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HIGH–ENERGY SINTERED (Nd, Dy)–(Fe, Co)–M–B (M = (Re, W, Zr), (Al, Cr), (Al, Cr, Nb)) MAGNETS

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Simultaneous addition of (Re, W, Zr), (Al, Cr) or (Al, Cr, Nb) to the sintered (Nd, Dy)–(Fe, Co)–B magnets affects: refinement of microstructure, high coercivity, thermal stability and improving intrinsic corrosion resistance. This is due to the replacing of conventional Nd–rich constituents by Nd–Co and formation M–(Fe, Co), M–(Fe, Co)–B (M = Cr, Nb, W, Zr) phases along and/or within the grains. The adding elements strongly influence coercivity mechanism.

Key words: NdFeB–type magnets; microstructure; magnetic properties; thermal stability; corrosion resistance; coercivity parameters.

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I. INTRODUCTION

The NdFeB type magnets based on the tetragonal $Nd_2Fe_{14}B$ intermetallic compound exhibit the highest energy density products (420 kJ/m^3 [1]) obtained so far. Likewise the chemical composition of a magnet is vital to obtaining optimum magnetic properties and corrosion resistance. Microstructure is also important in dictating the magnets overall quantity. The microstructure of a real sintered magnet is based on the phases present in the Nd–Fe–B system such as: the ferromagnetic main phase $Nd_2Fe_{14}B$ (the ϕ phase), the $Nd_{1.1}Fe_4B_4$ boride (the η–phase), Nd–rich constituents (the n–phase), oxide Nd_2O_3, additional phases stabilized by impurities or additions, α–Fe and pores. A certain fraction of boundaries of ϕ grains is not filled with non-ferromagnetic phases which may affect a magnetic decoupling of the exchange interaction of neighbouring ϕ grains. Certain elements have to be added in order to optimize the coercivity, to increase the Curie temperature and improve the corrosion resistance (see review papers [1–3]).

The purpose of the present work is to study the influence of partial substitution of Fe by (Re, W, Zr), (Al, Cr) or (Al, Cr, Nb) in sintered (Nd, Dy)–(Fe, Co)–B magnets on: (i) metallurgical characteristics, (ii) magnetic properties and thermal stability, (iii) coercivity and (iv) corrosion properties.

II. EXPERIMENTAL DETAILS

A. Samples Preparation

The

$$Nd_{14.5}Dy_{1.5}Fe_{71.5}Co_5B_{7.5},$$

$$Nd_{14.5}Dy_{1.5}Fe_{69.5}Co_5Re_{0.5}W_1Zr_{0.5}B_{7.5},$$

$$Nd_{14.5}Dy_{1.5}Fe_{68}Co_5Al_{1.5}Cr_2B_{7.5}$$

and

$$Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_{1.5}Cr_2Nb_2B_{7.5}$$

designed as magnet 1, 2, 3 and 4, respectively, have been prepared by the conventional powder metallurgy method. The material was prepared by vacuum induction melting of pure (($\geq$ 99.9 wt %) metals and Fe–B alloy containing 20 wt % B. The cast ingots were crushed in liquid freon to a coarse powder (240 μm) and then ground in the vibrating ball mill into a fine powder and subsequently sieved to get particles $\leq$ 5 μm in diameter. The powder was aligned in magnetic field of 1.6 MA/m and isostatically pressed at 100 MPa. Afterwards it was vacuum sintered at temperatures between 1320 K and 1420 K. The magnetic properties were optimized by annealing in argon atmosphere at different temperatures in the range of 1150 K to 770 K for 2 to 24 hours followed by furnace cooling.

B. Experimental Technique

Microstructural observations were performed by optical microscope and scanning electron microscope (SEM). Phase composition and element distribution were analyzed by an energy dispersive X–ray analyzer (EDX); light elements were not detected.

The densities of sintered magnets were determined by comparing their weight in air and in toluene.

Magnetic measurements were performed in a vibrating sample magnetometer (VSM) in the temperature range from 293 K to 493 K. The maximum magnetized field was 1200 KA/m. Specimen used for VSM measurements were disks, 2 mm in diameter and 1 mm thick, cut from sintered block. The anisotropy field (H_A) was determined in pulse field by the singular detection technique [4]. The temperature coefficients of remanence (M_r) and coercivity ($_MH_c$), α and β, respectively were determined from demagnetization curves. They are defined as follows [5]:

$$\alpha, \beta = \frac{100[Q(T_2) - Q(T_1)]}{Q(T_1)(T_2 - T_1)}, \tag{1}$$

where Q denotes quantity represented by M_r and $_MH_c$ at elevated temperature T_2 and room temperature T_1, respectively. Before measurement at each of the different temperatures, the samples were fully remagnetized in a 8000 kA/m pulsed field at room temperature. The irreversible losses of magnets with load lines $B\mu_\circ H = -1.0$ were determined from the measurement of the remanent magnetization at room temperature after heating the magnets for 2 hours at selected temperatures up to 493 K. The Curie temperature of magnets was determined by a low field thermomagnetic analysis (TMA) with a 500 kHz field of about 0.08 kA/m amplitude; the average sweep rate was 1.6 K/s. The measuring error of these quantities did not exceed 1 %.

Intrinsic corrosion resistance was quantified by means of weight gain on bare magnets after exposure of samples to steam saturated air containing 3 mg SO_2/l at 313 K – accelerated test of corrosion in "industrial" atmosphere. More details concerning the procedure of the corrosion tests as well as apparatus and measuring system can be found in our earlier paper [6].

III. RESULTS AND DISCUSSION

A. Microstructure

Studies of the microstructure of the tested multicomponent system magnets proved them to be somewhat similar; they display a clear refinement of grains (for example see microstructure for magnets 1 and 4 in Fig. 1). The mean grain size for both multicomponent system magnets (magnets 2 – 4) are approximately about 5 μm, compared with the 20 μm of magnet 1. In the picture of microstructure equiaxial grains of the matrix ϕ–phase are visible, divided by grain boundary containing Nd_3Co and $NdCo_2$ phases earlier described in [6, 7]. Moreover, a small amount of grains of the η phase is apparent. The Dy does not form additional phases, but it enters the composition of ϕ and η phases; only negligible amounts of Dy are detected in Nd–Co phases. Co exists in the composition of both ϕ and η phases. However, the latter phase contains a greater amount of this element. The content of Al in the ϕ–phase is similar to that of the bulk composition and in the Nd–Co grain boundaries phases are relatively low (0.12 at %). The η phase dose not dissolve any detectable amount of Al. The ϕ and η phases contains exactly the same quantity (2.4 at %) of Cr, but the Nd–Co phases does not practically contain Cr. In turn, Nb is insignificantly soluble in the main phases of the magnet, i.e. ϕ, η and the Nd–Co phases contain only up to 0.1, 0.2 and 0.1 at % of Nb, respectively. The Re and Zr dissolve in ϕ and Nd–Co phases, and does not dissolve in any detectable amount in the η phase, which is consistent with the results of earlier works [8–10]. The W concentration in ϕ and Nd–Co phases is in the same proportion (1 at%) and in the η phase it dissolves only in minor quantities.

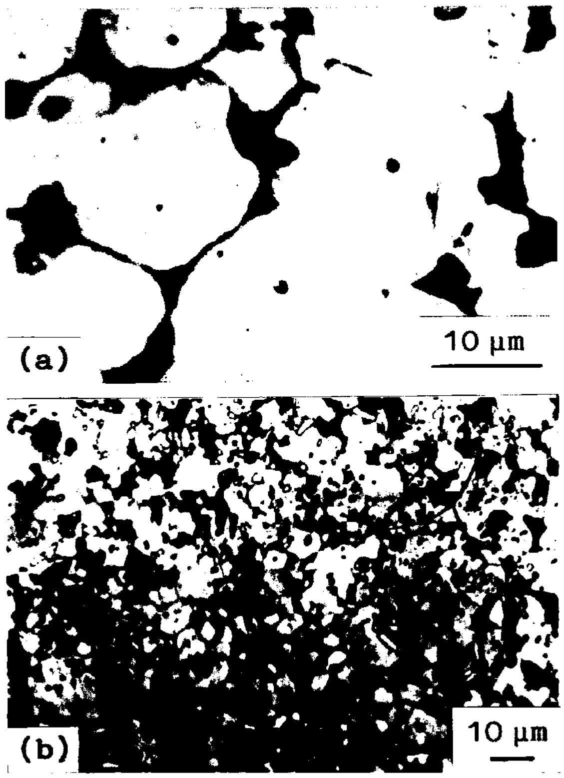

Fig. 1. Microstructure of the sintered $Nd_{14.5}Dy_{1.5}Fe_{71.5}Co_5B_{7.5}$ (a) and $Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_{1.5}Cr_2Nb_2B_{7.5}$ (b) magnets.

Because Cr, Nb, W and Zr are not completely dissolved in the main phases of the sintered magnets this results in precipitations of the additional binary M–(Fe, Co) ternary M–(Fe, Co)–B phases, such as phases: $Cr(Fe, Co)_2$, $Nb(Fe, Co)_2$; Cr(Fe, Co)B, Nb(Fe, Co)B, W(Fe, Co)B, Zr(Fe, Co)B and Cr_2(Fe, Co)B, W_2(Fe, Co)B alone and/or in the ϕ grains.

B. Room Temperature Magnetic Properties and Thermal Stability

The density of studied sintered magnets range from 7.42 ± 0.05 to 7.55 ± 0.05 [g/cm^3].

The demagnetization curves of a new family of sintered magnets 1–4 and for comparison the $Nd_{16}Fe_{78}B_8$ magnet are plotted in Fig. 2. The temperature coefficients α and β of the investigated magnets for the temperature range of 293 K–493 K are listed in Table 1. From Fig. 2 it is apparent that the coercivities of the magnets with alloying (Re, W, Zr), (Al, Cr) and (Al, Cr, Nb) (magnets 2–4) are significantly higher than that of the magnet without this alloying (magnet 1). Especially the (Al, Cr, Nb) alloying brings about a substantial increase in $_{\rm M}H_c$, but the remanence and Curie temperature decrease by 6 % and 5 %, respectively at the greatest. A significant decrease of β of the multicomponent system magnets 3 and 4 is mainly provoked by the Al alloying [11]. It is worth noting that the temperature coefficient of the coercivity β is not improved by adding Nb, as it was shown in [12]. The improved temperature stability of Nb containing magnets as published by Tokunaga et al. [13] may be due to a smaller grain size. Also alloying (Re, W, Zr) only sightly decreases or does not change α and β, respectively. The dependence of irreversible losses of multicomponent system magnets 2–4 on the temperature demonstrates that a maximum operating temperature about 483 K may be possible for magnets with a load line $B\mu_\circ H = -1.0$; the irreversible losses are less than 5 %.

The remanence is not seriously affected by the (Re, W, Zr), (Al, Cr) and (Al, Cr, Nb) alloying; the $\mu_\circ M_{\rm r}$ decreases maximum by about 8 %. As mentioned above, this low value should be attributed to the fact that the Fe–M (M = Cr, Nb, W, Zr) phases are not added, but replace the η phase. Partial substitution of Fe by Co in the NdFeB sintered magnet do not alter the remanence, in coherence with the dependence of the spontaneous magnetization on the Co content in the ϕ phase [6]. A partial substitution of Fe by Cr, Al, Nb, Re as well as by W decreases and increases only slightly the saturation magnetization, similarly as observed in papers [14–19].

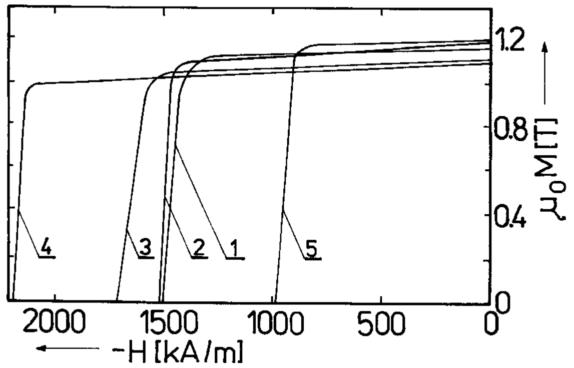

Fig. 2. The demagnetization curves of the sintered magnets:
1 - $Nd_{14.5}Dy_{1.5}Fe_{71.5}Co_5B_{7.5}$,
2 - $Nd_{14.5}Dy_{1.5}Fe_{69.5}Co_5Re_{0.5}W_1Zr_{0.5}B_{7.5}$,
3 - $Nd_{14.5}Dy_{1.5}Fe_{68}Co_5Al_{1.5}Cr_2B_{7.5}$,
4 - $Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_{1.5}Cr_2Nb_2B_{7.5}$

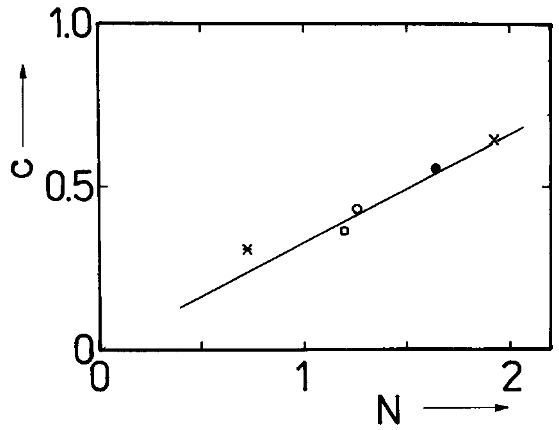

Fig. 3. The relation between coercivity parameters c and N for the sintered magnets: $Nd_{14.5}Dy_{1.5}Fe_{71.5}Co_5B_{7.5}$ (□), $Nd_{14.5}Dy_{14.5}Fe_{69.5}Co_5Re_{0.5}W_1Zr_{0.5}B_{7.5}$ (o), $Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_{1.5}Cr_2B_{7.5}$ (×) and $Nd_{11}Dy_3Fe_{76.8}Al_{0.7}B_{7.5}$ (*) — the results of Fukunga et al. [21].

No.	Composition (at%)	T_c (K)	α (%/K)	β (%/K)
1	$Nd_{14.5}Dy_{1.5}Fe_{71.5}Co_5B_{7.5}$	650	-0.115	-0.51
2	$Nd_{14.5}Dy_{1.5}Fe_{69.5}Co_5Re_{0.5}W_1Zr_{0.5}B_{7.5}$	646	-0.110	-0.50
3	$Nd_{14.5}Dy_{1.5}Fe_{68}Co_5Al_{1.5}Cr_2B_{7.5}$	632	-0.102	-0.48
4	$Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_{1.5}Cr_2Nb_2B_{7.5}$	630	-0.108	-0.45

Table 1. Curie temperature (T_c), temperature coefficients of the remanence (α) and the coercivity (β) of the studied sintered magnets.

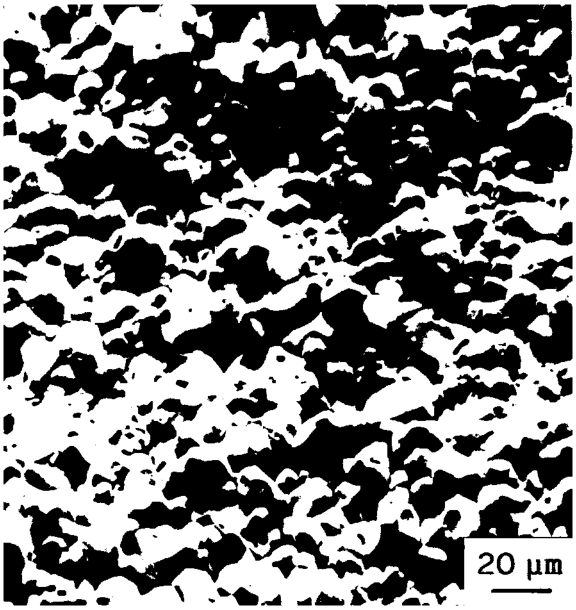

Fig. 4. SEM image of surface of the sintered $Nd_{16}Fe_{76.5}B_{7.5}$ magnet after 360 s exposure in the 0.5 M H_2SO_4 solution.

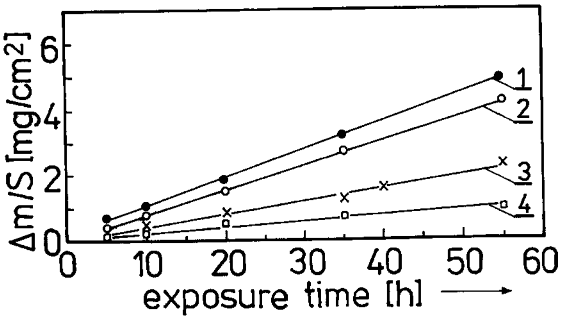

Fig. 5. The accelerated atmospheric corrosion test in the "industrial" environment of the sintered magnets: $Nd_{14.5}Dy_{1.5}Fe_{71.5}Co_5B_{7.5}$ (1), $Nd_{14.5}Dy_{1.5}Fe_{69.5}Co_5Re_{0.5}W_1Zr_{0.5}B_{7.5}$ (2), $Nd_{14.5}Dy_{1.5}Fe_{68}Co_5Al_{1.5}Cr_2B_{7.5}$ (3), $Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_1Cr_2Nb_2B_{7.5}$ (4).

C. Coercivity Parameter

In the theory of micromagnetism the coercivity of Nd–Fe–B–type permanent magnets in general can be described by the relation [4–6]:

$$\mu_{oM}H_c = c\mu_o H_A - NM_s, \tag{2}$$

where H_A denotes the anisotropy field $2K_1/M_s$, K_1 and M_s are the anisotropy constant and the spontaneous magnetization of $Nd_2Fe_{14}B$ phase, respectively, c and N are two constants which are different from one sample to

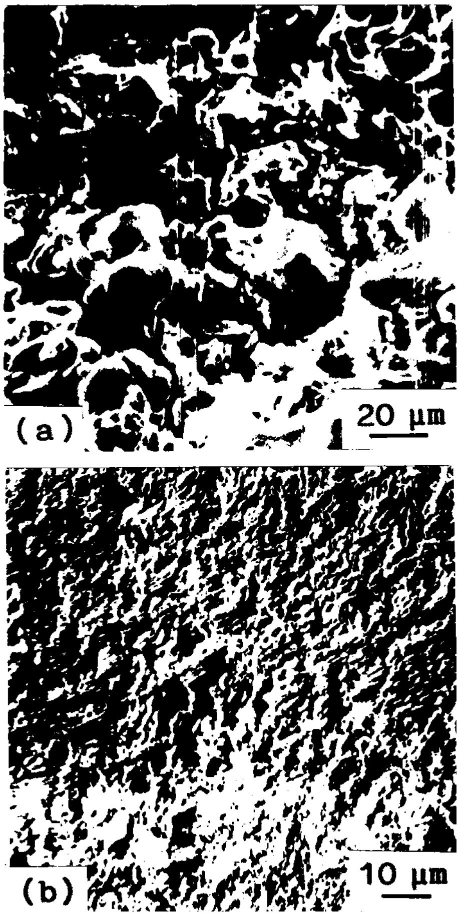

Fig. 6. SEM images of surface of the sintered $Nd_{14.4}Dy_{1.5}Fe_{71.5}Co_5B_{7.5}$ (a) and $Nd_{14.5}Dy_{1.5}Fe_{66}Co_5Al_{1.5}Cr_2Nb_2B_{7.5}$ (b) magnets after 90 s exposure in 0.5 M H_2SO_4 solution.

another, μ_o is the permeability. The first term in eq. (2) is considered to be related to the easiness of nucleation of reversal domains near the grain boundaries and the second to the demagnetization field at the grain surface. The parameter c is determined by the underlying magnetization reversal mechanism (nucleation or pinning of domain walls, nucleation of rotation modes, ...) and is related to microstructural features. N is determined by internal demagnetizing field in these chemically and magnetically heterogeneous materials. According to eq. (2) the microstructural parameters c and N can be determined in a $\mu_{oM}H_c(T)/M_s(T)$ versus $\mu_o H_A(T)/M_s(T)$ plot under the assumption of temperature independent values c and N [20]. In Fig. 4 shows the relation between the coercivity parameters c and N for the four magnets mentioned above and, for comparison, for the $Nd_{12}Dy_3Fe_{76.8}Al_{0.7}B_{7.5}$ sintered magnets [21]. It can be seen from this figure that between these two parameters the simple proportionality exists. It is necessary to take into account that the higher coercivity, the larger the values of both c and N. To discuss these results one has to keep in mind that a partial substitution of Fe by (Re, W, Zr), (Al, Cr) or (Al, Cr, Nb) in the sintered (Nd, Dy)–(Fe, Co)–B magnet provoke:

- an increase of c value, by reducing the average grain size and increase the isolation of the magnetic ϕ grains, making the density of defects decreasing, this in turn increases the difficulty for nucleation of reversed domains,
- large value of N in causing large demagnetization field results surrounding ϕ grains by paramagnetic phases.

This also leads to an increase of the coercivity of sintered (Nd, Dy)–(Fe, Co)–M–B magnets.

D. Intrinsic Corrosion Resistance in Industrial Atmosphere

The sintered NdFeB type magnets exhibit lack of resistance to corrosion particularly in acid media, thus, in environments temporarily acidified (e.g. in industrial conditions) the material undergoes degradation. The poor behaviour in such environments manifests itself in lack of passive state and in mechanical deterioration of the magnetic material due to hydrogenation. The susceptibility to atmospheric corrosion can be evaluated on the basis of weight gain of the samples due to oxidation of the magnet surface. The oxidizing agents (O_2, H_2O, H^+) owing to weak adherence of the corrosion products to the surface can easily penetrate to the inner parts of the magnet which causes fast corrosion of intergranular Nd–rich phase and sometimes takes on catastrophic forms (pulverization; for example see Fig. 4).

The results of accelerated test of the kinetics of corrosion in "industrial" atmosphere of the investigated magnets are presented in Fig. 5. As can be seen, the atmospheric corrosion rate decreases in sequence: magnet 1 $\rightarrow$ magnet 2 $\rightarrow$ magnet 3 $\rightarrow$ magnet 4. It seems that the process of oxidation of the intergranular region is strongly inhibited by the presence of Nd–Co phases in it and the rate of the process is distinctly reduced by the net of M–(Fe, Co) and M–(Fe, Co)–B phases embedded in this region. As a consequence, the multicomponent sintered Nd–Fe–Co–M–B type magnets show clearly better resistance to the atmospheric corrosion attack as compared with the magnets without M alloying (see Fig. 6).

[1] J. F. Herbst, Rev. Mod. Phys. **63**, 819 (1991).
[2] K. H. J. Buschow, Rep. Prog. Phys. **54**, 1123 (1991).
[3] H. Bala, S. Szymura, G. Pawłowska, Arch. Mater. Sci. **17**, 225 (1996).
[4] G. Asti, S. Rinaldi, J. Appl. Phys. 45, 3600 (1974); G. Asti, F. Bolzoni, J. Appl. Phys. **58**, 1923 (1985).
[5] H. F. Mildrum, K. M. D. Wong, in *Proceedings 2nd Int'l Workshop on Rare Earth Permanent Magnets and their Applications*, edited by K. J. Strnat (University of Dayton, Dayton, OH, 1976) p. 35.
[6] S. Szymura, H. Bala, G. Pawłowska, Yu. M. Rabinowvich, V. V. Sergeev, D.V. Pokrovski, J. Less - Common Met. **175**, 185 (1991).
[7] S. Szymura, J. J. Wysłocki, H. Bala, J. Moscow Phys. Soc. **7**, 101 (1997).
[8] M. Jurczyk, J. Magn. Magn. Mater. **83**, 237 (1990).
[9] R. J. Pollard, P.J. Groundy, S. F. M. Parker, G. P. Lord, IEEE Transact. Magn. **24**, 1626 (1988).
[10] S. Szymura, H. Bala, M. Malik, Yu. M. Rabinovich, V. V. Sergeev, D. V. Pokrovski, Mater. Chem. Phys. **30**, 93 (1991).
[11] Y. Xiao, S. Liu, H. F. Mildrum, K. J. Strnat, A. E. Ray, J. Appl. Phys. **63**, 3516 (1988).
[12] W. Rodewald, E. Wall. J. Magn. Magn. Mater. **80**, 57 (1989).
[13] M. Tokunaga, H. Kogure, M. Endoch, H. Harada, IEEE Transact. **23**, 2287 (1987).
[14] W. Rodewald, W. Fernengel, IEEE Transact. Magn. **24**, 1638 (1988).
[15] M. Jurczyk, IEEE Transact. Magn. **24**, 1942 (1988).
[16] M. Jurczyk, J. Magn. Magn. Mater. **83**, 237 (1990).
[17] M. Leonowicz, J. Magn. Magn. Mater. **83**, 211 (1990).
[18] W. Rodewald, P. Schrey, J. Magn. Magn. Mater. **83**, 206 (1990).
[19] Cheng–Hao Lin, T. S. Chin, Y. H. Huang, J. M. Yau, K. H. Cheng, T. Y. Chu, IEEE Transact. Magn. **29**, 2785 (1993).
[20] M. Sagawa, S. Hirosawa, in *Proceeding of the 5th Int'l Symposium on Magnetic Anisotropy and Coercivity in Rare Earth Transition Metal Alloys, Part I*, edited by C. Herget, H. Kronmüller, R. Poerschke (Deutsche Physikalische Gesellschaft, Bad Honnef, 1987), p. 229.
[21] A. Fukunga, K. Hirose, T. Yoeyama, J. Appl. Phys. **67**, 4750 (1990).

ВИСОКОЕНЕРҐЕТИЧНІ МЕТАЛОКЕРАМІЧНІ МАГНЕТИКИ (Nd, Dy)–(Fe, Co)–M–B (M = (Re, W, Zr), (Al, Cr), (Al, Cr, Nb))

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Одночасне додавання (Re, W, Zr), (Al, Cr) чи (Al, Cr, Nb) до металокерамічних (Nd, Dy)–(Fe, Co)–B магнетиків впливає на поліпшення мікроструктури, високу коерцитивність, термічну стабільність та підвищення опору внутрішній корозії. Цього досягають завдяки заміні компонентів, багатих на Nb, сполукою Nb–Co та утворенням фаз M–(Fe, Co), M–(Fe, Co)–B (M = Cr, Nb, W, Zr) уздовж і/або всередині зерен. Додаткові компоненти мають вагомий вплив на механізм коерцитивности.