

Powder Surface Modification as a Method of Corrosion Rate Limitation of the Magnetic RE-M-B Composite in an Acid Medium with Different pH

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Abstract. This paper presents the results of research on the effects of chemical treatment of the magnetic powder particles surface on the corrosion resistance of composites based on $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder bonded with an epoxy resin. In the studies, a magnetic material formed of a commercial MQP-B powder has been used and subjected to chemical modification in such aqueous solutions as acetic acid, EDTA, citric acid and oxalic acid. Chemical treatment of the powder particles surface was applied for etching the oxide paramagnetic phases formed on the surface as an effect of spontaneous oxidation of the alloy elements (Nd and Fe) in the presence of oxygen and moisture. On the basis of changes in the polarization resistance value, which were recorded for a series of samples in 0.5M acidic sulphate solutions (pH = 2, 3 and 4), it has been found that the proposed pre-treatment has beneficial effect on the stability of the material in acid environments.

Introduction

Magnetic permanent RE-M-B materials contain rare earth metals (RE, e.g. Nd, Dy) and transition group metals (M, e.g. Fe, Co, Ni) in their composition, which ensures excellent magnetic properties. Due to a wide range of possibilities to control functional properties by production technologies, this kind of magnetic materials are successfully used in various technical fields (elements of hard drives, equipment devices in cars, components of qualified equipment for magnetic resonance imaging, retention systems in dentistry, orthodontics, prosthetics, etc.) [1-3]. The major limitation to their use is unsatisfactory stability under the use conditions. A multi-phase structure, segregation of chemical components, large differences in electrochemical potential of individual phases and considerable porosity are the main causes of poor resistance to corrosion and a significant degradation of the structure [4-7]. The unique properties of the RE-M-B magnetic material are determined by the presence of the $\text{RE}_2\text{M}_{14}\text{B}$ ferromagnetic phase (2:14:1, e.g. $\text{Nd}_2\text{Fe}_{14}\text{B}$). On the other hand, phases enriched with boron (B-rich) and neodymium (Nd-rich) are also present in a typical structure of the RE-M-B sintered materials [1, 3-9]. Segregation of B and Nd in the structure is the reason why the phase which contains approx. 95% of neodymium is considered to be the one that is most easily degraded - the most active phase, whereas the phase in which boron is the predominant component is considered as the most noble. The structure modeling is possible by using alloying additives, which together with neodymium create more noble phases. Co, Ni and Cu [3, 5, 8] have to be among the most commonly used alloying additives (which replace the alloy composition of the main component, i.e. Fe). Other methods of reducing corrosion susceptibility of the RE-M-B materials are focused on the use of various production technologies. Among them, magnetic powders consolidation using a metal of low melting point or of an organic binder (epoxy resin, polyester resin, nylon) are worth mentioning. Magnetic powder bonding with an organic binder (caring about sufficient homogenization of the components), makes it possible to isolate individual powder particles, which is particularly important for powders of an alloy containing a large amount of Nd [4,

6, 9]. It is known that alloys based on rare earth metals easily oxidize even in the presence of trace amounts of oxygen and moisture [10,11], and the presence of paramagnetic oxide phases on the powder particles surface adversely affects the adhesive connections stability, and thus resistance to corrosion of bonded magnets [6,10]. Increasing the adhesion of the binder to the surface of the particles of magnetic powder has beneficial effects on many levels as it reduces porosity structure and limits the penetration of the corrosive medium into the material. The use of appropriate chemical modification of the magnetic powder particle surface prior to the consolidation process can help to improve not only corrosion resistance but also mechanical properties and magnetic material. It should be noted that reducing the corrosion rate of materials based on rare earths is becoming an increasingly important aspect. Technologies for the recovery of rare earths from used equipment are already being sought [12, 13].

The aim of this study is to determine the effectiveness of powder particle surface modification (chemical modification) and its effect on the corrosion rate. To evaluate the effect of a bonded magnetic material on corrosion properties, a series of tests in the solution of 0.5M Na₂SO₄ acidified to pH = 2, 3 and 4 were carried out.

Experimental

The Nd-M-B magnetic powder-based composite with the MQP-B manufacturer symbol (Magnequench) and Nd₁₂Fe₇₇Co₅B₆ chemical formula (subscripts indicate atomic percentages) has been used as the experimental material. According to the manufacturer information, the powder was prepared in three main steps: rapid solidification of the alloy from a molten state, thermal treatment of the received tapes (short-term annealing at the temperature of 600 °C) and mechanical crushing. Heat treatment allows for obtaining a nanocrystalline structure of the intermetallic compound, single-phase Nd₂M₁₄B structure (M - transition metal) and mechanical fragmentation results in the "lamellar" powder particles shape. As the presence of oxides on the powder particles surface may considerably limit the adhesion of the binder to the surface, the powder was subjected to preliminary etching. Digestion of the powder was carried out in aqueous solutions and this process can be seen as a type of chemical modification of the powder. As the etching media were selected aqueous solutions of the compounds strongly complexing metal ions or weak acid anions of the complexing properties, as follows: acetic acid, sodium edetate (EDTA), citric acid, oxalic acid.

The etching of the Nd₁₂Fe₇₇Co₅B₆ powder aimed at removing paramagnetic oxide phases, which are formed on the powder surface during storage under exposure to air and humidity. The powder was digested in a solution of acetic, citric and oxalic acid until the appearance of the first bubbles of gas (H₂) at the surface of the powder particles. Exposure times were various for different applied solutions. For solutions of acetic, citric and oxalic acid it was approx. 20, 15 and 5 minutes (at 20 °C).

The prepared magnetic powder has been bonded by two kinds of epoxy resins in the form of acetone solutions. In both cases the resin content in the magnetic composite was 2.5 wt. %: epidian 100 (Method B) - thermosetting resin, (Method C) – chemosetting resin. Resins used as a binder have been prepared as an acetone solution, to cover the surface of the powder particles with a thin adhesive layer (microencapsulation), thereby increasing the homogenization of the composition. For epoxy resin cure, the samples made with the B method have been annealed at 180°C for 2 h and the samples prepared with the C method have been allowed to stand for 48 hours in a dessicator. The effect of the powder surface etching has been determined on the basis of potentiokinetic tests and characteristic parameters of magnetic materials in sulphate solutions having three different pH values. The corrosion current density has been appointed by two methods: the method of extrapolation of Tafel's straight sections and the polarization resistance method based on linear overvoltage changes at potentials close to the corrosion potential - accordingly to the Stern-Hoar equation.

Results and discussion

The corrosion current density values (i_{corr}) determined by the anode Tafel plot extrapolation, and by polarization resistance are shown in Tables 1 and 2, while Figure 1 illustrates the $\log i_{\text{corr}}$ relation in pH function. In all the presented cases (Figure 1), the increase of pH leads to a reduction in corrosion rate and the slope of a linear relation ($\log i_{\text{corr}} = f(\text{pH})$) for i_{corr} values appointed by the Tafel plot extrapolation is approx. $-0.67 \div -0.40$, which is in analogy with literature data for pure iron (at $\text{pH} = 0 \div 2$). In contrast, the slope of a linear relation ($\log i_{\text{corr}} = f(\text{pH})$) for i_{corr} values appointed by polarization resistance has a value of $-0.30 \div -0.17$.

Table 1. The values of the parameters determining the corrosion resistance of the materials from the $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder in sulphate solutions of pH 2, 3 and 4. The powder $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ priory bonding coated with a film of thermosetting epoxy resin – the B method

0.5 M SO_4^{2-}	modifying solution	E_{corr} [V]	i_{corr} extrapolation [$\text{mA}\cdot\text{cm}^{-2}$]	R_p [$\Omega\cdot\text{cm}^2$]	i_{corr} resistance polarization [$\text{mA}\cdot\text{cm}^{-2}$]
pH = 2	without modification	-0.58	2.5	3.9	3.3
	acetic acid	-0.56	2.4	4.0	3.3
	EDTA	-0.66	2.8	5.0	2.6
	citric acid	-0.58	2.1	5.4	2.4
	oxalic acid	-0.58	2.0	5.4	2.4
pH = 3	without modification	-0.60	0.73	7.6	1.7
	acetic acid	-0.62	0.71	9.1	1.4
	EDTA	-0.67	0.99	7.2	1.8
	citric acid	-0.62	0.89	9.7	1.3
	oxalic acid	-0.60	0.65	9.9	1.3
pH = 4	without modification	-0.66	0.29	19	0.91
	acetic acid	-0.64	0.18	20	0.87
	EDTA	-0.68	0.28	18	0.97
	citric acid	-0.64	0.10	22	0.79
	oxalic acid	-0.65	0.087	24	0.73

As it can be seen, the differences in inclination are quite significant. It seems that the main cause lies in the accepted method of determining i_{corr} value, not taking into account the course of curves in the cathodic field. The fact that the hydrogen evolution (consumption of H^+ ions) in the cathode area must lead to an increase in pH near the surface, the stronger then pH of the solution (with stronger buffer capacity of the solution). It can therefore be expected that the actual value of the pH at the surface (pH_s) varies in time (during a reference potential). In the highly cathodic potential range, the value of pH_s may be, for example, 1-2 units higher than in the solution volume (pH_v). With changes in the potential (E) through the anode range, due to rapid mixing forces probably $\text{pH}_v \approx \text{pH}_s$. Because the polarization resistance method takes into account the cathode/anode transition, one can guess that this method is more subject to errors caused by the increase of the pH near the surface. On the other hand, it should be noted that the value of the $\partial \log i_{\text{corr}} / \partial \text{pH}$ partial derivative of iron decreases with the increasing pH. The literature values of the derivative at $\text{pH} = 2$ are close to 0.4, hence it is not entirely clear whether measurements using the polarization resistance of the $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ ($-0.3 \div -0.17$) alloy are less reliable. The lowest corrosion rate values in the sulfate solution (Table 1 and 2) were observed for the bonded magnetic material based on powder whose

surface was pre-etched in an aqueous solution of citric acid and oxalic acid. The $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder etching in a solution of acetic acid has little effect on the corrosion inhibition of the fabricated composite, while the corrosion current density of the composite based on the powder whose surface was modified with EDTA has comparable or higher values than the magnetic powder in the supply condition.

Table 2. The values of the parameters determining the corrosion resistance of the materials from the $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder in sulphate solutions of pH 2, 3 and 4. The powder $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ priory bonding coated with a film of chemosetting epoxy resin – the C method

0.5 M SO_4^{2-}	modifying solution	E_{corr} [V]	i_{corr} extrapolation [$\text{mA}\cdot\text{cm}^{-2}$]	R_p [$\Omega\cdot\text{cm}^2$]	i_{corr} resistance polarization [$\text{mA}\cdot\text{cm}^{-2}$]
pH = 2	without modification	-0.57	2.4	4.7	2.8
	acetic acid	-0.57	2.1	5.2	2.5
	EDTA	-0.61	2.5	4.8	2.7
	citric acid	-0.57	1.9	6.5	2.0
	oxalic acid	-0.57	1.7	6.5	2.0
pH = 3	without modification	-0.63	0.82	8.8	1.5
	acetic acid	-0.64	0.79	10	1.3
	EDTA	-0.70	0.69	13	1.0
	citric acid	-0.63	0.55	16	0.81
	oxalic acid	-0.62	0.51	18	0.72
pH = 4	without modification	-0.66	0.15	17	1.0
	acetic acid	-0.65	0.12	21	0.83
	EDTA	-0.69	0.18	16	1.1
	citric acid	-0.65	0.091	23	0.76
	oxalic acid	-0.64	0.077	24	0.73

Among the used solutions, EDTA has the strongest complexing facilities and acetic acid the weakest. It should be noted that EDTA (edentate sodium salt) is almost neutral (pH \sim 7), while the other solutions of organic acids have a pH \approx 2 (out of the three selected acids, the oxalic acid has relatively maximum power).

The most beneficial powder etching effect of the oxalic acid should therefore be attributed to both considerable acidity (pH $<$ 2) and good complexing ability of metal cations. The process of oxide phases removing from the surface of the powder particles involves acid digestion, wherein the complexing anions stimulate this process and do not allow for passivating the surface of the particles.

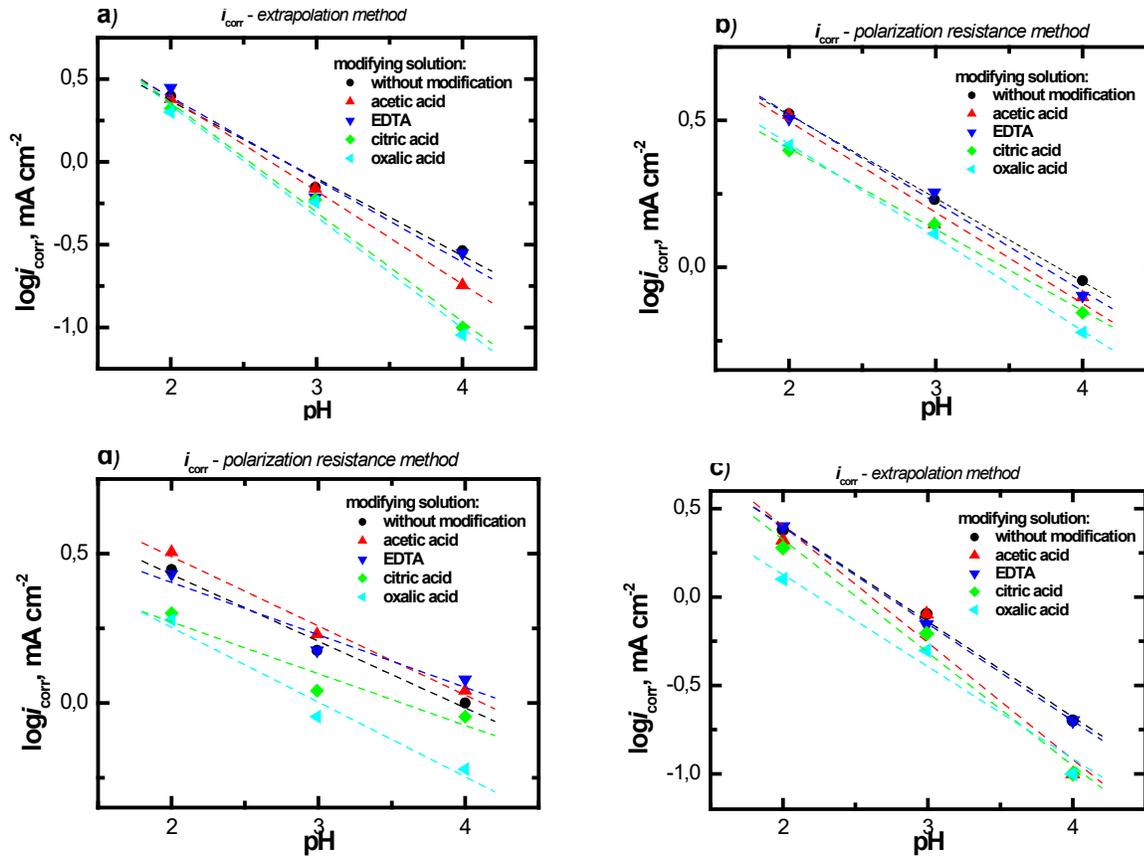


Fig. 1. The corrosion rate of magnetic materials as a function of 0,5 M SO₄²⁻ solution pH (i_{corr} value determined by: a, c) extrapolation, b, d) polarization resistance): a, b) - the B method; c, d) - the C method

Conclusions

The presented results show that chemical treatment of a powder particles surface in a complexing acid solution quite significantly improves corrosion characteristics of magnetic materials based on Nd₁₂Fe₇₇Co₅B₆, as evidenced is the reduction in the corrosion current density and polarization resistance increase in the sulphate environments. Removal of oxide phases spontaneously arising during storage in air from the surface of a powder ensures good adhesion of the binder directly to a metal substrate, effectively reducing the contact of individual particles in the composite structure. The elimination of oxide layers prevents the formation of gaps between particles and the binder in the conditions of acidic environment, which obviously inhibits corrosion processes.

References

- [1] R. Ulewicz, E. Wysocka, Magnets: History, the current state and the future, METAL 2015 - 24th International Conference on Metallurgy and Materials, Conference Proceedings, 1680-16862, Brno, Czech Republic
- [2] P. Ceruti, S. Ross Bryant, Lee Jun-Ho, M.I. MacEntee, Magnet-Retained Implant-Supported Overdentures: Review and 1-Year Clinical Report, J Can Dent Assoc. 76 (2010) 52

- [3] John J. Croat, Rapidly Solidified Neodymium-Iron-Boron Permanent Magnets, Elsevier Science, Woodhead Publishing Series in Electronic and Optical Materials, 2017
- [4] K. Loewe, D. Benke, C. Kübel, T. Lienig, K.P. Skokov, O. Gutfleisch, Grain boundary diffusion of different rare earth elements in Nd-Fe-B sintered magnets by experiment and FEM simulation, *Acta Materialia*, 124 (2017) 421–429. <https://doi.org/10.1016/j.actamat.2016.11.034>
- [5] T. T. Sasaki, T. Ohkubo, K. Hono, Structure and chemical compositions of the grain boundary phase in Nd-Fe-B sintered magnets, *Acta Materialia*, 115 (2016) 269–277. <https://doi.org/10.1016/j.actamat.2016.05.035>
- [6] D. Klimecka-Tatar, H. Bala, B. Ślusarek, K. Jagielska-Wiaderek, The effect of consolidation method on electrochemical corrosion of polymer bonded Nd-Fe-B type magnetic material, *Arch Metall Mater*, 54/1 (2009)247-256
- [7] G.A.Zickler, P. Toson, A. Asali, J. Fidler, Nanoanalytical TEM Studies and Micromagnetic Modelling of Nd-Fe-B Magnets, *Physics Procedia*, 75 (2015) 1442–1449. <https://doi.org/10.1016/j.phpro.2015.12.164>
- [8] L. Z. Zhao, Q. Zhou, J. S. Zhang, D. L. Jiao, Z. W. Liu, J. M. Greneche, A nanocomposite structure in directly cast NdFeB based alloy with low Nd content for potential anisotropic permanent magnets, *Materials & Design*, 117 (2017) 326–331. <https://doi.org/10.1016/j.matdes.2017.01.008>
- [9] K. Radomska, G. Pawłowska, D. Klimecka-Tatar, Profilometry surface analysis of bonded magnets based on biencapsulated Nd-(Fe,Co)-B powder, *Ochrona przed Korozją* 4 (2014) 142-146
- [10] D. Klimecka-Tatar, G. Pawłowska, M. Sozańska, The Effect of Powder Particle Biencapsulation with Ni-P Layer on Local Corrosion of Bonded Nd-(Fe,Co)-B Magnetic Material, *Archives of Metallurgy and Materials*, 60/1 (2015) 153-157. <https://doi.org/10.1515/amm-2015-0024>
- [11] A. A. El-Moneima, O. Gutfleisch, A. Plotnikov, A. Gebert, The Influence of Co and Ga on the Corrosion Behavior of Nanocrystalline NdFeB-Based Magnets *J. Magn. Magn. Mater.* 248 (2002) 121-133. [https://doi.org/10.1016/S0304-8853\(02\)00286-X](https://doi.org/10.1016/S0304-8853(02)00286-X)
- [12] K. Kapustka, G. Ziegmann, D. Klimecka-Tatar, Technological and ecological safety in aspect of chemical properties of recycled neodymium magnets – electric motors and hard disk, *Production Engineering Archives*, 17/ 4 (2017) 36-39. <https://doi.org/10.30657/pea.2017.17.08>
- [13] K. Kapustka, G. Ziegmann, S. Sdrenka, T. Elwert, D. Klimecka-Tatar, Microscopic characteristic of Nd-Fe-B magnets structure - magnets recovered from electric motors, *Archiwum Wiedzy Inżynierskiej*, 2/1 (2017) 39-41