

THE EFFECT OF Nd₁₂Fe₇₇Co₅B₆ POWDER ELECTROLESS BIENCAPSULATION METHOD ON ATMOSPHERIC CORROSION OF POLYMER BONDED MAGNETIC MATERIALDorota KLIMECKA-TATAR ^a, Grażyna PAWŁOWSKA ^b, Klaudia RADOMSKA ^b^a *Institute of Production Engineering, Czestochowa University of Technology, Poland, EU, klimt@wip.pcz.pl*^b *Department of Chemistry, Czestochowa University of Technology, Poland, EU, pawlow@wip.pcz.pl, klaudia_radomska@poczta.onet.pl***Abstracts**

In the study has been evaluated the effect of Nd-(Fe,Co)-B particles biencapsulation method on bonded magnetic material atmospheric corrosion behavior. Bonded magnets were prepared from Nd₁₂Fe₇₇Co₅B₆ magnetic powder after biencapsulation. In this work three kind of biencapsulation method (double layer coating of powder particles) were applied. The powder biencapsulations with bilayers of Ni-P/epoxy resin, phosphate/epoxy resin and Cu/epoxy resin, was carried out to protect the surface of the powder particles against oxidation during manufacturing process. In the paper the results of accelerated gravimetric tests were carried out in so called artificial industrial atmospheres. Experimental conditions of the chosen environments were as follows: aerosol produced from aqueous solution of 3 mg/dm³ SO₂, at temperature of 40 °C. The corrosion rates were determined on the basis of sample's mass gain per surface unit in order to relationship of Δm/S versus time. It has been established that used method of magnetic powder pretreatment satisfactory encapsulates individual particles of the powder and consequently, significantly inhibits corrosion processes of the final material in artificial industrial atmospheres but only in case when used coating layer tightly cover entire particle surface (Ni-P/epoxy resin and phosphate/epoxy resin). There is no improvement in the case of use the encapsulation with Cu/epoxy resin, because the Cu layer does not cover entire surface of powder surface.

Keywords: Neodymium magnets, dielectromagnets, biencapsulation, Nd-Fe-B, bonded magnets**1. INTRODUCTION**

Highcoercivity nanocrystalline permanent magnets based on rare earth elements (RE) and transition metals (M) using the properties of intermetallic phases RE₂M₁₄B (e.g. Nd₂Fe₁₄B) are increasingly used in wide variety of industry for almost 30 years (e.g. electronic, automatics, automobiles, computers and medical devices) [1-2]. 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 [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). Dielectromagnets are the group of magnets produced by consolidation of hard magnetic powders with dielectric binder [7]. 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 [7-9]. Additionally, technology of bonded magnets production makes it possible to produce small elements with complicated shape without expensive mechanical treatment. 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. The binder dielectric properties also give the ability to use of bonded magnets in direct neighborhood of the fast changing magnetic fields [2].

There are many ways to obtain the magnetic powders, among others, by the hydrogenation/disproportionation/desorption/recombination (HDDR), hydrogenation/ disproportionation (HD), mechanical alloying (MA), and also by melt quenching (MQ) methods [1,2]. The main advantages of producing

powders by melt-spun ribbon, is the possibility to produce a magnetic powder with single-phase structure - in this case randomly oriented RE₂Fe₁₄B, with high uniaxial anisotropy, which effect on beneficial magnetic properties.

The properties of Nd-Fe-B bonded magnets depend mainly on their composition: 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 [10,11].

One of the problem with Nd-Fe-B magnets use 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. ENd³⁺/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. It is also known that as a result of some 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 Nd₂O₃ or Nd(OH)₃) which is prone to decrease of magnets losses [13,17-21].

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 further increases corrosive medium penetration into the material [8, 22]. To increase the 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 (bilayer), i.e. metallic layer of protective coating, and thin layer of resin (bonding material) [23-25].

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

2. MATERIAL PREPARATION, ENCAPSULATION PROCEDURE

The bonded magnetic materials were prepared from powder Nd-(Fe,Co)-B (commercial MQP-B, Magnequench). Base on the producer information, the powder contain about 12 % at. Nd, 5 % at. Co, 77 % at. Fe, 6 % at. B, and was produced by melt spinning. 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 [8,24,25]. To protect the etched powder surface against atmospheric agents in the later stages of sample preparation the encapsulation processes.

The deposition of a layer (encapsulation) takes place as following through three methods: chemical reduction, exchange or autocatalytic process [27,28].

The encapsulation (powder surface coating) of powder was performed as follow:

- Ni-P coating was carried out in an bath containing in its composition NiCl₂·6H₂O, NH₄Cl, NaH₂PO₂·H₂O, and sodium citrate - deposition was carried out at 90°C for 5, 15 or 30 minutes. In this case the sodium hypophosphite NaH₂PO₂·H₂O take the role of nickel ions reductor whilst the metallic powder surface is the catalyst
- phosphate coating was carried out in a solution with presence of phosphate anions of two different pH values: 3 or 7 - in both cases the phosphating time was 72 h.

- The powder encapsulation with Cu coating was carried out in a bath containing in its composition 5 g/dm³ CuSO₄·5H₂O at temperature 25 °C. There were prepared two kinds of powders, the powder were subjected for 1 or 5 minutes.

The presented three encapsulated methods allow to obtain the coated particles, which have been separated from modification solution on paper filter, thoroughly washed distilled water and acetone and dried in Ar atmosphere.

However, the effect of the powder particles biencapsulation (bilayers powder surface coating) was obtained through the use of an acetone solution of a thermosetting epoxy resin, which after evaporation of the solvent uniformly cover the particle surface. The content of binder in the composition (after evaporation of acetone) was about 3 % by mass. In order to create the samples shape, the compositions of powder were pressed at a pressure of 800 MPa, and heated at 180 °C for 2 hours to setting the resin (optimal parameters for shaping and hardening this type of powder [11]). The test specimens have the cylindrical shape with the following dimensions: $\varnothing = 8$ mm and $h = 10$ mm. In **Fig. 1 (a-c)** the images of encapsulated with Ni-P, phosphate and Cu coating powders are presented.

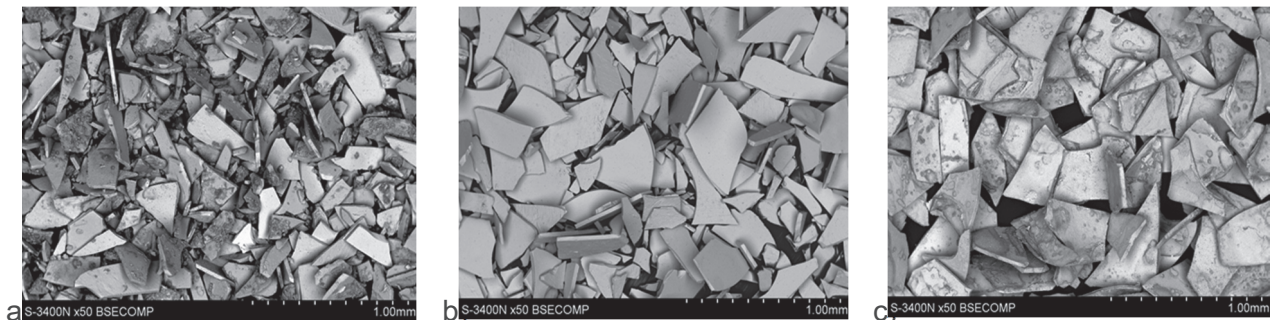


Fig. 1 The Nd₁₂Fe₇₇Co₅B₆ powder particles encapsulated with: a) Ni-P/epoxy resin, b) phosphate/epoxy resin, c) Cu/epoxy resin

3. ACCELERATED ATMOSPHERIC TESTS

For the samples prepared with three kind of proposed biencapsulated method accelerated gravimetric tests were carried out in so called artificial industrial atmospheres. Experimental conditions of the chosen environments were as aerosol produced from aqueous solution of 3 mg·dm⁻³ SO₂, at temperature in 40 °C, over the nine cycles exposure (each cycle ran 10 hours). Sample's mass gain per surface unit was being measured after each exposure cycle in order to relationship of $\Delta m/S$ versus time to be determined.

In **Fig. 2** results of accelerated atmospheric corrosion tests for bonded magnets with the applied techniques are presented. The mass of the particular samples linearly increases with exposure time only in the first four cycles (**Fig. 2 a-c**). The slopes of respective straight lines are the measure of corrosion rate in this time range. All obtained curves are compared to the curve of bonded magnet based on Nd₁₂Fe₇₇Co₅B₆ powder without any surface chemical modification (without biencapsulation - as received). As it results from literature data, the main atmospheric corrosion products of Nd-Fe-B type magnets are white Nd(OH)₃ and "brown rust": Fe(OH)₂ or FeO(OH) compounds [13,15]. According to most of authors, Nd(OH)₃ predominates in corrosion products. Simplifying the problem, the main reaction responsible for the atmospheric corrosion process is:



Assuming that the mass gain (measured Δm) during atmospheric corrosion process is mainly equal to mass of OH- groups in corrosion products and that the in first 40 hours of accelerated test the mass gain has linear character, one can calculate that the real corrosion rate is:

$$r_{\text{corr}} = \frac{\Delta m}{\Delta t \cdot S} \cdot \frac{M_{\text{Nd(OH)}_3}}{3M_{\text{OH}^-}} \quad (2)$$

Where $M_{\text{Nd(OH)}_3}$ and M_{OH^-} and OH⁻, are molar weights of Nd(OH)₃ respectively. The slopes of straight lines read from **Fig. 4** allow to determine magnets corrosion rate:

$$r_{\text{corr}} = \text{slope} \times 3.53 \quad (2a)$$



Fig. 2 Mass gain as a function of time during exposure of Nd₁₂Co₅Fe₇₇B₆ epoxy resin bonded magnetic material in industrial atmosphere; powder biencapsulated with: a) Ni-P/epoxy resin, b) phosphate/epoxy resin, c) Cu/epoxy resin

Corrosion rates [$\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$] of the tested samples in atmospheric environment evaluated on the basis of eq. 2a are listed in **Table 1**.

Table 1 Corrosion rates of bonded magnetic material (based on nd12fe77co5b6 encapsulated powder) in artificial industrial atmosphere

Nd ₁₂ Fe ₇₇ Co ₅ B ₆ powder biencapsulation before bonded magnets consolidation	Encapsulation parameters	Corrosion rate, $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$
as received	-	139.7
Ni-P/epoxy resin	5 min, temperature 90 °C	128.3
	15 min, temperature 90 °C	112.9
	30 min, temperature 90 °C	98.8
phosphate/epoxy resin	pH = 3, 72 hours	90.4
	pH = 7, 72 hours	95.3
Cu/epoxy resin	1 min, temperature 25 °C	183.6
	5 min, temperature 25 °C	169.4

As can be concluded, the applied of Nd₁₂Fe₇₇Co₅B₆ powder particles biencapsulation affects on the rate of atmospheric corrosion of bonded magnets. It should be noted that the used biencapsulation methods (biencapsulation with Ni-P/epoxy resin and phosphate/epoxy resin) have the favorable effect on the stability of the material in a corrosive medium. The corrosion rate decrease is more over the 30 %. However, it is also apparent that the powder particles biencapsulation with Cu/epoxy resin contributed to increasing the corrosion

rate of a bonded material. A significant increase in the corrosion rate results both from the large difference in electrochemical potentials of the alloy components and of the applied protective layer, but also with the morphology of the copper layer.

As can be seen in **Fig. 3**, the copper layer easy spalling, cracking and chipping from the surface of the powder particles. The emergence of such cracks contributes to the microcells, which is primarily exposed to corrosive factors, resulting in an increase in corrosion rate of up to 30%.

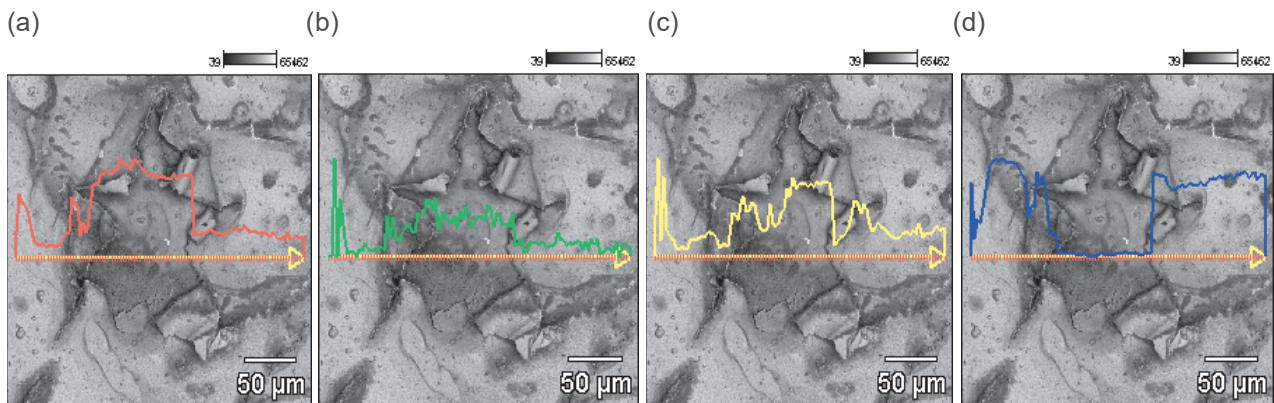


Fig. 3 Profiles of chemical elements concentration on the Cu coated $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ powder surface iron (a), cobalt (b), neodymium (c) and copper (d) distribution across the $\text{Nd}_{12}\text{Co}_5\text{Fe}_{77}\text{B}_6$ particle surface encapsulated with Cu

SUMMARY

Bienapsulation of $\text{Nd}_{12}\text{Co}_5\text{Fe}_{77}\text{B}_6$ nanocrystalline powder with Ni-P/epoxy resin, phosphate/epoxy resin and Cu/epoxy resin before compacting clearly affect on the atmospheric corrosion behaviour (industrial environment) of the final bonded magnets.

The accelerated atmospheric corrosion tests of $\text{Nd}_{12}\text{Co}_5\text{Fe}_{77}\text{B}_6$ material bonded create from powder bienapsulated with different layers indicate that corrosion processes are inhibited in case when used coating layer tightly cover entire particle surface. And the best results are for bienapsulation with phosphate/epoxy resin coating.

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