

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

BIENKAPSULACJA CZĄSTEK PROSZKU POWŁOKAMI Ni-P JAKO SPOŚÓB POPRAWY ODPORNOŚCI WIĄZANYCH MAGNESÓW Nd-(Fe,Co)-B NA KOROZJĘ LOKALNĄ

Effect of the Nd-(Fe,Co)-B powder particle biencapsulation with Ni-P layer on bonded magnetic materials corrosion behaviour has been investigated. Bonded magnets were prepared from single-phase, nanocrystalline magnetic $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder. Powder particles before consolidation were preliminary etched and then coated with bilayer (powder biencapsulation). The powder surface was coated as a first with autocatalytic applied Ni-P layer during 5, 15 and 30 minutes in Ni(II) containing bath and the second layer was thermosetting epoxy-resin. Impact of the used biencapsulation process was rated on the basis of polarization curves recorded in phosphate environment with addition of chloric ions. It has been established that the used biencapsulation method satisfactorily isolate individual particles of the powder and consequently, significantly inhibits corrosion processes of the final material, especially in passivating environment containing Cl^- .

Keywords: Nd-Fe-B bonded magnets, biencapsulation, local corrosion, Ni-P layer

W pracy zaprezentowano wyniki badań nad wpływem bienkapsulacji cząstek proszku powłokami Ni-P/żywica epoksydowa na odporność korozyjną magnesów wiązanych. Materiały magnetyczne zostały przygotowane z jednofazowego, nanokrystalicznego proszku $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$. Cząstki proszku przed konsolidacją były wstępnie trawione, a następnie pokryte podwójną warstwą (bienkapsulacja proszku). Powierzchnia proszku w pierwszej kolejności została poddana 5 i 30 minutowemu autokatalitycznemu nanoszeniu warstw Ni-P. Drugą warstwę stanowił materiał spoiwa, czyli żywica epoksydowa. Dokonano oceny wpływu zastosowanej metody bienkapsulacji na odporność na korozję lokalną na podstawie krzywych polaryzacji zarejestrowanych w środowisku fosforanowym (0,5M, pH = 3) z dodatkiem jonów chlorowy. Stwierdzono, że zastosowane metody bienkapsulacji zadowalająco izolują pojedyncze cząstki proszku, a co za tym idzie, hamują proces korozji materiału końcowego, zwłaszcza w środowisku pasyującym zawierającym Cl^- .

1. Introduction

Highcoercivity materials based on rare earth metals (RE) and transition metals (M), using the properties of intermetallic phases $\text{RE}_2\text{Fe}_{14}\text{B}$ are used for almost 30 years in wide variety of industry (e.g. electronic, automatics, automobiles, computers and medical devices) [1-3]. They are used for many precise and expensive devices, and are many factors have the effect on their applications stability, reliability and durability. They should possess not only advantageous magnetic parameters, but also the required mechanical properties and resistance to the corrosion environment. Improvement of these properties allow to extend lifetime of magnets [3-6]. Among contemporary Nd-Fe-B materials such as sintered magnets, suction casting magnets and bonded magnets, especially interesting are Nd-Fe-B permanent magnets bonded with polymer binder (often called dielectromagnets). Consolidation of hard magnetic powders with dielectric thermo or chemical setting resin

is very promising owing to their advantageous magnetic properties and low material and production costs [7-9]. There are many ways to obtain the magnetic powders, among others, by the hydrogenation/decrepitation/desorption/recombination (HDDR), hydrogenation/decrepitation (HD), mechanical alloying (MA), and also by melt quenching (MQ) methods [1,2]. The main advantages of producing powders by crushing rapidly cooled metallic strips is possibility to produce a magnetic powder with single-phase structure - in this case randomly oriented $\text{RE}_2\text{Fe}_{14}\text{B}$, with high uniaxial anisotropy, which effect on beneficial magnetic properties.

The polymer binder used for making dielectromagnets is able to provide sufficient mechanical strength to hold powder particles together and to improve corrosion resistance as a result of particles isolation [7-11]. The binder dielectric properties also give the ability to use them in direct neighborhood of the fast changing magnetic fields [2]. The properties of Nd-Fe-B bonded magnets depend mainly on their com-

* CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, INSTITUTE OF PRODUCTION ENGINEERING, CZESTOCHOWA, POLAND

* CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF CHEMISTRY, CZESTOCHOWA, POLAND

* SILESIA UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS ENGINEERING AND METALLURGY, POLAND

position: amount of high coercivity powder and epoxy resin concentration as well as manufacturing technology [7]. As it was shown in earlier publications, application of various kinds of resin and various homogenization and pressing method of the composition has a visible effect on the magnetic and mechanical properties, as well as corrosion resistance of these materials [8,9].

Significant problem with Nd-Fe-B magnets is their corrosion susceptibility. It is a consequence of the presence about 30 wt.% of rare earth elements in magnet composition. It is known that the RE elements belong to the most electrochemically active metals (e.g. $E_{Nd^{3+}/Nd} = -2.43$ V) [4,12]. As many authors indicate [4,12-16], in most acidified environments the Nd-Fe-B type material dissolves activationally, which is particularly undesired. However, in acidified phosphate solution, as well as in neutral and alkaline solutions the magnets effectively passivate. Ionic-conductive passive film which is formed on the magnet surface effectively isolates the material from aggressive media [10,13,17]. It is also known that as a result of same accelerated corrosion tests (i.e. boiling water, autoclave or salt spray test) the Nd-Fe-B type magnets easily cover with thin, protective film of oxides or hydroxides (mainly Nd_2O_3 or $Nd(OH)_3$) which is prone to decrease of magnets losses [13,18-21].

The appearance of oxidized paramagnetic phases on powder particles surface decrease adhesive force between powder grains and binder which deteriorates both magnetic properties and corrosion resistance [20] and it is possible to reduce of properties decrease by preliminary powder surface etching in solutions of weak organic acids or complexing agent solutions [8, 22]. To increase the thermodynamic stability of the structural components of the Nd-Fe-B material, the novel process named the biencapsulation is proposed. The biencapsulation is the method used to isolate the particle surface with two layers (bielayer), i.e. metallic layer of protective coating, and thin layer of resin (bonding material) [8,11,13,22].

The purpose of present paper is to evaluate the effect of powder particle biencapsulation method on the local corrosion development in bonded magnetic materials based on Nd-(Fe,Co)-B alloy.

2. Experimental

The bonded magnetic materials were prepared from powder Nd-(Fe,Co)-B. The powder contained 12% at. Nd, 5% at. Co, 77 % at. Fe, 6 % at. B, and was produced by rapid quenching. 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 specimens preparation was the powder particles surface etching in a 5% oxalic acid aqueous solution, analogously to study [8,22]. To protect the etched powder surface against atmospheric agents in the later stages of sample preparation the encapsulation processes were used. 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 effect of the powder particles biencapsulation was obtained through the use of an acetone solution of a thermosetting epoxy resin, which (after evaporation of the solvent) uniformly cover the particles 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 Figure 1 and 2 the image of encapsulated with Ni-P coating and biencapsulated with Ni-P/epoxy resin coating powders are presented.



Fig. 1. Morphology of $Nd_{11}Fe_{77}Co_5B_6$ powder after encapsulation with Ni-P

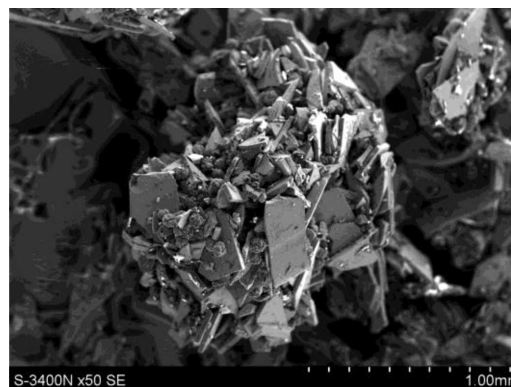


Fig. 2. The agglomerate of $Nd_{11}Fe_{77}Co_5B_6$ powder after biencapsulation with Ni-P/epoxy resin



Fig. 3. The structure of bonded magnets based on $Nd_{11}Fe_{77}Co_5B_6$ powder after biencapsulation with Ni-P/epoxy resin

After powder treatment composition was pressed under the pressure of 800 MPa [9] and the cylindrical shaped samples ($\phi = 5$ mm and $h = 10$ mm) were annealed at 180°C for 2 hours to setting the resin. In Figure 3 the structure of bonded magnet is presented.

The influence of biencapsulation method with Ni-P/epoxy resin coating on corrosion behaviour has been evaluated according to the potentiokinetic polarization curves measured in 0.5 M phosphate acidified to pH = 3 solution containing 0.001 ± 0.1 M of chloride ions. Potentiokinetic tests have been carried out in temperature of 20°C and the disk electrode rotation speed equal to 21 rps., with potential change from cathodic to anodic direction, ranging from -1.5V to +2.0V with a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$. All potentials are expressed vs. Ag/AgCl auxiliary electrode.

3. The results and discussion

The corrosion resistance of examined samples based on $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder biencapsulated with Ni-P/epoxy resin was determined on the basis of potentiokinetic test, which resulted in polarization curves. From the course of curves were read the following values: E_{corr} (V) – corrosion potential, $i_{\text{min,pass}}$ (mA/cm^2) – minimal value of current density in passive range and E_{pit} (V) – pitting potential.

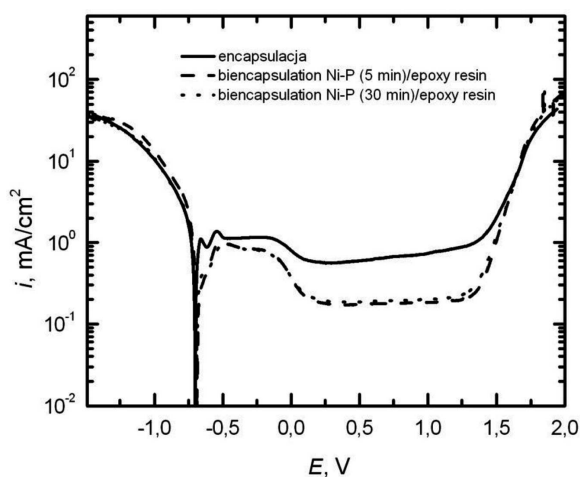


Fig. 4. Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Ni-P/epoxy resin) $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3), 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps

In Fig. (4-8) the polarization behaviours of the tested samples in 0.5 M phosphate solution containing 0 ± 0.1 M chloride ions are presented. As it has been shown in our previous papers the RE magnets passivate effectively in acidified phosphate solutions, most probably due to formation of insoluble layer of lanthanide phosphates on corroding surface. In case of sintered and nanocrystalline Nd-Fe-B magnets, in phosphate solutions anodic currents within a passive range were found on the order of $10^{-1} \text{ mA}/\text{cm}^2$. As its results from Figures, anodic currents in passive range for epoxy resin bonded magnets are tenfold greater, as confirms general property of compacted metal powders to show limited resistance in passive state [26].

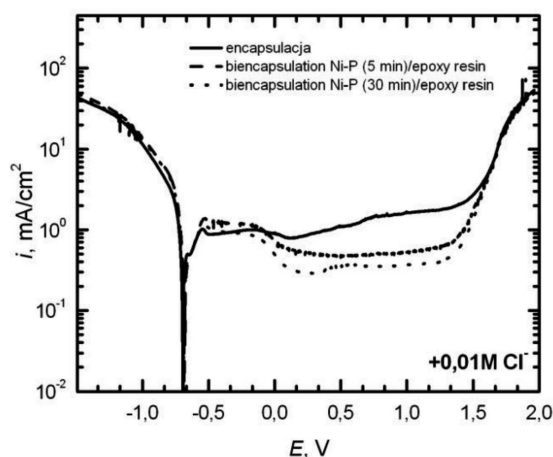


Fig. 5. Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Ni-P/epoxy resin) $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0,01 M Cl^- addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps

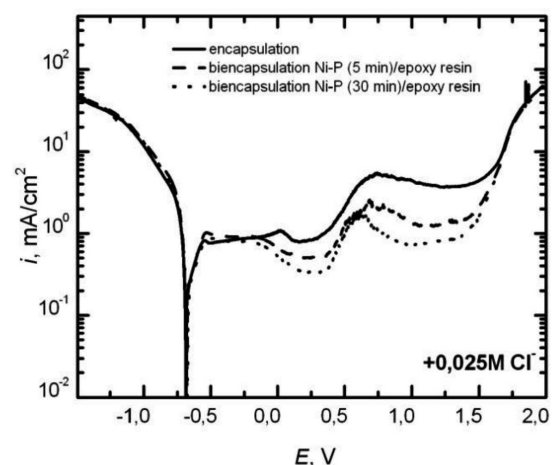


Fig. 6. Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Ni-P/epoxy resin) $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0,025 M Cl^- addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps

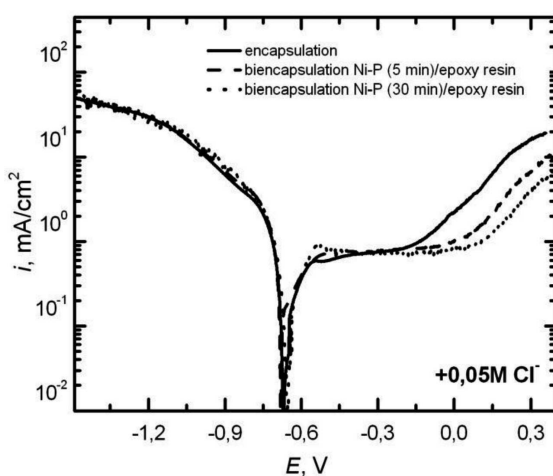


Fig. 7. Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Ni-P/epoxy resin) $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0,05 M Cl^- addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps

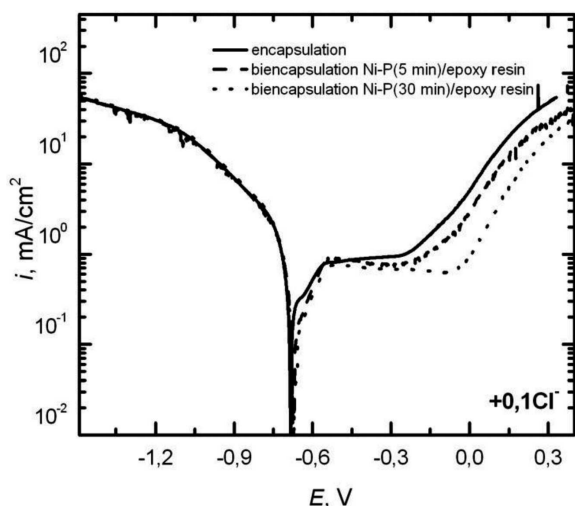


Fig. 8. Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Ni-P/epoxy resin) $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder. Experimental conditions: 0.5 M phosphate solutions ($\text{pH} = 3$) with 0.1 M Cl^- addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps

From the course of curves shows that the applied powder coating technologies (biencapsulation with Ni-P/epoxy resin) have not substantial effect on the cathode curves course and the value of the corrosion potential varies in the range of -0.67 V to -0.69 V (Fig.4). The differences are observed after crossing the corrosion potential ($E_{\text{corr}} = -0.67 \div -0.69$ V) in the passive state. The anodic current density in the passive range in phosphate solution for the sample after encapsulation, is only about 0.55 mA/cm². While for samples after biencapsulation when autocatalytically applying the Ni-P coating the current value of: 0.17 mA/cm² for 5 min bath. and 0.18 mA/cm² for 30 min bath. Above the potential of 1.4 V is observed a rapid increase in the anodic current density, due to the evolution of oxygen (Fig. 4).

The following curves (Fig. 5 and 6) show that both the addition of 0.01 M Cl^- and 0.025 M Cl^- do not change the potential range of the material passive state. Thus, in those cases the contents of chloride ions do not even breakdown the passive layer. However, it should be noted that in both cases, the current density in the passive state distinctly increase. Thus with the addition of 0.01 M Cl^- sample after encapsulation minimum current in passive state ($i_{\text{min,pass}}$) is 0.76 mA/cm² and for samples after biencapsulation with Ni-P/epoxy resin (5 min) $i_{\text{min,pass}} = 0.47$ mA/cm² and (30 min) $i_{\text{min,pass}} = 0.27$ mA/cm². With the chloride ion content of 0.025 M (Fig. 7) the further increase of the current density in the passive range is observed. With concentration of chloride ions equal to 0.05 M Cl^- the beginning of local corrosion is observed. The pitting nucleation potential (E_{pit}) to the sample after encapsulation equal about -0.150 V for the samples after biencapsulation with Ni-P/epoxy resin 0.015 V (5 minute) and 0.081 V (30 minute) (Fig. 7). Further increase in the concentration of chloride ion results in more negative values of pitting potential. For a concentration of 0.1 M Cl^- break of the passive layer for samples after encapsulation is visibly in potential value -0.21 V, for the samples after biencapsulation in -0.14 V (5 min) and -0.03 V (30 min) (Fig. 8).

4. Conclusions

- The use of a $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder particles two-step coating (biencapsulation with Ni-P/epoxy resin) before the process of bonding, positively effect on the thermodynamic resistance of passive layers on the finished bonded magnets (according to magnets obtained from $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder particles single-step coated - encapsulation).
- Longer time of autocatalytic protective Ni-P surface coating has an effect on $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$ bonded magnets corrosion characteristics in environments conducive to their passivation, and the pitting nucleation potential is more positive.
- Proper insulation of individual $\text{Nd}_{11}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder particles is an effective method to improve the corrosion resistance of epoxy-bonded magnets.

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