15$ kOe. The contents of rare-earth element and oxygen in magnets do not exceed 30 and 0.20 wt %, respectively. High magnetic hysteresis properties are gained by optimization of chemical and phase compositions of magnets, as well as their microstructure. The grain size of the main $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is approximately $3.5\text{ }\mu\text{m}$, and, according to the X-ray analysis, the amount of additional Nd-rich phases (NdO_x and Nd_2O_3) does not exceed 2.5%. Phase (C) with the composition $(\text{Nd,Fe,M})\text{O}_x$ is localized at triple junctions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains; it is connected through its acute angles with the Nd-rich thin layers of intergranular boundaries and can significantly affect their composition. In phase (C), oxygen content is negligible ($x \leq 0.05$), however, it contains large amount of iron, and the ratio $r = \text{Fe}/(\text{Nd} + \text{Dy})$ can reach ~ 3 . The angular dependences of coercivity of magnets shows that the magnetic hysteresis is characterized by a mixed process combining both the nucleation and pinning mechanisms.

ACKNOWLEDGMENTS

Magnetic and structural properties were measured using equipment of Collaborative Access Center “Testing Center of Nanotechnology and Advanced Materials” IMP UB RAS.

FUNDING

The work is performed in the framework of state assignment of the Ministry of Education and Science of Russia (theme “Magnet,” No. AAAA-A18-118020290129-5).

OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

REFERENCES

1. S. Sugimoto, “Current status and recent topics of rare-earth permanent magnets,” *J. Phys. D, Appl. Phys.* **44**, No. 6, 064001 (2011).
2. G. H. Yan, R. J. Chen, Y. Ding, S. Guo, D. Lee, and A. R. Yan, “The preparation of sintered NdFeB magnet with high-coercivity and high temperature-stability,” *J. Phys., Conf. Ser.* **266**, No. 1, 1–6 (2011).
3. K. Hono and H. Sepehri-Amin, “Strategy for high-coercivity Nd–Fe–B magnets,” *Scr. Mater.* **67**, No. 6, 530–535 (2012).
4. H. Nakamura, “The current and future status of rare earth permanent magnets,” *Scr. Mater.* **154**, 273–276 (2018).
5. J. M. D. Coey, “Perspective and prospects for rare earth permanent magnets,” *Engineering* **6**, No. 2, 119–131 (2020).
6. M. Sagawa, S. Hirosawa, K. Tokuhara, H. Yamamoto, S. Fujimura, Y. Tsubokawa, and R. Shimizu, “Dependence of coercivity on the anisotropy field in the Nd₂Fe₁₄B-type sintered magnets,” *J. Appl. Phys.* **61**, No. 8, 3559–3561 (1987).
7. J. Fidler and T. Schrefl, “Overview of Nd–Fe–B magnets and coercivity (invited),” *J. Appl. Phys.* **79**, 5029–5034 (1996).
8. F. Vial, F. Joly, E. Nevalainen, M. Sagawa, K. Hiraga, and K. T. Park, “Improvement of coercivity of sintered NdFeB permanent magnets by heat treatment,” *J. Magn. Magn. Mater.* **242–245**, 1329–1334 (2002).
9. Y. Shinba, T. J. Konno, K. Ishikawa, K. Hiraga, and M. Sagawa, “Transmission electron microscopy study on Nd-rich phase and grain boundary structure of Nd–Fe–B sintered magnets,” *J. Appl. Phys.* **97**, No. 5, 053504 (2008).
10. W. Mo, L. Zhang, Q. Liu, A. Shan, J. Wu, and M. Komuro, “Dependence of the crystal structure of the Nd-rich phase on oxygen content in an Nd–Fe–B sintered magnet,” *Scr. Mater.* **59**, No. 2, 179–182 (2008).
11. W. F. Li, T. Ohkubo, and K. Hono, “Effect of post-sinter annealing on the coercivity and microstructure of Nd–Fe–B permanent magnets,” *Acta Mater.* **57**, No. 5, 1337–1346 (2009).
12. H. Sepehri-Amin, T. Ohkubo, T. Shima, and K. Hono, “Grain boundary and interface chemistry of an Nd–Fe–B-based sintered magnet,” *Acta Mater.* **60**, No. 3, 819–830 (2012).
13. T. H. Kim, S. R. Lee, S. Namkung, and T. S. Jang, “A study on the Nd-rich phase evolution in the Nd–Fe–B sintered magnet and its mechanism during post-sintering annealing,” *J. Alloys Compd.* **537**, 261–268 (2012).
14. W. Q. Liu, C. Chang, M. Yue, J. S. Yang, D. T. Zhang, Y. Q. Liu, J. X. Zhang, X. F. Yi, and J. W. Chen, “Coercivity enhancement of sintered Nd–Fe–B magnets by grain boundary diffusion with DyH₃ nanoparticles,” *J. Magn.* **18**, No. 4, 400–404 (2013).
15. T. T. Sasaki, T. Ohkubo, and K. Hono, “Structure and chemical compositions of the grain boundary phase in Nd–Fe–B sintered magnets,” *Acta Mater.* **115**, 269–277 (2016).
16. N. Tsuji, H. Okazaki, W. Ueno, Y. Kotani, D. Billington, A. Yasui, S. Kawaguchi, K. Sugimoto, K. Toyoki, T. Fukagawa, T. Nishiuchi, Y. Gohda, S. Hirosawa, K. Hono, and T. Nakamura, “Temperature dependence of the crystal structures and phase fractions of secondary phases in a Nd–Fe–B sintered magnet,” *Acta Mater.* **154**, 25–32 (2018).
17. T. T. Sasaki, Y. Takada, H. Okazaki, T. Ohkubo, T. Nakamura, T. Sato, A. Kato, Y. Kaneko, and K. Hono, “Role of Ga on the high coercivity of Nd-rich Ga-doped Nd–Fe–B sintered magnet,” *J. Alloys Compd.* **790**, 750–759 (2019).
18. A. Mazilkin, B. B. Straumal, S. G. Protasova, S. Gorji, A. B. Straumal, M. Katter, G. Schütz, and B. Barezky, “Grain boundary oxide layers in NdFeB-based permanent magnets,” *Mater. Des.* **199**, 109417 (2021).
19. T. Nakamura, A. Yasui, Y. Kotani, T. Fukagawa, T. Nishiuchi, H. Iwai, T. Akiya, T. Ohkubo, Y. Gohda, K. Hono, and S. Hirosawa, “Direct observation of ferromagnetism in grain boundary phase of Nd–Fe–B sintered magnet using soft x-ray magnetic circular dichroism,” *Appl. Phys. Lett.* **105**, No. 20, 202404 (2014).
20. H. Kronmüller, K. D. Durst, and M. Sagawa, “Analysis of the magnetic hardening mechanism in RE–FeB permanent magnets,” *J. Magn. Magn. Mater.* **74**, No. 3, 291–302 (1988).
21. M. Sagawa, K. Hiraga, H. Yamamoto, and Y. Matsuurra, “Permanent magnet materials based on the rare

- earth-iron-boron tetragonal compounds (invited)," IEEE Trans. Magn. **20**, No. 5, 1584–1589 (1984).
22. K. Hono and H. Sepehri-Amin, "Prospect for HRE-free high coercivity Nd–Fe–B permanent magnets," Scr. Mater. **151**, 6–13 (2018).
 23. A. N. Bogatkin, E. N. Tarasov, S. V. Andreev, A. G. Popov, and N. V. Kudrevatykh, "Improvement of the technology of obtaining permanent magnets from Nd–Fe–B alloys," Metally, No. **2**, 86–90 (1996).
 24. V. P. Menushenkov and A. G. Savchenko, "Annealing behavior of coercivity in (Nd,Dy)–Fe–B based sintered magnets," Phys. Met. Metallogr. **91**, No. Supplement **1**, S249–S253 (2001).
 25. V. P. Menushenkov and A. G. Savchenko, "Effects of post-sintering annealing on magnetic properties of Nd–Fe–B sintered magnets," J. Magn. Magn. Mater. **258–259**, 558–560 (2003).
 26. A. G. Popov, T. Z. Puzanova, V. S. Gaviko, D. Yu. Vasilenko, and V. P. Vyatkin, "Formation of a high-coercive state in sintered Nd–Fe–B–Ga magnets by thermocycling," Phys. Met. Metallogr. **101**, No. 6, 538–546 (2006).
 27. V. P. Piskorskii, G. S. Burkhanov, S. A. Mel'nikov, A. P. Parshin, R. A. Valeev, I. S. Tereshina, and S. I. Ivanov, "Influence of neodymium content on the properties of nanostructured materials (NdPr)–Fe–B, obtained by binary technology," Perspektivnye Mater., No. 9 (2010).
 28. A. A. Lukin, N. B. Kol'chugina, G. S. Burkhanov, N. E. Klyueva, and K. Skotnitseva, "Significance of terbium hydride additions in the microstructure formation and magnetic properties of sintered Nd–Pr–Dy–Fe–B magnets," Fiz. Khim. Obr. Mater., No. 1, 70–73 (2012).
 29. A. V. Brykin and S. V. Churikov, *The Main Development Trends of the Permanent Magnet Market*, Kon'yunktura Tovarnykh Rynkov Marketing i Logistika, No. 2, 9–12 (2012).
 30. A. G. Popov, N. B. Kudrevatykh, V. P. Vyatkin, D. Y. Vasilenko, D. Y. Bratushev, T. Z. Puzanova, and E. G. Gerasimov, "Preparation of high-power permanent magnets from platelike Nd–Fe–B alloys," Phys. Met. Metallogr. **109**, No. 3, 238–246 (2010).
 31. J. Bernardi, J. Fidler, M. Sagawa, and Y. Hirose, "Microstructural analysis of strip cast Nd–Fe–B alloys for high $(BH)_{\max}$ magnets," J. Appl. Phys. **83**, No. 11, 6396–6398 (1998).
 32. S. Sasaki, H. Hasegawa, and K. Nakajima, U.S. Patent No. 20070095438, 2007.
 33. D. Yu. Vasilenko, A. V. Shitov, A. V. Vasyuga, A. G. Popov, N. V. Kudrevatykh, and N. V. Pechishcheva, "Microstructure properties of Nd–Fe–B alloys obtained by strip casting and permanent magnets made from them," Metalloved. Term. Obr. Met. **613**, No. 11, 10–16 (2014).
 34. W. F. Li, T. Ohkubo, K. Hono, and M. Sagawa, "The origin of coercivity decrease in fine grained Nd–Fe–B sintered magnets," J. Magn. Magn. Mater. **321**, No. 8, 1100–1105 (2009).
 35. B. B. Straumal, Y. O. Kucheev, I. L. Yatskovskaya, I. V. Mogilnikova, G. Schutz, A. N. Nekrasov, and B. Baretzky, "Grain boundary wetting in the NdFeB-based hard magnetic alloys," J. Mater. Sci. **47**, No. 24, 8352–8359 (2012).
 36. B. B. Straumal, A. A. Mazilkin, S. G. Protasova, G. Schutz, A. B. Straumal, and B. Baretzky, "Observation of pseudopartial grain boundary wetting in the NdFeB-based alloy," J. Mater. Eng. Perform. **25**, No. 8, 3303–3309 (2016).
 37. H. Okazaki, D. Billington, N. Tsuji, W. Ueno, Y. Kotani, S. Kawaguchi, K. Sugimoto, K. Toyoki, T. Fukagawa, T. Nishiuchi, K. Hono, S. Hirose, and T. Nakamura, "Quantitative identification of constituent phases in a Nd–Fe–B–Cu sintered magnet and temperature dependent change of electron density of Nd₂Fe₁₄B studied by synchrotron X-ray diffraction," Acta Mater. **181**, 530–536 (2019).
 38. T. H. Kim, T. T. Sasaki, T. Ohkubo, Y. Takada, A. Kato, Y. Kaneko, and K. Hono, "Microstructure and coercivity of grain boundary diffusion processed Dy-free and Dy-containing Nd–Fe–B sintered magnets," Acta Mater. **172**, 139–149 (2019).
 39. W. F. Li, H. Sepehri-Amin, T. Ohkubo, N. Hase, and K. Hono, "Distribution of Dy in high-coercivity (Nd,Dy)–Fe–B sintered magnet," Acta Mater. **59**, No. 8, 3061–3069 (2011).
 40. T. Kohashi, K. Motai, T. Nishiuchi, and S. Hirose, "Magnetism in grain-boundary phase of a NdFeB sintered magnet studied by spin-polarized scanning electron microscopy," Appl. Phys. Lett. **104**, No. 23, 1–6 (2014).
 41. H. Sepehri-Amin, S. Hirose, and K. Hono, "Advances in Nd–Fe–B based permanent magnets," in *Handbook of Magnetic Materials*, 1st ed. (2018), Vol. 27, pp. 269–372.
 42. Y. Matsuura, J. Hoshijima, and R. Ishii, "Relation between Nd₂Fe₁₄B grain alignment and coercive force decrease ratio in NdFeB sintered magnets," J. Magn. Magn. Mater. **336**, 88–92 (2018).
 43. Y. Matsuura, T. Nakamura, K. Sumitani, K. Kajiwar, R. Tamura, and K. Osamura, "Angular dependence of coercivity in isotropically aligned Nd–Fe–B sintered magnets," AIP Adv. **8**, No. 5, 056236 (2018).
 44. S. Bance, H. Oezelt, T. Schrefl, G. Ciuta, N. M. Dempsey, D. Givord, M. Winklhofer, G. Hrkac, G. Zimanyi, O. Gutfleisch, T. G. Woodcock, T. Shoji, M. Yano, A. Kato, and A. Manabe, "Influence of defect thickness on the angular dependence of coercivity in rare-earth permanent magnets," Appl. Phys. Lett. **104**, No. 18 (2014).

Translated by O. Golovnya