Electrochemical corrosion tests of Nd-Fe-B-based magnetic materials with modified structure

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Abstract. The wide application of Nd-Fe-B permanent magnets in addition to the rare-earth metal resource constrains determine the necessity of their recycling. One of approaches to magnet-to-magnet recycling consists in using the grain boundary modification of sintered magnet material, which includes the grain-boundary diffusion (GBD) and grain-boundary structuring (GBS). The preparation of magnets with the modified structure determines a need for research their corrosion resistance. The corrosion resistance of magnets prepared by powder blending techniques, namely, magnets, which were recycled from hard-disk drivers, in using Dy/NdH₂ additions in the powder mixture and magnets, which were prepared from strip-casting alloy, in using TbH₂ hydride in the powder mixture, is studied. The corrosion potential and polarization resistance were measured, and the average corrosion rate was estimated based on polarization measurements of the magnet samples in the aqueous solution 0.1 M NaCl. Furthermore, a pitting resistance corrosion test was conducted and the values of pitting and repassivation potential were determined. The corrosive properties of the magnet samples are discussed from the viewpoint of the phase compositions of the material.

1. Introduction
Sintered Nd–Fe–B permanent magnets are widely used in many fields because of their excellent magnetic properties. Their wide application in addition to the rare-earth metal resource constrains determine the necessity of the development of resource-saving technologies and efficient technologies for recycling sintered Nd-Fe-B permanent magnets. One of approaches to solving the problems consists in using the grain boundary modification of sintered magnet material [1–2], which includes the grain-boundary diffusion (GBD) and grain-boundary structuring (GBS) and can be applied both in manufacturing the magnets and in their recycling by magnet-to-magnet technology [1].

The undesirable corrosion properties of Nd-Fe-B magnets and, in particular, recycled materials can be positively or negatively changed by the grain boundary modification of the magnet compositions.

The poor corrosion resistance of Nd–Fe–B magnets is attributed to the coexistence of several phases in the microstructure and, in particular, to the presence of the Nd-rich grain boundary phase in the alloys. Just this phase is subjected to the compositional and structural modification upon grain-boundary structuring and magnet-to-magnet recycling. The major phase is the Nd₂Fe₁₄B matrix and there is a lesser amount of the Nd rich grain boundary phase. Under electrochemical conditions, the Nd rich phase surrounding the matrix phase becomes anodic to the later. The formation of a galvanic couple between the Nd rich phase and the matrix phase takes place (corrosion microbattery): the Nd rich phase corrodes preferentially, leading to intergranular corrosion. The reason for formation of a
galvanic couple between the above phases is due to the fact that neodymium (Nd = -2.43 V), which is present in the grain boundaries is considerably more electrochemically active than boron (B = -0.87 V) or iron (Fe = -0.44 V); so the corrosion is focused at the intergranular regions of the Nd–Fe–B magnets [3].

The Nd-rich phases at the surface of the magnets react with water vapor and oxygen in a hot, humid atmosphere (Eqs. (1) and (2)). The reaction product H then diffuses into the grain boundaries and reacts with the Nd-rich phases to form NdH$_3$ (Eq. (3)). The NdH$_3$ hydride causes the volume expansion of the grain-boundary phases. Therefore, local stresses are induced, which lead to the spalling of the matrix Nd$_2$Fe$_{14}$B grains [4].

\[
\begin{align*}
\text{Nd} + 3\text{H}_2\text{O} & \rightarrow \text{Nd(OH)}_3 + 3\text{H} & (1) \\
4\text{Nd} + 3\text{O}_2 & \rightarrow 2\text{Nd}_2\text{O}_3 & (2) \\
\text{Nd} + 3\text{H} & \rightarrow \text{NdH}_3 & (3)
\end{align*}
\]

In [4], it was found that the humid-heat resistance of the magnets was obviously improved by partially substituting Dy for Nd. The refinement of grains also can increase the corrosion resistance [5]. The copper-containing additions Cu(60)Zn(40) [6], Al(85)Cu(15) [7], Mg-containing addition Mg(7)Zn(3) [8] (favors the uniform distribution of Nd-rich phase, enhances the electrochemical potential of Nd-rich phase, and refines grains), as well the decrease in the content of Nd-rich phase [9] (to restrict the oxidation propagation and suppress the oxidation) by spark plasma preparation technique improve the corrosion resistance.

The use of binary powder blending technique, where the composition of the master alloy was close to the stoichiometric Nd$_2$Fe$_{14}$B compound, while the sintering aid (SA) had a composition of MM$_{38.1}$Co$_{46.4}$Ni$_{15.4}$ [10], showed that by decreasing the amount of Nd-rich grain boundary phases and substitution of some Fe atoms by Co and Ni, an improvement in the corrosion resistance of the magnets was observed.

All the above measures are among the grain boundary structuring technique used, in particular, in recycling Nd-Fe-B magnets. Generally, the corrosion resistance of the magnetic materials depends mainly on the chemical composition as well as the processing technique

The application of hydrogen decrepitation for recycling of magnets determines the necessity of consideration of the hydrogen effect on the corrosion resistance [11]. The excessive hydrogen contents are harmful to the corrosion resistance of the magnets. The influences of residue hydrogen contents on the corrosion resistance of magnets dominate only when the residue hydrogen content exceeds 1300 parts per million [10].

The aim of the present study is to investigate the electrochemical behavior of Nd-Fe-B magnets prepared by powder blending technique in using rare-earth metal hydrides in the powder mixture and initial Nd-Fe-B powders prepared from strip-casting alloy and recycled magnets.

2. Materials and experiment

For the investigation, we used samples of magnets prepared by recycling of magnets from hard disk drives (HDD) in using 2.5 wt DyH$_2$ in powder mixture (samples 1, 2, 3) and magnets prepared from strip-casting alloy (Nd, Pr)-Fe-B and 2 in using 2 and 4 wt % TbH$_2$ added to the powder mixture at the fine milling stage [12]; The average grain size of all magnets is ~15 μm. Magnets from HDD were subjected to hydrogen decrepitation; the coating was separated by sieving. The optimum heat treatment of all magnets consists in heating to 500°C and holding for 1 h.

The structure of magnets was studied using an Quanta 450 FEG high-resolution field emission gun scanning electron microscope equipped with energy dispersive (EDX, EDAX) analyzer.

The corrosion resistance of the magnets in the demagnetized state was studied by electrochemical corrosion tests. The samples were stored in closed plastic containers in alcohol to prevent atmospheric corrosion in air before the tests. The dimensions of the samples and initial weights are shown in Table 1. A non-alloy steel sample (ČSN 11321, EN 1.0330, EU DC01) was used as a reference for
comparison. The surfaces of the test magnet samples were not grinded or otherwise modified before the tests.

The electrochemical corrosion tests were conducted in the following order: measurement of the corrosion potential ($E_{cor}$), measurement of the polarization resistance value ($R_p$), pitting corrosion test with polarization curve recording and measurement of the conventional value of the pitting potential ($E_p$), repassivation ($E_r$).

The samples were cleaned with an alcohol-gasoline mixture and rinsed in demi-water just before the polarization measurement. The samples were then attached to a specialized corrosion cell with a three-electrode connection and sealed from the outside with a silicone seal. The exposed cylindrical surface ($S = 0.312 \text{ cm}^2$) was defined by a $\varnothing 6.3 \text{ mm}$ hole in the cell. A potentiostat-galvanostat PGP 201 controlled by a PC with the Volta-Master 1 program was used for measuring and processing the measured values of electrochemical corrosion. The potential values were measured in relation to a saturated calomel electrode (SCE).

Table 1. Dimensions and initial weights of the samples.

| Sample no. | dimensions (mm) | mass (g) | density (g/cm$^3$) | note appearance of the sample |
|------------|----------------|----------|--------------------|------------------------------|
| 1 HDD + 2.5 wt. % DyH$_2$ | 8.4x7.4x7.4 | 3.4666 | 7.54 | metallic, shiny |
| 2 HDD + 2.5 wt. % DyH$_2$ | 8.2x7.5x7.4 | 3.4282 | 7.53 | metallic, shiny |
| 3 HDD + 2.5 wt. % DyH$_2$ | 8.4x7.5x7.5 | 3.4999 | 7.40 | metallic, shiny |
| 4 2 wt. %TbH$_2$ | 7.6x7.5x7.4 | 3.1397 | 7.44 | rust on all surfaces |
| 5 4 wt. %TbH$_2$ | 7.5x7.4x7.4 | 3.0832 | 7.51 | rusty stains on one surface |
| Fe-C | 38.0x25.4x1.0 | 9.7556 | 7.8 | steel 11321, refer. glossy pattern |

The conditions and parameters of the test: aqueous solution 0.1 M NaCl, volume 60 ml, temperature 25°C, open air, without stirring. The selected range of the potentials for the measurement of the polarization curve for the evaluation of pitting corrosion, were from $E_{cor} - 50 \text{ mV (SCE)}$ to the return potential (at a current density of 1.0 mA/cm$^2$) and back with the speed of polarization of 0.50 mV/s to the corrosion potential.

The electrochemical corrosion tests were performed according to the following standards: ČSN EN ISO 17475, ASTM G59, ASTM G61.

3. Results and discussion

3.1. Structure and appearance of magnet samples

All samples of magnets investigated in terms of present study are characterized by modified structure, namely, core-shell structure of the main magnetic phase grains. The structure of the magnets is given in Figure 1.

The use of REM hydrides in the powder mixture determines the presence of active (Dy, Tb) powder and diffusion of the REMs into the $\text{R}_2\text{Fe}_{14}\text{B}$ main magnetic phase lattice. The diffusion of heavy REM atoms leads to edging Nd atoms and increase in both the Nd content within the intergranular phase and volume of fraction of the phase.

Figure 2 shows images of the sample surface before corrosion tests.

3.2. Electrochemical corrosion tests
The values of the corrosion potential $E_{\text{cor}}$ were measured at the beginning of the time interval, the values of $E_{\text{cor}}$ at the end of the given interval (Table 2), which was defined by the condition of change of potential 2 mV per minute, i.e. approximately after reaching a steady state, within a few minutes.

![Image](image1)

Figure 1. (a) Microstructure (SEM, secondary electron mode) of magnet prepared from the powder mixture with 4 wt. % TbH$_2$, (b) variations of element content along the scanning line; areas marked by digits 1 and 2 are depleted of and enriched in Tb, respectively. (c) Microstructure (SEM, secondary electron mode) of magnet (sample 3) prepared from the powder mixture containing HDD powder and 2.5 wt. % DyH$_2$ and (d) dysprosium distribution.

The $E_{\text{cor}}$ values enable the comparison of possible corrosion from a thermodynamic point of view. In general, the lower the $E_{\text{cor}}$ values, the less noble is the metal (alloy, magnet), i.e. more corrosive, corrodes more easily in a given environment. The $E_{\text{cor}}$ values can also tell us whether the metal is in an active or passive state ($E_{\text{cor}}(\text{act}) < E_{\text{cor}}(\text{pas})$), differences of hundreds of mV). The kinetics of corrosion can be evaluated by the polarization resistance $R_p$, which is indirectly proportional to the corrosion rate ($r_c$), while relation $r_c = B/R_p$, where B is a parameter dependent on material and environment.

The polarization resistance $R_p$ was determined in two ways, according to the ASTM G59 standard and also from the initial part of the polarization curve using the Stern method. The corrosion potential measurement was followed by cyclic linear polarization in the range ± 30 mV from the corrosion potential value (ASTM G59) and the $R_p$ values were determined using the VoltaMaster 1 program, the measurement was repeated 3 times at certain exposure time intervals. There was a considerable spread in the individual measured values $R_p$. Table 2 presents the average values $R_p$. After measuring the polarization curve for determining the pitting parameters, the Stern method was used to determine the
$R_{pb}$ values. The $R_{pb}$ values determined at the end are several times smaller than $R_{pa}$ values, which can be explained by a change in the actual surface during dissolution (corrosion) of the active phases rich in Nd in the magnetic material due to the formation of corrosion pits, crevices etc. The decrease in the $R_p$ value over time of exposure corresponds to a decrease in the corrosion resistance of the magnets. In comparison to the original surfaces, a higher proportion of black spots and grains (pores, microscopic pits after corrosion, i.e. dissolution of phases rich in Nd and RE, falling out of grains (powder particles) of a more resistant basic ferromagnetic phase) was observed on the microscope.

![Figure 2](image)

Figure 2. Appearance of samples (a) 1 and (b) 4 after storage in alcohol and before the electrochemical test.

Next, the value of the average corrosion rate $r_c$ was calculated using the $R_{pb}$ value; the molar mass of the dissolved or corroding phase and its density value would be required to achieve a more accurate value. The molar mass of 63.6 g/mol (for Nd$_2$Fe$_{14}$B) and the average density of the material according to Table 1 were used for a simplified approximate calculation. The intervals for calculating $r_c$ were chosen subjectively (the range on the anodic part of the curve was chosen to be 150 mm, the correlation interval 50 mm, identically for all samples). The $r_c$ values, therefore, need to be assessed and compared with caution, especially in cases of uneven corrosion where the maximum corrosion penetration rate is several times higher than the average. The values of corrosion current density were also determined, which are proportional to the corrosion rate in accordance with Faraday’s law (they are not included in Table 2).

| Sample no. | $E_{cor1}$ | $E_{cor2}$ | $R_{pa}$ | $R_{pb}$ | $r_c$ | Order according to: |
|-----------|-----------|-----------|---------|---------|------|------------------|
| 1         | -735      | -739      | 68,5    | 6,07    | 182  | 4-5 2 4          |
| 2         | -720      | -725      | 5,92    | 1,41    | 243  | 3 6 6 6          |
| 3         | -857      | -876      | 85,15   | 13,8    | (210)? | 6 1 5         |
| 4         | -564      | -591      | 9,18    | 2,52    | 112  | 2 4 2          |
| 5         | -726      | -743      | 8,9     | 1,59    | 124  | 4-5 5 3          |
| 6         | -777      | -784      | 7,7     | 1,8     | 259  |                 |
| Fe-C      | -380      | -448      | 13,3    | 2,74    | 60   | 1 3 1          |
The measured values of corrosion electrochemical parameters also enable us to determine the order of corrosion resistance, which according to $E_{cor}$ (thermodynamic variant) is different from the order according to $R_p$, or $r_c$ (kinetic aspect). It is not possible to single out the most resistant sample from the tested magnetic materials; it depends what value (weighting factor) we attach to the individual parameters. When $E_{cor}$ and $R_p$ are of equal weight according to the average order (weighting factors $w_i = 0.50 = 50\%$) the samples 2%Tb and No. 1 appear to be the most resistant magnets; on the contrary, the worst samples appear to be No. 2 and 4% Tb. It was also confirmed that non-alloy steel, i.e. iron as the prevalent element in magnets, showed the higher resistance than that of magnets.

3.3. Resistance of magnets to pitting corrosion

Resistance to pitting corrosion is usually compared according to the values of the pitting potential (depassivation) and repassivation (protection). In general, the higher the values of these potentials, the better the resistance to pitting (local) corrosion. The differences between the named potentials and the corrosion potential can be used as an auxiliary criterion. In the case of magnetic materials of the type Nd(RE)-Fe-B, the phases rich in Nd and similar elements (R - some lanthanides, rare earth metals) dissolve first, leaving irregular microscopic pits or, in some cases, intercrystalline corrosion in their place.

![Figure 3](image)

**Figure 3.** Surface of samples (1, 2, 3, 4, 5) after corrosion electrochemical test and storage in alcohol. Corrosion points and stains on the surface.

Figure 3 shows images of the surface of samples after the tests in aqueous 0.1 M NaCl solution and corrosion macromorphology. It can be seen that there are pits in the surface of the corroded specimens, and a particle-shaped (or powder-shaped), brown corrosion product.

The polarization curves of magnet samples 1, 2, 3, 4, and 5 are given in Figure 4. All the curves are typical of pitting corrosion.

When comparing the resistance to pitting corrosion, the relatively best resistance among the tested magnets was demonstrated by sample 2 % Tb, on the contrary, the worst corrosion resistance was demonstrated by sample no. 3. (Table 3). All polarization curves had a loop shape, typical of pitting or crevice corrosion, which occurred mainly on the steel sample.

As was noted above, the corrosion of Nd-Fe-B magnets mainly is due to the existence of Nd-rich phase. This phase is pathways for the oxidation propagation, and the intergranular oxidation process occurs.
The processes used in the present study for manufacturing Nd-Fe-B magnets (diffusion of REMs formed by decomposition of REMH$_2$) deal with the modification of the Nd-rich phase. The heavy REMs (Tb, Dy) alloy main magnetic phase grains; this leads to the thickening of Nd-rich phase and its enrichment in Nd. These factors are unfavourable for the corrosion resistance of magnets. In this case, the lesser addition of heavy REM (sample 4 with 2 wt. % TbH$_2$) determines the higher corrosion stability of the sample. Despite the fact that the binary powder blending technique results in careful adjustment of the microstructure and microcomposition of the alloys, the corrosion resistance of such magnets can be decreased by the diffusion of Nd into grain boundaries and increased hydrogen content in the manufacturing process [11].
Table 3. Conventional values of pitting potential ($E_p$) and repassivation ($E_r$), order of resistance to pitting corrosion according to measured potential values ($E_p$ and $E_r$).

| Sample no. | $E_p$ (mV) | $E_r$ (mV) | $E_p - E_r$ (mV) | Order of resistance |
|------------|------------|------------|------------------|---------------------|
| HDD + 2.5 wt.% DyH$_2$ | -670 | -760 | 90 | 3 |
| HDD + 2.5 wt.% DyH$_2$ | -689 | -765 | 76 | 4 |
| HDD + 2.5 wt.% DyH$_2$ | -790 | -903 | 113 | 6 |
| 2 wt. % TbH$_2$ | -451 | n | | 2 |
| 4 wt. % TbH$_2$ | -693 | -780 | 87 | 5 |
| Fe-C | -722 | -782 | 60 | 1 |

Note: $n$ - value could not be determined from the polarization curve recording. After the tests, the measured weights of the samples were the same as in their initial state (Table 1), i.e. weight changes were not detected on the Sartorius CP224 S-OCE digital scale.

It is likely that the worst corrosion resistance (among considered samples) demonstrated by sample 3 is related to the lowest density (Table 1) of the sample and existence of pathways for oxidation propagation.

According to [13], the pitting corrosion is due to the existence of spots of high conductivity (electronic or redox) act as precursor sites for initiation of pits. It can be rationalized that iron inclusions are responsible for the high susceptibility of Nd–Fe–B magnets to pitting corrosion. In the case of our magnets prepared from wastes and by powder blending technology, the presence of iron inclusions was not detected [2, 12].

4. Conclusions
The easily corroding materials Nd-Fe-B magnets would suffer from rapid oxidation involving the development of pits.

The overall corrosion values - corrosion potential values, polarization resistance and approximate average corrosion rate were determined based on polarization measurements of the selected magnet samples made according to standards in the aqueous solution 0.1 M NaCl. Furthermore, a pitting resistance corrosion test was conducted and the values of pitting and repassivation potential were determined in a conventional manner. Non-alloyed low-carbon steel was used for comparison with magnets, compared to which it demonstrated greater resistance. An order of the individual parameters and types of corrosion was made depending on the resistance of the magnetic materials.

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References
[1] Zakotnik M and Tudor C O 2015 Waste Manag. 44 48
[2] Kolchugina N B, Prokofev P A, Skotnitsova K, Burkhanov G S, Kursa M, Zheleznyi M V, Dormidontov N, Cegan T, Bakulina A S, Koshkidko Yu S and Smetans B 2020 *Materias* **13** (14) 3049

[3] Gurrappa I, 2006 Corrosion Eng. Sci. Technol. 2006, **41**(1), 57

[4] Li J J, Li A H, Zhu M G, Pan W and Li W 2011 *J. Appl. Phys.* **109** (7) 07A744

[5] Tu S J, Yan M, Cui X G, Ni J J and Jin Y B A 2010 *Rare Met. Mater. & Eng.* **39** (10) 1777

[6] Wu Y R, Ni J J, Ma T Y and Yan M 2010 *Physica B-Condensed Matter* **405** (16) 3303

[7] Ni J J, Ma T Y, and Yan M 2010 *J. Magn. Magn. Mater.* **322** (22) 3710

[8] Wu Y R, Ni J J and Yan M 2010 *Rare Met. Mater. & Eng.* 39 (Suppl. 1) 487

[9] Liu W Q, Yue M, Wang G P, Zhang D T and Zhang J X 2010 *Corrosion* **66** (5) 055004

[10] Madaah Hosseini H R, Dadoo A, Dolati A and Kianvash A 2006 *J. Alloys Compd.* **419** 337

[11] Guo S, Zhou Q Y, Chen R J, Lee D and Yan A R 2011 *J. Appl. Phys.* **109** (7) 07A734

[12] Lukin A A, Kolchugina N B, Burkhanov G S, Klyueva N E and Skotnicova K 2013 *Inorg. Mater. Appl. Research* (4) 256

[13] Malik M A and Kulesza P J 2007 *Analyt. Chem.* **79** (11) 3996