Chapter 3

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VERIFICATION OF Nd-(Fe,Co)-B PARTICLE POWDER BIENCAPSULATION METHOD BASED ON IMPEDANCE MEASUREMENTS

Abstract: In the paper the effect of the biencapsulation metod with Ni-P/epoxy resin and phosphate/epoxy resin on corrosion resistance of bonded magnets – based on impedance spectra. The values of charge transfer resistance of materials made of powder coated with binder (encapsulation with epoxy resin) in relation to the value of the resistance of materials made of powder after biencapsulation (with NiP/epoxy resin, phosphate/epoxy resin) are larger, reflecting the inhibition of corrosion.

Key words: biencapsulation, corrosion resistance, impedance

3.1. Introduction

The unique magnetic properties of RE-M-B materials makes that their attractiveness is not decreasing over the years. Over the time, these materials were subject to modification in terms of chemical composition, structure and there are also developed of new methods for magnets preparation. In Following this change underwent their properties, which are a derivative of manufacturing technology (KASZUWARA W. 2003., PAWŁOWSKA G. 2011).

In most of the methods used for the RE-Fe-B materials preparation in first step the highcoercivity powders is obtained (each single powder particle is a magnet). The material in this form is not applicable in practice. Therefore, it is necessary to consolidate the powder to obtain a solid material with predetermined shape, mechanical properties and the

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most apparent density, while preserving an optimized phase structure. Due to the fact that small grains have a metastable character the consolidation method using a high temperature have limited application (e.g., in this way cannot be obtained the nanocrystalline materials, couse the grain growth at elevated temperatures results in loss of magnetic properties of these materials). Bonded RE-Fe-B materials are usually performed through powders consolidation by mechanical alloying (MA), mechanical milling (MM) or by binding with organic binder powders formed from rapidly cooled (rapid solidification - RS). For the production of composite magnetswhere the the binder is a polymeric material, there are two methods of molding: injection or compression (LEONOWICZ M., WYSŁOCKI J.J. 2005, ŚLUSAREK B. 2001). In the first method into the mold the mixture of the magnetic powder with plasticized polymer is injected. While the second method involves compressing a powder composition of the hard magnetic with chemically- or thermosetting resins. To the binder most commonly used are included epoxy resins. The epoxy resin are fragile solids or viscous liquids which just due to cross-linking during the setting process become insoluble and infusible polymeric materials with high mechanical strength, good dielectric properties, thermal insulation, and high chemical resistance. A characteristic feature of structural epoxy resin is an epoxy group (also called etoksylinową, oxirane), a three-membered ring composed of two carbon atoms and one oxygen. Due to the number of epoxy groups, the resins can be divided into low molecular weight and high molecular weight. The first group of chemically set resins are resins which hardening takes place by reaction with a suitable coupling so-called activator - crosslinking agent (e.g., Z1) and the second group of resins are thermosetting resins, wherein the crosslinking of the resin is thermally activated.

According to the Ślusarek (ŚLUSAREK B., DUDZIKOWSKI I. 2002), to maintain good magnetic properties the required minimum content of the resin to bind powder particles is 2.5 wt%. Additional ingredients may be incorporated into the base composition of the magnetic powder and resin in order to control the mechanical and magnetic properties of the final product (DOBRZAŃSKI L. A., DRAK M. 2004).

The pressure produced during compression should be sufficient to under influence of powder particles be easily packed and binder filled spaces between the particles precisely. Discontinuities in the form of pores in the structure of the magnets are exposed to corrosive environments, especially where adjacent powder particles are not tightly coated with resin. While too high pressure makes that the flake particles are breaking, at the same time within the individual particles appear microcracks (KLIMECKA-TATAR D., BALA H., ŚLUSAREK B., JAGIELSKA-WIADEREK K. 2009).

The consolidated materials with resin, are characterized by a high resistance to acid corrosion due to the powder particles isolation. This allows for a significant reduction (advantage over sintering) the threat of selective corrosion occurring due to the rapid dissolution of neodymium phase (present at the grain boundaries of sintered magnets). In contrast, bounded materials have a density much lower than the sintered material. Obtained bonded magnets have a density less than the theoretical caused mainly by binder additive but also by the formation of voids in the structure of the magnet, void which are not filled by either the binder or the small particles of the powder.

In the technological process of bonded magnets main difficulty is that, in the presence of small amounts of oxygen magnetic powders (comprising highly active rare-earth element) are oxidized rapidly, and the presence of paramagnetic oxide phases on the surface of powder particles has a negative impact on the properties of the magnets (ŚLUSAREK B., KLIMECKA-TATAR D., BALA H., GĘSIARZ K. 2005, GUTFLEISCH O., DRAZIC G., MISHIMA C., HONKURA Y. 2002, GARRELLA M., SHIHB A.J., MA M., LARA CURZIOD E., SCATTERGOODE R.O. 2003). Surface oxidation of the powder particles takes place both in the preparation and hardening of powder compacts prepared at elevated temperatures (ok. 150 - 200ºC).

It should be noted that the oxides in the powder material can be regarded as desirable or undesirable, depending on the stage of the manufacturing process. Oxide layer in the preparation of the powder may be desirable as it may reduce the risk of explosion of powder during the contact with the air. The ideal scenario is one where oxide is present during the preparation of the powder, and then removed before the stage of consolidation.

The presence of oxide layers on the powder surface may limited high-coercivity wettability of the powder particles surface by the binder. Sufficiently weakly tight-fitting covering powder with binder makes the final material is more porous. The removal of the oxide layer from the surface of the individual particles increases the wettability of the polymer and results in a noticeable improvement in the corrosion resistance of the finished magnet (PAWŁOWSKA G., BALA H., SZYMURA S., RABINOVICH YU. M. 1999, PAWŁOWSKA G., BALA H. 1998.). Loosely bound on the surface the oxide products of the magnetic powder can be removed by etching. The beneficial effect of digestion on the corrosion resistance of the material found in the works (KLIMECKA-TATAR D., BALA H., ŚLUSAREK B., JAGIELSKA-WIADEREK K. 2009, KLIMECKA-TATAR D. 2009).

The consolidation process of high-coercivity powder particles with resin reduces to some extent the access of oxygen and moisture to the surface of materials, however, uneven distribution of the binder does not protect it enough. To prevent re-oxidation of the surface of the powder particles is necessary to protect them by applying a protective coating. Isolation with two layers of powder particles (biencapsulation) layer of protective coating (inorganic or metallic) and tight with a layer of resin (bonding material) effectively reduces the corrosion rate of bonded magnets RE-MB (KLIMECKA-TATAR D., PAWŁOWSKA G., SZYMURA S. 2010).

The aim of this study was to compare the effect of biencapsulation with NiP/epoxy resin and phosphate/epoxy resin coating on the corrosion resistance of bonded magnets based on impedance measurements.

3.2. Experiments

3.2.1. Material preparation methodology

Bonded magnetic materials were prepared from commercial powder RE-M-B. The powder contained 12% at. Nd, 5% at. Co, 77 % at. Fe, 6 % at. B, and was produced by rapid solidification from the liquid alloy. In the process, the amorphous strip are mechanically ground, and in order to obtain a nanocrystalline structure undergo heat treatment at a temperature of approximately 600°C.

The preliminary stage of speciments preparation were the powder particles surface etching in a 5% oxalic acid aqueous solution. To protect the surface of the fabricated powder against atmospheric agents in the later stages of sample preparation used the methods of encapsulation and biencapsulation. The first method of encapsulation has been carried out to applying the protective layer of Ni-P, while the second type of encapsulation method had to create the phosphate conversion layer. The encapsulation of powder with Ni-P coating was carried out in an universal bath containing in its composition $NiCl_2 \cdot 6H_2O$, NH_4Cl, $NaH_2PO_2 \cdot H_2O$, and sodium citrate - deposition was carried out at 90°C for 5, 15 or 30 minutes. However, the encapsulation process with phosphate coating was carried out in a bath of the phosphate of two different pH values: 3 or 7 - in both cases the phosphating time was 72h.

The effect of the powder particles biencapsulation obtained through the use of an acetone solution of a thermosetting epoxy resin, which after evaporation of the solvent particles uniformly cover the surface. The concentration of the acetone solution and the procedure has been designed in such way that the content of binder in the composition (after evaporation of acetone) was 3 mass %. In order to shape samples, the compositions of powder pressed at a pressure about 800 MPa, and were annealed at 180°C for 2 hours to setting the resin. The test specimens have the shape of cylinders with the following dimensions: $ø = 5$ mm and $h = 10$ mm.

3.2.2. Impedance measurements

Impedance measurements were performed in 0.5 M sulfate solution acidified to pH = 3.0, at open circuit potential mode, without stirring. Measurement was started after 1.5 hours from the time of immersion into the solution. At this time, the corrosion potential were determined and constant - indicating almost stationary condition, necessary for the correct interpretation of the results. The tests were performed using a set of CHI Instruments. Measurements carried out in a three-electrode system, wherein the reference electrode was a saturated calomel electrode and the auxiliary electrode - platinum grid. Used frequencies in the 0.01-10000 Hz. The amplitude of the voltage signal was 10 mV and the results were analyzed using ZSimpWin 3.50.

3.3. The results and discussion

During the galvanic corrosion occur microscopic various processes such as the formation of elementary electrochemical cells, transport of electrons in the electron conductor, an electron transfer at the interface of a charged or neutral molecules as a result of oxidation or reduction reaction, the flow of ions in the electrolyte solution. The intensity of the flow of charged particles in an electric circuit depends on the resistance of the corrosive material and the electrolyte and the intensity of the reaction occurring at the interface of metal - electrolyte. The electrical current present in the system, wherein the electrochemical corrosion processes take place, allows the testing of such circuits by modeling the EIS, with electrical circuits.

Impedance is characterized by a number of parameters, such as: $|Z|$, Z' – real component of impedance, Z''- imaginary impedance component, ω – frequency circular, φ – phase angle, f – signal frequency, which can be represented by different types of dependence. The most commonly used diagrams are: Nyquist diagram (parametric plot of a frequency response used in automatic control and signal processing), illustrates the relationship $Z'' = \mathrm{f}(Z')$ (parameter is the frequency of the AC signal). Commonly used method of data analysis is to match the impedance of electrical equivalent circuit. Determining the electrical and electrochemical properties of the materials and processes based on electrochemical direct relation that exists between the behavior of the real system and its idealized model in the form of an electric circuit. For the analysis of graphs presented In Fig. 3.2-3.3 the $R_1(CPE_2(R_2(CPE_2 (R_3W))))$ electrical impedance equivalent circuit were used (where: R_1 - solution resistance R_2 - the resistance of the electrolyte in the pores, R_3 charge transfer resistance, W - Warburg impedance reproduces the impact of the diffusion of the reactants in the corrosion process.

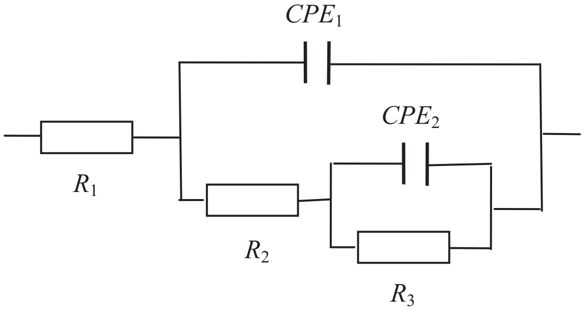

Fig. 3.1. Equivalent circuit used to interpret the impedance spectra obtained for the bonded materials Nd-(Fe, Co)-B based on powder biencapsulated with NiP/epoxy resin and phosphate/ epoxy resin coatings. R_1 – solution resistance, R_2 – electrolyte resistance in the pores, CPE_1 i CPE_2 –fixed angle elements, R_3 – charge transfer resistance.

Source: own study

In Fig. 3.2-3.4 the results if impedance research are presented (in Nyquist’ system). Measuring points are shown beside the points obtained from the equivalent circuit of electrical fitting to experimental data.

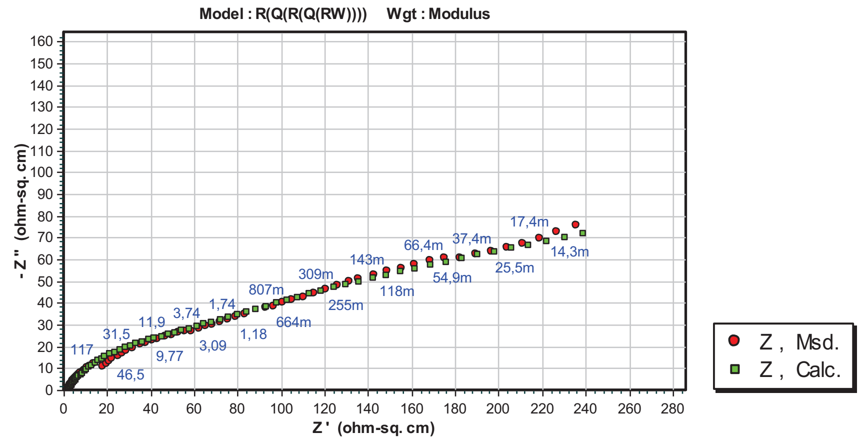

Fig. 3.2. Impedance spectrum of the Nd-(Fe,Co)-B material (powder encapsulation with epoxy resin) in Nyquist' system (per 1 cm^2 area of the sample).

Source: own study

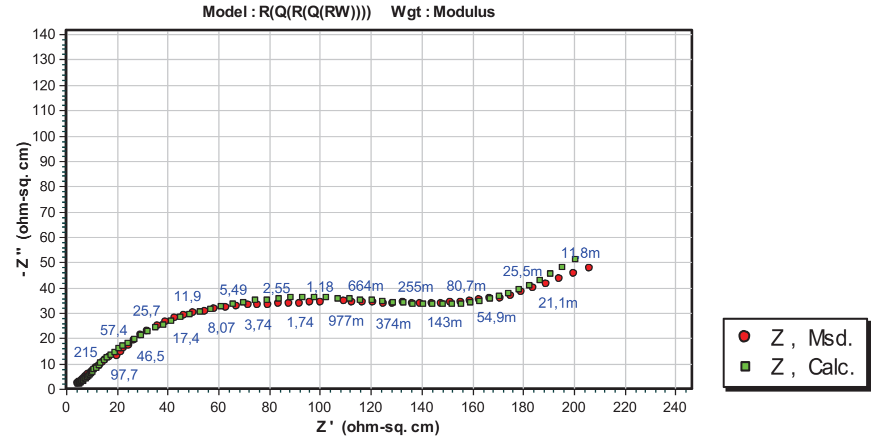

Fig. 3.3. Impedance spectrum of the Nd-(Fe,Co)-B material (powder biencapsulation with Ni-P/epoxy resin) in Nyquist' system (per 1 cm^2 area of the sample).

Source: own study

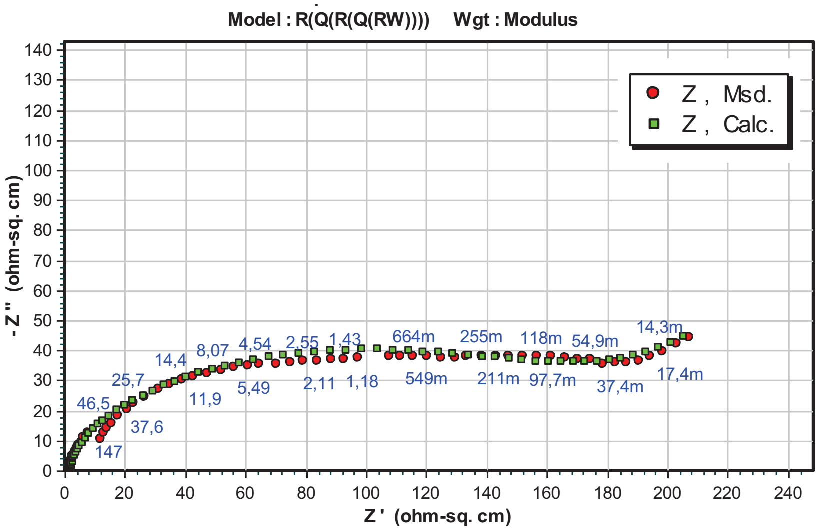

Fig. 3.4. ***Impedance spectrum of the Nd-(Fe,Co)-B material (powder biencapsulation with phosphate/epoxy resin) in Nyquist' system (per 1 cm^2 area of the sample).***

Source: own study

On the graphs representing the results of electrochemical impedance measurements are visible semicircles with center outside the real axis.Such behavior may be associated with inhomogeneity of surface layers (Barsoukow Eds. E., Macdonald J. R. 2005). Significant flattening of semicircle representing on Nyquist diagram experimentally determined, indicates the state of the metal surface and suggests the existence of a surface zone, characterized by a high degree of porosity and surface development. In contrast, linear part of the plot in the low-frequency excitation signal suggests that the corrosion process is controled by the diffusion of reagents. Exposed due to spalling of cracked particles, the surfaces of powders Nd-Fe-B are particularly exposed to destruction, as it is in cases not covered with protective coatings samples (reference - Fig. 3.2).

Powder particles biencapsulated with Ni-P/eopxy resin and phospahte/epoxy resin additionally protected against contact with an aggressive environment. The presence of the coating or the lack of it affects the value of the charge transfer resistance R_3 (Table 3.1).

Table 3.1. The parameters obtained by fitting the electrical equivalent circuit $R_1(Q_1(R_2(Q_2(R_3W))))$

	Encapsulation with epoxy resin, reference (A)	***Biencapsulation with Ni-P/epoxy resin (B)***	***Biencapsulation with phosphate/epoxy resin (C)***
χ^2	$3.3\cdot10^{-3}$	$6.8\cdot10^{-4}$	$3.2\cdot10^{-3}$
R_1, Ωcm^2	$2{,}6\cdot10^{-3}$ ±0,002	$1{,}3\cdot10^{-3}$± 0,003	$1{,}2\cdot10^{-3}$ ±0,002
Y_{o1}	$5{,}4\cdot10^{-3}$± 0,001	$1{,}676\cdot10^{-3}$± 0,0	$2{,}103\cdot10^{-3}$ ± 0,0
n_{01} $(0<n<1)$	0,15 ± 0,04	0,39 ± 0,08	0,43 ± 0,03
R_2, Ωcm^2	2,011 ± 0,5	2,8 ± 0,6	2,6 ± 0,3
Y_{02}	$4{,}3\cdot10^{-4}$ ± 0,0	$2{,}7\cdot10^{-4}$±0,0	$4{,}7\cdot10^{-5}$ ± 0,0
n_{02}, $(0<n<1)$	0,71±0,03	0,7 ±0,08	0,99 ± 0,03
R_3, Ωcm^2	167,1±10,0	183,6±6,8	202,2 ± 4,7
W_3	0,045 ±0,001	0,057±0,004	0,078 ± 0,018

Source: own study

To evaluate the corrosion resistance of the materials based on powder after biencapsulation with NiP coatings/epoxy resin and phosphate/epoxy materials been classified according to increasing values of charge transfer resistance R_3 corresponding to the polarization resistance - inversely proportional to the corrosion rate. Arrangement of the material in the direction of decreasing corrosion resistance (from highest to lowest value R_3) showed that the most effective protection provides a preliminary phosphate coating (Fig. 3.5).

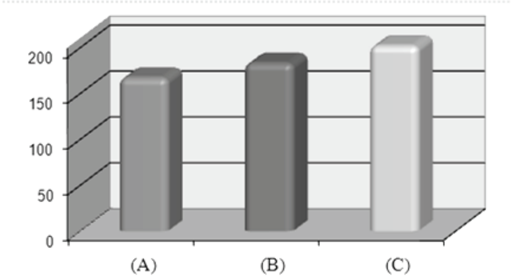

Fig. 3.5. Charge transfer resistance values R_3 of Nd-(Fe,Co)-B bonded magnets based on encapsulated/biencapsulated powder: (A) encapsulation with epoxy resin, (B) biencapsulation with Ni-P/epoxy resin, (C) biencapsulation with phosphate/epoxy resin

Source: own study

3.4. Summary

Application of the powder particles biencapsulation before their bonding process greatly affects on corrosion resistance. The values of charge transfer resistance of materials made of powder coated with binder (encapsulation with epoxy resin) in relation to the value of the resistance of materials made of powder after biencapsulation (with NiP/epoxy resin, phosphate/epoxy resin) are larger, reflecting the inhibition of corrosion.

Such a limitation of the corrosion process can results from tight insulation of the $Nd_{12}Fe_{77}Co_5B_6$powder particles from the external environment. The coatings on the powder particles to a certain extent limited penetration of corrosive media into the structure of the material. It should be noted that the biencapsulation application is not limited in case of damaged or crushed metallic particles but it can significantly reduce the further penetration of corrosive medium into the composite.

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