PECULIARITIES IN ELECTROCHEMICAL HYDROGENATION OF Nd-Fe-B-TYPE PERMANENT MAGNETS

STEFAN SZYMURA[1]*, YURII M. RABINOVICH[2], HENRYK BALA[3],
TATYANA K. SERGEYEVA[4], ALEKSANDER A. LUKIN[5]

The effect of composition and processing parameters of sintered Nd-Fe-B-type permanent magnets on the parameters of hydrogen absorption and desorption were studied. The interaction of these alloys with hydrogen is strongly related to the alloy composition. The results show that the decrepitation of the magnets containing different alloy additions depends not only on the amount of hydrogen absorbed but also on the form of its occurrence. The lowest absorption of hydrogen, in comparison to that of high-strength steels, has been found for the $Nd_{15}Dy_{1}Fe_{69.5}Co_{5}(W, Re)_{1.5}Zr_{0.5}B_{7.5}$ permanent magnet.

Key words: RE-Fe-B permanent magnets, electrochemical hydrogenation, hydrogen desorption kinetics

OSOBITOSTI ELEKTROCHEMICKEJ HYDROGENIZÁCIE PERMANENTNÝCH MAGNETOV TYPU Nd-Fe-B

Študovali sme vplyv zloženia a parametrov spracovania spekaných permanentných magnetov typu Nd-Fe-B na parametre absorpcie a desorpcie vodíka. Interakciu týchto zliatin s vodíkom uvádzame do úzkeho vzájomného vzťahu so zložením zliatiny. Výsledky ukazujú, že rozpad magnetov, ktoré obsahujú rôzne legujúce prvky, závisí nielen od množstva absorbovaného vodíka, ale aj od podoby jeho výskytu. Najnižšiu absorpciu vodíka, v porovnaní s jeho absorpciou vo vysokopevných oceliach, sme zistili pri permanentnom magnete $Nd_{15}Dy_{1}Fe_{69,5}Co_{5}(W, Re)_{1,5}Zr_{0,5}B_{7,5}$.

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[1] Department of Physics, Technical University of Opole, PL 45-370 Opole, Poland; Institute of Physics, University of Opole, ul. Oleska 48, PL–45–052 Opole, Poland

[2] Metallotherm Company, 105095 Moscow, Russia

[3] Department of Chemistry, Technical University of Czestochowa, PL 42-200 Czestochowa, Poland

[4] Institute of Quality Steel, Central I. P. Bardin Ferrous Metallurgy Research Institute, 107005 Moscow, Russia

[5] Centre of Magnetic Technologies, 117246 Moscow, Russia

* corresponding author

1. Introduction

The interest of studying the interactions of hydrogen with the Nd-Fe-B-type permanent magnets arises from the following [1–3]:

(a) *processing* such as hydrogen decrepitation (HD), sintering in hydrogen atmosphere, hydrogenation-disproportionation-desorption and recombination (HDDR) processes, and related to the ability of hydrogen absorption;

(b) *the search for new applications* such as precision electro-mechanical devices including: magnetoelastic and moment motors, hydroscope devices, sensors, etc., based on the effects of a hydrogen containing medium on magnetic and mechanical properties of permanent magnets.

The reactivity of the sintered Nd-Fe-B-type magnets with respect to hydrogen has been attributed to the presence of Nd-rich phases at the grain boundaries. It is well known that the amount of hydrogen in sintered Nd-Fe-B-type permanent magnets is strongly related to the composition and microstructure of permanent magnets [1–7].

In this paper, we study the effect of alloy additions and processing conditions on the electrochemical hydrogen absorption behaviour of sintered Nd-Fe-B type permanent magnets.

2. Experimental

2.1 Tested material and its preparation

Various sintered RE-(Fe, M)-B permanent magnets differing in the contents of RE (Nd, Dy, Tb, Pr) and M (transition metals or Al), in the ratios of B_r/H_c and in their structures due to variations in the processing conditions, have been employed in the present study.

RE-(Fe, M)-B alloy ingots of various composition were prepared by vacuum induction melting of stoichiometric amounts of the constituent elements. After melting, the ingots were homogenized at 1100 °C for 20 hours in vacuum and crushed into powder of particle size not exceeding 200 μm and, then, they were ground in a vibrational ball-mill to a fine powder. The powder was compacted at a pressure of 200 MPa in a magnetic field of 2.4 MA/m applied perpendicularly to the pressing direction. After pressing, the samples were sintered in a vacuum furnace. The sintering temperature of the tested samples was adjusted in a manner to achieve their relative density of 96–99 % in comparison to the as-cast alloy[†]. The generally applied heat treatments consisted from a double-stage treatment (1 hour for each stage) and final air-cooling on a metallic plate. The milling time and sintering

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[†] The densities of the tested magnets were determined within the accuracy of 0.01 g/cm^3 by comparing their weight in air and in toluene.

Table 1. Chemical composition, magnetic properties and processing conditions of the sintered RE-(Fe, M)-B type permanent magnets

Alloy No.	Chemical formula (numbers denote atomic percentages)	Magnetic properties			Processing schedule			
		Remanence B_r [T]	Coercive force $_BH_c$ [$kA \cdot m^{-1}$]	Intrinsic coercivity $_iH_c$ [$kA \cdot m^{-1}$]	Milling duration [h]	Sintering temp. [°C]	Heat treatment (1h – 1h) [°C]	
1	$Nd_{14}DyFe_{69.5}Co_5Cr_2AlB_{7.5}$	1.10	815	1080	3.5	1115	900	560
2	*Idem*	1.05	760	960	3.0	1115	900	560
3	*Idem*	1.00	736	920	2.0	1115	900	560
4	*Idem*	1.06	720	760	2.0	1140	900	560
5	$Nd_{14}DyFe_{67}Co_5Nb_3Al_2B_8$	1.05	760	1440	4.0	1065	900	560
6	$Nd_{13}Dy_2Tb_2Fe_{70}Co_5AlB_7$	1.05	745	1600	3.5	1065	880	560
7	$Nd_{13.8}Tb_{0.8}Fe_{72.7}Co_5Nb_{0.7}B_7$	1.25	800	920	3.5	1065	880	560
8	$(Nd,Pr)_{16}Fe_{67}Co_5Al_4B_8$	1.06	850	1160	3.5	1065	880	560
9	$Pr_{16}Fe_{71}Co_5B_8$	1.15	560	680	3.5	1065	880	560
10	$Nd_{15}Fe_{76}ZrB_8$	1.18	736	895	3.5	1065	880	560
11	$Nd_{14}Dy_2Fe_{61.5}Co_{12}Al_3B_{7.5}$	1.8	760	1200	3.5	1065	880	560
12	$Nd_{15}DyFe_{69.5}Co_5(W,Re)_{1.5}Zr_{0.5}B_{7.5}$	1.15	765	1085	3.5	1065	900	560

temperatures of the tested permanent magnets were varied. Table 1 shows chemical composition, magnetic properties and employed processing conditions of the magnets studied in this work.

2.2 Experimental procedures

To study the hydrogen absorption and desorption behaviour of the tested RE-(Fe, M)-B permanent magnets, the following techniques were employed:

(a) *Hydrogen absorption ability.* Prismatic specimens were electrolytically (under galvanostatic conditions) hydrogenated in 0.5 M solution of sulphuric acid with thiourea (1.5 g/l) as a hydrogen uptake stimulator. The external current density was 40 mA/cm^2; the anode (in a spiral form) was made of platinum and the tested specimen served as a cathode.

(b) *Determination of diffusively mobile hydrogen.* After hydrogenation, the amount of absorbed hydrogen was determined by separating it into *diffusively mobile* hydrogen and the *retained* one. The amount of the diffusively mobile hydrogen was measured (continuously during two days) by the eudiometric technique using ethanol-glycerine mixture (1:1) at room temperature [8].

(c) *Determination of the retained hydrogen.* Specimens were subjected to the gas analysis in order to determine the amount of the total hydrogen introduced (diffusively mobile + irreversibly captured or chemically bounded). This was done by performing the reduction-melting step in the LECO type PH-1 analyser and by measuring the difference between the hydrogen concentration in the electrochemically hydrogenated sample and in the initial specimen. The retained hydrogen concentration was the difference between concentrations of the total hydrogen introduced and the diffusively mobile one.

(d) *Determination of reaction order and hydrogen desorption constants.* The experimental hydrogen-desorption kinetic curves for the hydrogenated permanent magnets were analysed using the kinetic first-order reaction equation:

$$\frac{\mathrm{d}c_{\mathrm{H}}}{\mathrm{d}t} = kc_{\mathrm{H}}, \tag{1}$$

where c_{H} is the diffusively mobile hydrogen concentration in the tested sample, t is the desorption time, and k is the desorption rate constant. After separation of the variables and integration of Eq. (1), we obtain a common first-order kinetic function:

$$\log \frac{c_{\mathrm{H}}^{0}}{c_{\mathrm{H}}} = \frac{kt}{2.303}, \tag{2}$$

where c_{H} is the diffusion hydrogen concentration corresponding to time t and c_{H}^{0} is the diffusively mobile hydrogen concentration obtained after hydrogenation (at

$t = 0$). The desorption rate constant k was determined from the slope of the rectilinear segments of the $\log(c_{\mathrm{H}}^{0}/c_{\mathrm{H}}) = f(t)$ curves. The constant k is related to the effective force bonding of the diffusively mobile hydrogen in the alloy.

3. Results and discussion

The diffusive hydrogen desorption kinetic curves and the calculated $\log(c_{\mathrm{H}}^{0}/c_{\mathrm{H}}) = f(t)$ curves for the tested permanent magnets are shown in Figs. 1 and 2, respectively. Table 2 summarises the main results of the hydrogen absorption and desorption parameters obtained for these permanent magnets.

The permanent magnets studied here can be classified into two groups according to the initial hydrogen concentration: (i) the first group – permanent magnets Nos. 1–9 – contain high amounts of fixed initial hydrogen (23–82 cm^3/100 g) and (ii) the second group – permanent magnets Nos. 10–12 characterized by *ca.* tenfold lower content of initial hydrogen (3.9–5.4 cm^3/100 g). Such a wide variation in the amount of hydrogen in the permanent magnets indicates that this characteristic

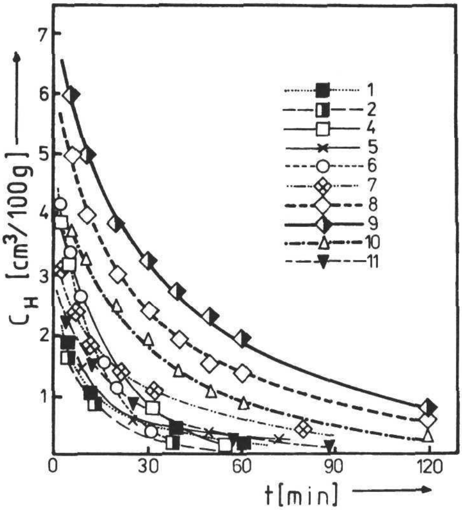

Fig. 1. Hydrogen desorption kinetic curves of the tested sintered RE-(Fe,M)-B type permanent magnets determined from eudiometric measurements. Curve numbers correspond to the alloy numbers in Table 1.

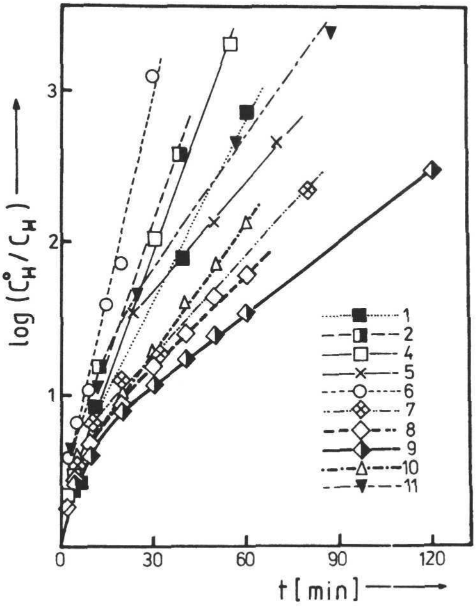

Fig. 2. First-order approximation for hydrogen desorption kinetic curves of the tested sintered RE-(Fe,M)-B type permanent magnets. Curve numbers correspond to the alloy numbers in Table 1.

Table 2. Initial hydrogen, hydrogen absorption and desorption parameters, and the degree of decrepitation following hydrogenation of the tested RE-(Fe, M)-B type permanent magnet

Alloy No.	Hydrogen content [$\text{cm}^3 \cdot 10^{-2}\ \text{g}^{-1}$]				Desorption rate constant [$10^{-4} \cdot \text{s}^{-1}$]	Decrepitation degree after hydrogenation
	Initial	After hydrogenation				
		Total introduced	Diffusively mobile (eudiometry)	Irreversibly captured (LECO)		
1	39.0	16.6	2.6	14.0	4.52	Moderate
2	46.0	16.1	2.6	13.5	4.89	Moderate
3	82.0	−24.7*	0.7	−25.4*	−**	Strong
4	32.5	18.5	5.3	13.2	3.70	Absent
5	41.0	−19.0*	3.3	−22.3*	2.40	Strong
6	24.5	53.0	7.6	45.4	6.21	Absent
7	23.0	14.7	4.1	10.6	1.60	Strong
8	58.0	50.7	7.7	43.0	1.58	Moderate
9	42.5	69.0	9.2	59.8	1.20	Moderate
10	3.9	41.6	6.6	35.0	1.87	Moderate
11	5.4	57.7	4.3	53.4	2.75	Moderate
12	5.0	12.3	3.3	9.0	–	Absent

* minus sign denotes activation and partial loss of the initial hydrogen (due to the alloy decrepitation and hydride decomposition)

** mixed order of desorption reaction; calculation of the rate constant was not possible

is strongly related not only to the alloy composition but also to the processing parameters (see permanent magnets Nos. 1–4). With increasing milling time and hence decreasing average grain size, the initial hydrogen content decreases. The smaller grain size, the greater amount of oxide phases at the grain boundaries. The surface oxide layers apparently inhibit the hydrogen uptake and limit the initial hydrogen concentration.

With increasing sintering temperature, the initial hydrogen content also decreases (compare permanent magnet samples Nos. 3 and 4). The initial hydrogen concentration influences both the electrolytic hydrogenation process and hydride decrepitation of the permanent magnets. After electrolytic hydrogenation, the permanent magnet No. 3, having a coarse-grained structure, contains a very small amount (0.7 $\text{cm}^3/100\ \text{g}$) of mobile hydrogen. This can be explained by the fact that the hydride phases formed by the initial hydrogen are mainly located close to the surface. Hence, during electrolytical hydrogenation they immediately delaminate and the unstable hydrides decompose outside of the permanent magnet. Delamination is accompanied by the "release" of initial hydrogen. This phenomenon reduces the total hydrogen content in the permanent magnets by approximately one third after electrolytical hydrogenation. Similar effect was observed for permanent magnet No. 5. However, for this magnet (after hydrogenation), mobile hydrogen amount was detected on a relatively high level (3.3 $\mathrm{cm}^3/100$ g). This result may be explained by assuming higher solubility of hydrogen in the matrix phase for this magnet. Sample No. 4, which was sintered at elevated temperature (1140 °C) and, thus, contained smaller amount (32.5 $\mathrm{cm}^3/100$ g) of initial hydrogen, exhibited greater ability to undergo hydrogenation in comparison to the same permanent magnet sample sintered at the temperature of 1115 °C. But, contrary to the sample No. 3, the latter one did not change its durability (no hydride decrepitation after hydrogenation).

Among the alloys of the first group, the permanent magnet sample No. 6 showed satisfactory resistance to the hydrogenation process. After hydrogenation the total concentration of hydrogen for this permanent magnet was equal to 53.0 $\mathrm{cm}^3/100$ g. However, the absorbed hydrogen was mostly in a form of irreversibly captured hydrogen (45.4 $\mathrm{cm}^3/100$ g), which was probably present in the matrix phase. The higher value of the desorption rate constant (6.1×10^{-4} s^{-1}) resulted in a higher value of the diffusion mobile hydrogen (7.6 $\mathrm{cm}^3/100$ g). The practical lack of decrepitation in the case of permanent magnet No. 6 indicates that hydrogen existed mainly in the form of dissolved hydrogen. By contrast, permanent magnets Nos. 8 and 9 intensively absorbed hydrogen during electrolytical hydrogenation. Thus, the amounts of the hydrogen present in these permanent magnets were 108.7 $\mathrm{cm}^3/100$ g and 111.5 $\mathrm{cm}^3/100$ g, respectively. These permanent magnets exhibited moderate decrepitation after hydrogenation.

Regarding permanent magnets of the second group, alloy No. 12 possessed minimum absorption ability, and it probably formed an optimum ratio of hydrogen (since hydrogen absorption by this alloy was comparable to that of the high-strength steel). In comparison to permanent magnets Nos. 10 and 11, the permanent magnet No. 12 absorbed three times smaller amount of hydrogen. Thus the simultaneous alloying by Co and (Re, W, Zr) seemed to be highly efficient in view of the permanent magnet resistance against hydrogen absorption. As it was found earlier and reported in previous papers [9, 10], the additions of Re, W and Zr tend to worsen slightly the resistance of permanent magnets to acid- and atmospheric corrosion, but they facilitate transition of the permanent magnets into passive state. As it was found in the present study, the permanent magnet containing Co and (Re, W, Zr) additions does not decrepitate after hydrogenation.

The unusual affinity of RE-containing permanent magnets to hydrogen is commonly known [1, 11, 12]. In our earlier papers [13–15], we paid special attention to the abnormal dissolution of RE-containing permanent magnets caused by cathodic hydrogenation. Hydrogen absorption of RE-Fe-B-type permanent magnets accelerated corrosion rate of these permanent magnets in many aggressive environments and deteriorated their magnetic properties [16–18]. On the other hand, the ability of a permanent magnet to undergo decrepitation following hydrogen absorption found application in the process of powderization. Recently, a sophisticated process for producing RE-Fe-B magnet powder that involves hydrogenation, disproportionation, desorption and recombination (HDDR), has been developed and attracted much attention [1, 7]. The hydrogenation makes the final powder finer than conventionally treated material. It seems also, that hydrogenated powder is more stable against oxygen than the non-hydrogenated one [19–22].

4. Conclusions

The main results obtained in the paper can be summarized as follows:

1. Parameters of hydrogenation have been determined for sintered RE-(Fe, M)-B-type permanent magnets, and the correlation between these parameters, as well as the processing conditions and chemical composition have been established. For permanent magnets intended for use in a hydrogen containing atmosphere, a simultaneous alloying by Co and (Re, W, Zr) is highly effective.

2. The decrepitation of sintered RE-(Fe, M)-B type permanent magnets following hydrogenation depends not only on the amount of absorbed hydrogen, but also on the form of its occurrence in the permanent magnet (i.e. whether it is diffusively mobile or chemically bounded). The form of the hydrogen depends on the chemical composition of the permanent magnet, its heat treatments (including sintering temperature) and the grain size.

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