SOME CORROSION ELECTROCHEMICAL PROPERTIES OF THE Nd-Fe-B TYPE MAGNETIC MATERIAL

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Abstract

Research in the field of magnetic materials based on Nd-Fe-B is focused on the improvement of certain magnetic characteristics by alloying of suitable elements (Co, Dy, Pr, Cu), extending the thermal stability of these permanent magnets, improving their corrosion resistance and the creation of nano-structure modifications. Magnets based on Nd-Fe-B are susceptible to corrosion, especially in humid atmospheres. The corrosion resistance of these magnets is a function of the structure, temperature, degree of environment humidity and Nd-rich phase reactivity. The paper is focused on determining and comparing the corrosion resistance of magnetic material NdPr-FeM-B (produced by powder metallurgy, M = Cu,Co,Al) in several environments. For comparative purposes, unalloyed carbon steel (C ≤ 0.1 wt.%) was tested under the same conditions. On the basis of electrochemical polarization measurements there were determined polarization curve, corrosion characteristics and parameters (corrosion potential, polarization resistance, pitting potentials, etc.) of mentioned selected materials in aqueous solutions (Na_2SO_4, NaH_2PO_4, $NaCl$). Salt spray test was also performed with these materials. The heterogeneous structure of magnetic material and uneven and/or localized corrosion was observed using microscopy. In the sodium chloride solution, a higher corrosion resistance reached steel in comparison with the magnet, in sodium sulfate solutions the results were not clear (depending on the pH, surface condition). The magnetic material exhibited a much higher resistance in the solution of NaH_2PO_4 in comparison with the corrosion resistance in other test solutions.

Keywords: Magnetic material, Nd-Fe-B, corrosion resistance, polarization test.

1. INTRODUCTION

RE-Fe-B base magnets contain rare earth (RE) elements: neodymium (Nd), dysprosium (Dy) or praseodymium (Pr). These excellent magnets allow substantial miniaturization of dimensions and cost reduction of many devices and industries [1]. They are also produced by sintering very finely ground powders, reaching the highest magnetic energy $(BH)_{max}$.

Application properties of these materials are dependent on their ability to maintain the magnetic properties, mechanical load transfer and also the resistance to corrosive environments. Magnets Nd-Fe-B are susceptible to corrosion in a humid atmosphere and it is also a factor in limiting their applicability.

Excellent magnetic properties of this material can be attributed to the ferromagnetic phase, $Nd_2Fe_{14}B$ matrix with a very high saturation polarization and high magnetic anisotropy. Neodymium rich and reactive phase coupling at the grain boundaries of these magnets provide adequate mechanical properties. Magnetic properties are to some extent influenced by the input material and production process [2].

Magnets based on Nd are very susceptible to corrosion in atmospheric humidity above 80 %. The corrosion sensitivity of these materials, however, has its cause in the material structure consisting of magnetic $Nd_2Fe_{14}B$ grains and grain boundary Nd-rich phase, see **Fig. 1**.

Neodymium phase is much more reactive than $Nd_2Fe_{14}B$ phase in the matrix, so that with sufficient moisture in the air there will be a localized galvanic reaction between Nd and $Nd_2Fe_{14}B$ phases. The reaction can then be initiated from neodymium phase as follows: anodic reaction: $Nd \rightarrow Nd^{3+} + 3e^-$ and cathodic reaction - $3/2H_2O + 3/4O_2 + 3e^- \rightarrow 3OH^-$. Final corrosion product is then $Nd(OH)_3$ or $Nd_2O_3 \cdot nH_2O$ according to conditions. In dry atmosphere, the surface of the magnet of Nd-Fe-B layer forms Nd_2O_3, which exhibits good insulation properties. In the case of moisture this layer is converted into $Nd(OH)_3$ which does not have protective properties. If the grain boundary covered on neodymium rich phase of sufficient thickness and exposed to wet air, the corrosion then proceeds continuously along the grain boundaries as shown in **Fig. 1**.
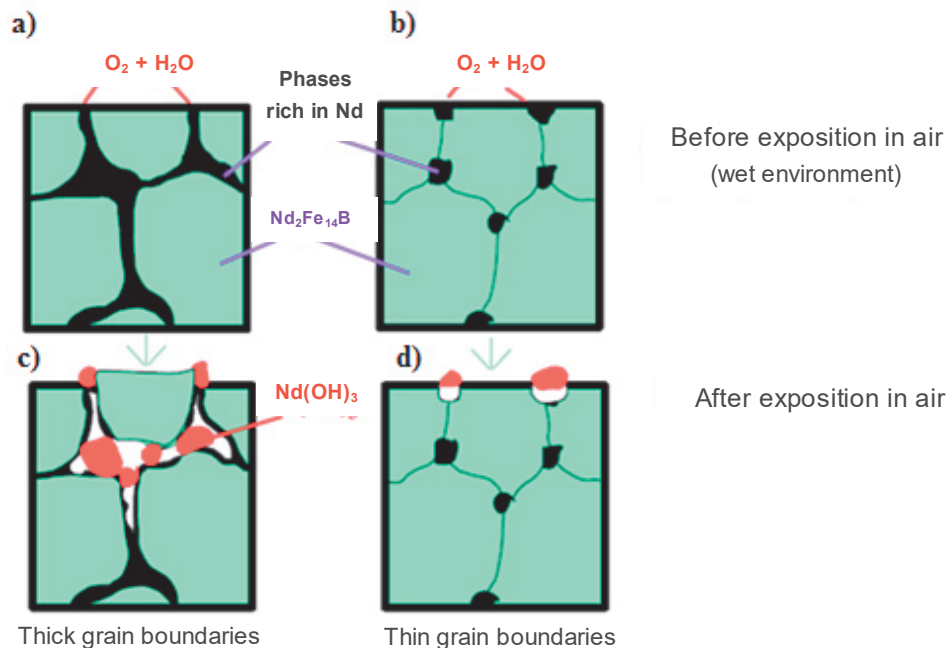
Fig. 1 Scheme of NdFeB corrosion process [3]

Corrosion rates of the individual phases of $Nd_2Fe_{14}B$, and $NdFe_4B_4$, Nd_4Fe with time initially increases and then is almost constant. The corrosion rate of the individual phases are in order in the acid solution: $Nd_{1+\varepsilon}Fe_4B_4$ (paramagnetic phase η), $Nd_2Fe_{14}B$ (ferromagnetic phase Φ), and Nd_4Fe (Nd-rich diamagnetic phase ρ). Knowledge of the corrosion behavior of the magnet and its phases are also needed to optimize surface preparation and design of corrosion protection, especially electroplating.

The main ways of protecting magnet type Nd-Fe-B corrosion:
- Use protective coatings on the surface of the magnet: galvanic metallic coatings, polymers, passive layers.
- Varying the internal corrosion properties of the material by adding alloying elements.

The corrosion rate of Nd-Fe-B materials containing Co, Al (replacing Fe), are lower than without these elements in many environments, from sulfuric acid to moist air [4].

There was also developed a new material modification of Nd-Fe-B type, in which the most reactive neodymium phase in the intergranular field was replaced by stable intermetallic compounds [5].

Access restructuring grain boundaries was based on improving corrosion resistance (Pr,Nd)-Fe-B sintered magnets due to intergranular exchange (Pr,Nd)-rich $(Pr,Nd)_6Fe_{13}Cu$ phase. In addition to improved corrosion resistance, restructured magnets also exhibit excellent magnetic performance. Phase type δ $(Pr,Nd)_6Fe_{13}Cu$ having more positive than the electrochemical potential (Pr, Nd)-rich phase also reduces the driving force for the corrosion reaction. The amorphous structure and uniform distribution of the intergranular phase improves both corrosion resistance and magnetic properties [6]. Addition of Cu causes a modification in the material phases - Nd-rich phase was replaced by phases containing Cu and boric phase can be eliminated, which

improves the corrosion resistance due to galvanic corrosion limitations. In the presence of Ni or Co $Nd_3(Ni,Cu,Co)$ phase may arise.

The aim of this paper is to evaluate the corrosion properties of selected magnetic material NdFeB, especially their corrosion-electrochemical properties in several environments and expand knowledge in the field of corrosion properties of magnetic materials based on Nd-Fe-B.

2. EXPERIMENTAL

2.1. Materials and samples

The main objective of this experimental work was to determine the corrosive properties of modified magnetic material of type Nd-Fe-B. As samples were cylindrical magnets of dimensions $\varnothing$ 8×8 mm having the chemical compositions listed in **Table 1**. Basic ferromagnetic phase ($Nd_8Pr_2Fe_{80}Al_3B_7$) corresponds to $(NdPr)_2Fe_{14}B$. The content of boron could not be determined by using x-ray microanalysis (usually 6-8 at.%). The minor and reactive phase is rich in Nd and Pr in total above 60 wt. %. Oxygen was bounded in the corrosion products. These magnets were produced by powder metallurgy, and therefore pores were also detected, **Figs. 2** and **3**. Magnetic material can be written as (NdPr-FeM-B), where M (Al, Cu, Co) - metals replacing Fe.

Table 1 The analyzed chemical composition (at.%) of the magnetic material (JEOL 6490 LV + EDX)

Name	O	Al	Si	Fe	Co	Cu	Pr	Nd
Phase 1	18.55	7.50	-	27.46	1.73	11.78	9.66	23.32
	14.09	8.82	-	35.87	1.93	6.98	9.18	23.13
Phase 2	-	3.46	-	86.16	-	-	2.34	8.05
	-	3.42	-	84.84	-	-	2.56	9.19
Phase 3	15.67	1.99	1.69	79.09	-	-	0.35	1.21
	21.81	1.56	3.15	69.47	-	-	0.92	3.10
	30.01	1.35	0.82	63.14	-	-	1.05	3.64

Along with magnets were prepared reference samples of low carbon steel (DC01 EN10130-91, CSN 11321) of dimensions 50×25×1 mm. The composition of steel in wt.%: max. 0.10 % C, 0.45 % Mn, 0.030 % P and 0.030 % S.
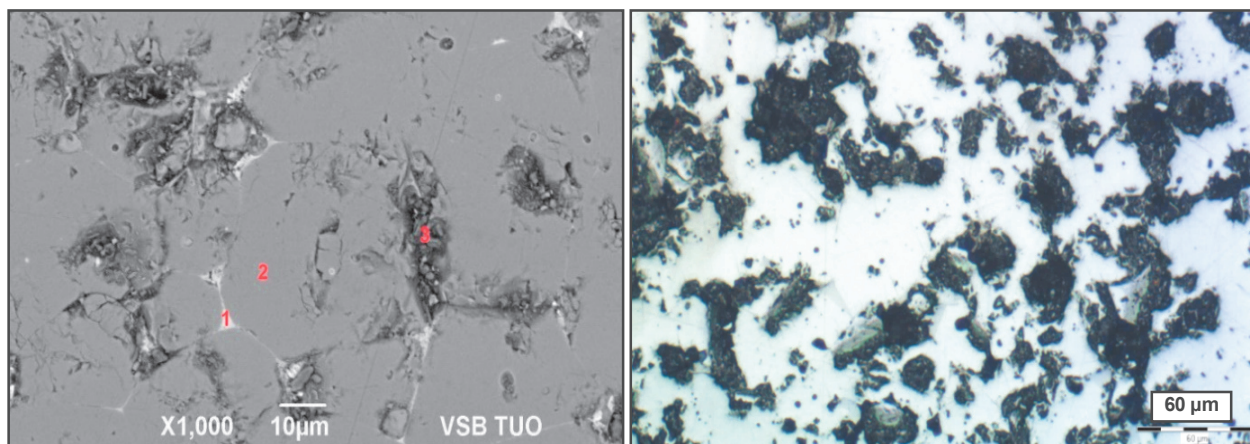
Fig. 2 Heterogeneous structure of magnetic material (after polishing), SEM and LM

2.2. Corrosion tests

To verify the corrosion properties of these permanent magnets following methods were used:

- Electrochemical polarization tests, cyclic potentiodynamic measurements [7]
- Accelerated salt spray test.

Corrosion electrochemical tests were carried out in solutions: 0.5 M Na_2SO_4, pH 5.6; 0.5 M Na_2SO_4, pH 3.0 (with the addition of H_2SO_4) and 0.5 M NaH_2PO_4, pH 4.3). Samples were tested with the supplied (as-received) and finally ground surface (SiC paper 1200). For comparison purposes, it was used demineralized water (pH 7). Electrochemical corrosion tests were performed using a potentiostat PGP201 and program VoltaMaster. The exposed area of the sample was 0.5 cm^2 and tests were carried out at room temperature (24°C). The reference electrode was a saturated calomel electrode (SCE), the auxiliary electrode was made of platinum. Potentiodynamic polarization measurements were carried out in the potential range from -1.0 to 2.0 V (SCE) at polarization rate of 5.0 mV·s^{-1}. The polarization resistance (R_p) and related parameters were calculated by Stern´s method.

To determine the resistance to pitting corrosion the neutral solution of 0.1 M and 0.5 M NaCl was used. Samples were used of NdPr-FeM-B material and said steel for comparison. Tests were carried out at room temperature from E_{cor} - 100 mV up to the return potential (at 2 mA·cm^{-2}) and back at a scan rate of 1.0 mV·s^{-1} in both directions.

Salt spray test was performed in accordance with standard [8]. After certain times of exposure, the samples were photographed and weighed for using the gravimetric method. After the test some samples were exposed in a pickling solution for removal of corrosion products. To determine the effects of the aggressive solution on the basic materials there were added reference samples of steel and the magnet.

3. RESULTS

On the basis of polarization curves (**Fig. 3**) were determined parameters of corrosion - see **Table 2**. Values of corrosion current density (J_{cor}) and corrosion rates ($r_{c.}$) are approximate and inversely proportional to the polarization resistance R_p. In NaH_2PO_4 solution there was found out much lower corrosion rate of tested magnet than in Na_2SO_4 and NaCl ones. Magnetic material (NdPr-FeM-B including Nd-rich phase), was not perfectly passivated in phosphate solution with anodic current density in the range 0.05-0.15 mA·cm^{-2}, that is 3 orders of magnitude lower than the current density in the analogous environment of sulfate (at a comparable pH), **Fig. 3.**
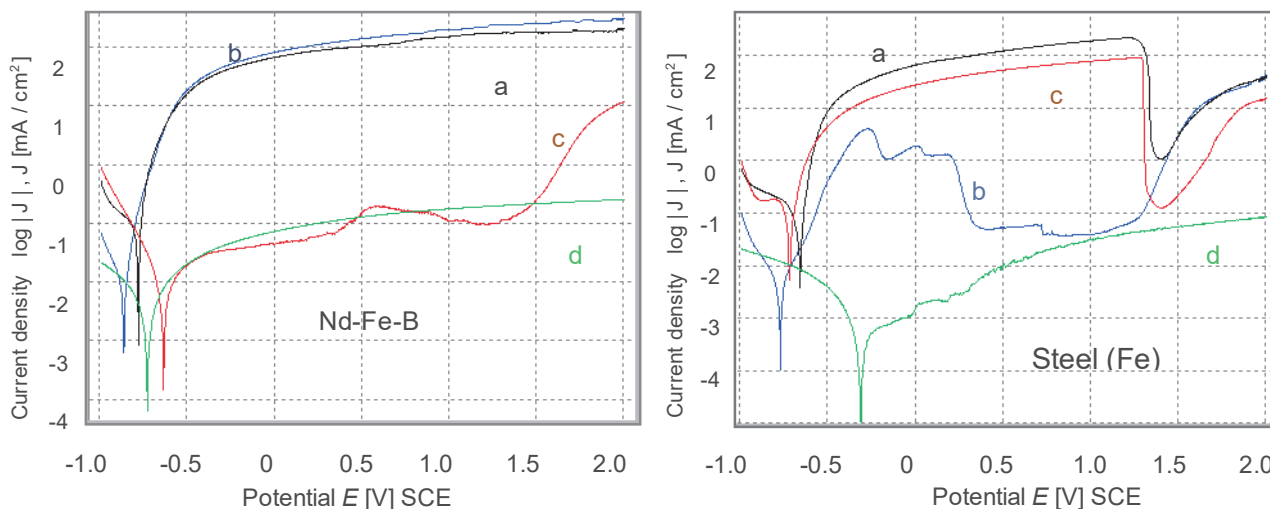
Fig. 3 The magnetic material of Nd-Fe-B and steel (Fe), the polarization curve in the environment: a) Na_2SO_4 (pH 3), b) Na_2SO_4 (pH 5.6), c), NaH_2PO_4 (pH 4.3) and d) H_2O (demineralized)

Initial surface conditions (as-received or after grinding) have reflected in the corrosion parameters differently according to each environment. Modified alloy magnetic material exhibits a much higher corrosion resistance than the basic Nd-Fe-B type. The lowest corrosion rates on both test materials were confirmed in pure water.

For comparison on the Nd-Fe-B material type without alloying were identified values of the parameters, which shows that the corrosion rate of the test modified material (NdPr-FeM-B) are much lower [4]. $Nd_{16}Fe_{76}B_8$ material in the sulphate solution at pH 3-6 had similar values E_{cor} = -0.81 to -0.75 V SCE. For $Nd_{15}Fe_{77}B_8$ material current density J_{cor} = 0.5 mA·cm^{-2} (pH 6) and for $Nd_{10}Fe_{84}B_6$ polarization resistance R_p = 2.5 to 7.7 Ω·cm^2 (in 0.5M SO$_4^{2-}$, pH≈3) were measured. On $Nd_xFe_{94-x}B_6$ materials R_p decreases from 10 to 5 Ω·cm^2 during growth of Nd content from 6 to 16% in the sulphate solution at pH=3. Passive state of $Nd_{15}Fe_{77}B_8$ was achieved in the range of 0-1.5 V SCE at a current density 0.3-0.4 mA·cm^{-2} in NaH_2PO_4 solutions (pH 2-5). Passive state for Nd-Fe-B ($Nd_{15}Fe_{77}B_8$) in phosphate solution at pH 4 would be formed by hardly soluble $NdPO_4$ [4].

**Table 2** The values of parameters obtained in polarization test

Material	solution	pH	surface	$E_{cor.}$ (mV)	R_p (kΩ·cm^2)	$J_{cor.}$ (μA·cm^{-2})	r_c. (mm·a^{-1})	corrosion
NdFeB type magnet	Na_2SO_4	5.6	supplied	-735	1.30	17.1	0.317	non-uniform
	Na_2SO_4	5.6	ground	-870	1.98	11.0	0.128	non-uniform, pits
	Na_2SO_4	3.0	ground	-781	0.297	83.1	0.972	non-uniform, pits
	NaCl	6.5	supplied	-811	2.07	6.7	0.079	pitting, 0.1M
	NaCl	6.5	ground	-776	1.30	11.6	0.136	pitting, 0.5M
	NaH_2PO_4	4.3	supplied	-662	4.10	5.66	0.077	passive
	NaH_2PO_4	4.3	ground	-575	4.89	4.07	0.048	passive
	H_2O	7.0	ground	-735	13.0	1.8	0.021	(pitting)
low carbon steel	Na_2SO_4	5.6	supplied	-695	1.04	29.8	0.349	non-uniform
	Na_2SO_4	5.6	ground	-595	6.01	4.2	0.049	non-uniform
	Na_2SO_4	3.0	ground	-638	0.385	69.8	0.817	uniform
	NaCl	6.5	supplied	-550	4.65	4.21	0.049	pitting, 0.1M
	NaCl	6.5	ground	-507	2.27	9.66	0.113	pitting, 0.5 M
	NaH_2PO_4	4.3	supplied	-695	0.283	73.9	0.812	uniform
	NaH_2PO_4	4.3	ground	-671	0.578	76.7	0.898	uniform
	H_2O	7.0	ground	-320	101.7	0.27	0.003	

The values of parameters of uniform corrosion in NaCl solution were determined before initiation of pitting. In NaCl water solution the potentials of depassivation (E_d) and repassivation (E_r) for magnetic material have lower values in comparison with steel, **Fig. 4**. The test was conducted in neutral 0.1 and 0.5 M (mol/l) NaCl water solutions. The differences in potentials in both solutions are relatively small. The lower values of measured potentials (E_d, E_r) and the difference of E_d - E_{cor} (E_r - E_{cor}), the smaller resistance to pitting corrosion.

Non-uniform corrosion with dimples on the magnet is documented in **Fig. 5**. In comparison with carbon steel, the modified magnetic material (NdPr-FeM-B) exhibits a higher resistance to corrosion in salt spray, but base material (Nd-Fe-B) has a lower corrosion resistance (**Fig. 6**) i.e. a higher corrosion rate.
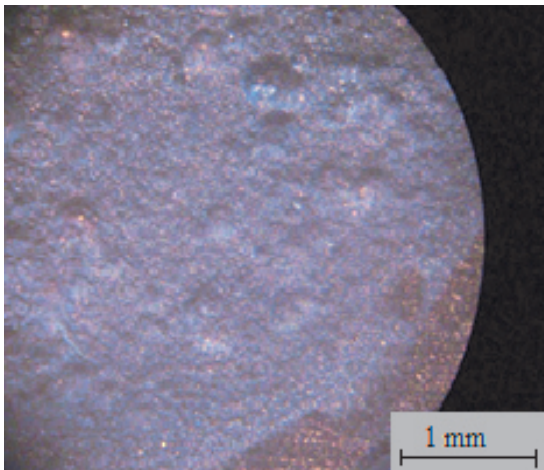
Fig. 4 Comparison of pitting parameters of tested materials in water solution of NaCl
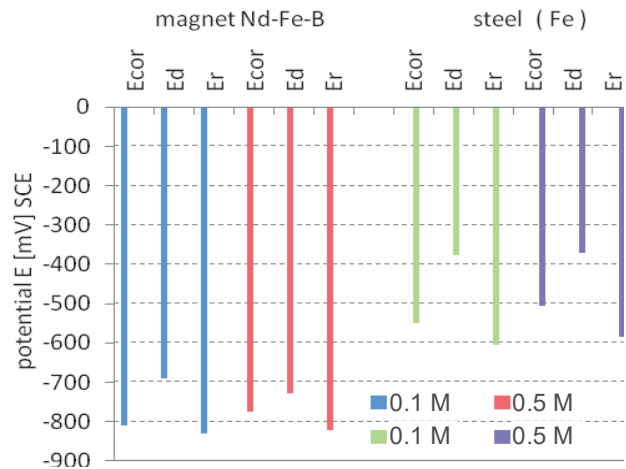
Fig. 5 The surface of the magnet after the test in solution of Na_2SO_4, pH 3
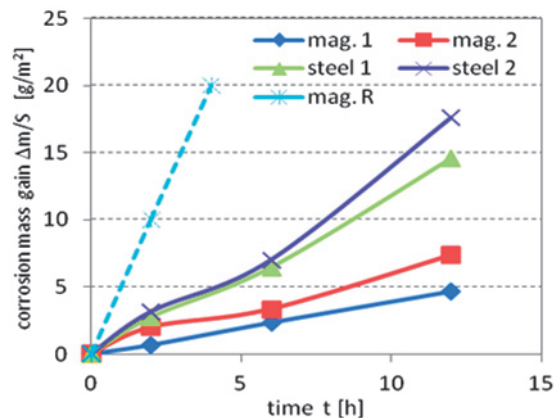
Fig. 6 The corrosion mass gains of magnetic material NdPr-FeM-B and carbon steel (C ≤ 0.10%) in salt spray test. Reference magnet (R) - the sintered material of Nd-Fe-B ($Nd_{15}Fe_{77}B_8$) [4], dashed line

4. CONCLUSION

Tested modified magnetic material has a heterogeneous structure comprising at least three different phases. Alloying of the magnetic material of the Nd-Fe-B type by suitable elements (Pr, Cu, Co, Al) led to the increased corrosion resistance in tested environments. The corrosion rate of tested magnet material in monosodium phosphate solution was much lower than in environments of sulphate and sodium chloride because of its tendency to passivity. On the contrary, the reference steel showed a higher corrosion rate in phosphate solution. Non-uniform corrosion and pitting were observed on the samples after the exposure in the sodium sulphate and sodium chloride. On the basis of potentiodynamic method, a lower resistance to pitting corrosion of the magnet compared with carbon steel was demonstrated. The modified magnetic material evinced a higher corrosion resistance than low-carbon steel or Nd-Fe-B magnet under salt spray test conditions.

ACKNOWLEDGEMENTS

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