

### **THE Nd-(Fe,Co)-B POWDER BIENCAPSULATION WITH Cu/EPOXY RESIN AND ITS EFFECT ON PITTING CORROSION RESISTANCE OF BONDED MAGNETS**

**Abstract:** In this chapter the effect of the Nd-(Fe,Co)-B powder particle biencapsulation with Cu layer on bonded magnetic materials corrosion behaviour has been investigated. Bonded magnets were prepared from nanocrystalline magnetic Nd<sub>11</sub>Fe<sub>77</sub>Co<sub>5</sub>B<sub>6</sub> powder. Powder particles before consolidation were preliminary etched with oxalic acid and then coated with bilayer (powder biencapsulation). The powder surface was coated as a first with Cu layer during 1 or 5 minutes in copper plating bath and the second layer was thermosetting epoxy-resin. The polarization curves in phosphate environment with addition of chloric ions were determined. It has been established that the used biencapsulation method not always satisfactorily isolate individual particles of the powder and consequently, significantly inhibits corrosion processes of the final material, especially in passivating environment containing Cl<sup>-</sup>.

**Key words:** biencapsulation, corrosion resistance, pitting corrosion, composite magnets, Nd-Fe-B magnets

#### **2.1. Introduction**

Magnetic materials which contain in their chemical composition rare-earth (RE) elements, such as: Nd, Sm, Dy and others exhibit excellent magnetic properties and are marked as e.g RE-Fe-B or RE-Co type magnets. The RE-magnets principal disadvantages is low corrosion resistance in many aggressive environments. The corrosion processes reduce reliability of the materials in operating conditions and decide about their life-

---

<sup>1</sup> Dr inż., Czestochowa University of Technology, Faculty of Management, Institute of Production Engineering, e – mail: klimt@wip.pcz.pl

<sup>2</sup> Dr hab., Czestochowa University of Technology, Faculty of Process, Materials Engineering and Applied Physics, Department of Chemistry, e – mail: pawlow@wip.pcz.pl

time (LEONOWICZ M., WYSŁOCKI J.J. 2005, BALA H., SZYMURA S. 1995, DOBRZAŃSKI L.A., DRAK M., TRZASKA J. 2005).

Either the poor corrosion resistance and very good magnetic properties of RE containing magnets directly are the result of strongly active RE elements presence (~35 wt.%) in their composition and also the multiphase structure, contact of intermetallic phases with considerable differences of electrochemical activity (BALA H., SZYMURA S. 1995, EL-MONEIMA A.A., GEBERT A., SCHNEIDER F., GUTFLEISH O., F.SHULTZ, 2002, EL-MONEIMA A.A., GUTFLEISH O., PLOTNIKOV A., GEBERT A. 2002). It is well known that, in solid state for alloys with basic chemical composition there exist three equilibrium intermetallic phases. Therefore for Nd-Fe-B type magnets, there are exist phases i.e. ferromagnetic ( $\text{Nd}_2\text{Fe}_{14}\text{B}$ ), boron-rich ( $\text{NdFe}_4\text{B}_4$ ) and neodymium-rich ( $\text{Nd}_4\text{Fe}$ ) phase but it is worth to mention, that in the presence of other additional elements in the alloy structure could create the others phases (LEONOWICZ M., WYSŁOCKI J.J. 2005).

Among many Nd-Fe-B materials (created with different technological proces) especially interesting are bonded nanocrystalline Nd-Fe-B permanent magnets. Their represents the magnetic materials with advantageous magnetic properties and low material- and production costs. The introduction of bonded magnetic materials fullfilled the large gap on the magnetic materials market, by the optimal (magnetic and economic), parameters (LEONOWICZ M., WYSŁOCKI J.J. 2005).

As it was listed the magnetic properties mostly depend on chemical composition of the alloy and its microstructure (grain size, phase composition) (EL-MONEIMA A.A., GEBERT A., SCHNEIDER F., GUTFLEISH O., F.SHULTZ, 2002, EL-MONEIMA A.A., GUTFLEISH O., PLOTNIKOV A., GEBERT A. 2002, RADA M., LYUBINA J., GEBERT A., GUTFLEISCH O., SCHULTZ L. 2005). To avoid appearance of equilibrium phases with large differences of corrosion potential, it is very important to match the chemical composition of alloy to stoichiometric composition of ferromagnetic  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase (i.e. Nd 12.3%, Fe 82.6%, B 5.4%), which is responsible for the unique magnetic properties of these materials. Thus,

it is most preferred to single-phase produce alloy (LEONOWICZ M., WYSŁOCKI J.J. 2005). Single-phase Nd-Fe-B magnets can be produced with different methods, e.g. by traditional powder metallurgy or by powder consolidation with polymer binders (LEONOWICZ M., WYSŁOCKI J.J. 2005, LEONOWICZ M., WOJCIECHOWSKI S. 1988, ŚLUSAREK B. 2001). Application of thermo- and chemically-setting epoxy-resin as a binder makes it possible to form a complicated shapes of magnetic elements without final mechanical treatment (ŚLUSAREK B. 2001). As it was showed in literature (KLIMECKA D. 2009, BALA H., TREPAK N.M., SZYMURA S., LUKIN A.A., GAUDYN V.A., ISAICHEVA L.A., PAWŁOWSKA G., ILINA L.A. 2001, SKULJ I., DOUVALIS A.P., HARRIS I.R. 2006, EDGLEY D.S., LE BRETON J.M., STEYAERT S., AHMED F.M., HARRIS I.R., TEILLET J. 1997) in manufacturing process of polymer-bonded magnets particularly important is powder surface preparation, because RE containing particles easily cover with thin film of oxides (mainly  $\text{Nd}_2\text{O}_3$ ), decreasing adhesive force between powder grains and binder. Due to isolation of magnetic particles with binder the polymer-bonded magnets are more stable in aggressive environment but in the case when the binder material uniformly and tightly cover the powder particle surface. To create the material with better corrosion resistance it is important to remove oxide film from powder surface before consolidation (KLIMECKA D. 2009).

In most acid environments the Nd-Fe-B type material dissolves activationally, which is particularly undesired (BALA H., SZYMURA S. 1995, KLIMECKA D. 2009, PAWŁOWSKA G. 2005). However, in acidified phosphate solution, and also in neutral and alkaline solutions the RE-containing magnets passivate effectively (KLIMECKA-TATAR D., PAWŁOWSKA G., SZYMURA S., BALA H. 2003, KLIMECKA-TATAR D., ŚLUSAREK B., BALA H., GĘSIARZ K. 2005, KLIMECKA D. 2009). Non-conductive passive film which is formed on the magnet surface, effectively isolates the material from aggressive media. From the passive layer stability point of view, especially disadvantageous is the presence of aggressive chloride ions in corrosion environments. Even small

amount of  $\text{Cl}^-$  ( $\geq 0.03 \text{ M}$ ) is prone to pit nucleation and development of pitting corrosion (SZKLARSKA-SMIALOWSKA Z. 2005, KLIMECKA D. 2009).

One of the corrosion resistance improve method of magnetic materials (bonded) is the use of surface multi-stage pre-treatment, which was presented in previous work of the team (KLIMECKA-TATAR D. 2011, KLIMECKA-TATAR D., PAWŁOWSKA G., RADOMSKA K. 2013, PAWŁOWSKA G., KLIMECKA-TATAR D., MAZIK A. 2013). The purpose of these treatments are sufficient isolation of individual particles providing, which in the first place cleans the surface of the powder particles of paramagnetic oxide-phase, protect it from re-oxidation during the production process and in result will be inhibited progressive into material corrosion destruction in the final magnet.

## **2.2. Experiments**

### **2.2.1. Material preparation methodology**

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 (KLIMECKA-TATAR D. 2009, KLIMECKA-TATAR D. 2011, KLIMECKA-TATAR D., PAWŁOWSKA G., RADOMSKA K. 2013, PAWŁOWSKA G., KLIMECKA-TATAR D., MAZIK A. 2013). To protect the etched powder surface against atmospheric agents in the later stages of sample preparation the encapsulation processes were used metallic Cu and epoxy binder. The powder encapsulation with Cu coating was carried out in a bath containing in its composition 5 g/dm<sup>3</sup>  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in temperature 25°C, 5 minutes. The above kind of encapsulated methods allow to obtain the coated particles, which have been

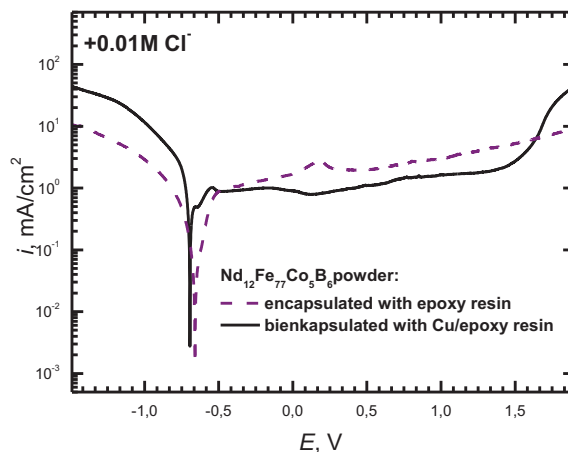
separated from modification solution on paper filter, thoroughly washed distilled water and acetone and dried in Ar atmosphere. The effect of the powder particles biencapsulation obtained through the use of an acetone solution of a thermosetting epoxy resin, which after evaporation of the solvent particles 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:  $\varnothing = 5$  mm and  $h = 10$  mm.

### 2.2.2. Potentiokinetic tests

The influence of biencapsulation method with Cu/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 0.01 ÷ 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 mV·s<sup>-1</sup>. All potentials are expressed vs. Ag/AgCl auxiliary electrode.

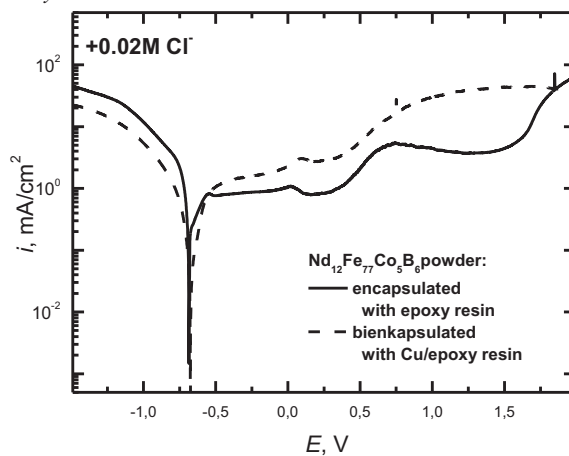
### 2.3. The results and discussion

The corrosion resistance of examined samples based on Nd<sub>11</sub>Fe<sub>77</sub>Co<sub>5</sub>B<sub>6</sub> powder biencapsulated with Cu/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:  $E_{\text{corr}}$  (V) – corrosion potential,  $i_{\text{min,pass}}$  (mA/cm<sup>2</sup>) – minimal value of current density in passive range and  $E_{\text{pit}}$  (V) – pitting potential.



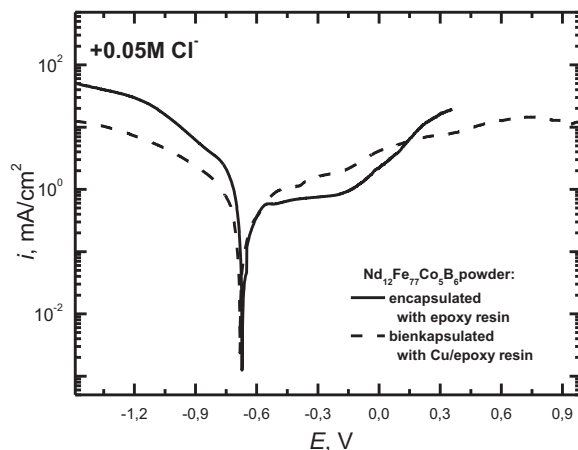
**Fig. 2.1.** Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Cu/epoxy resin)  $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$  powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0.01 M Cl<sup>-</sup> addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps.

Source: own study



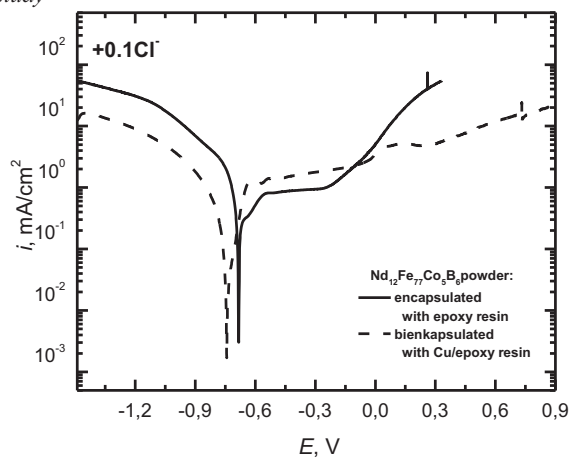
**Fig. 2.2.** Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Cu/epoxy resin)  $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$  powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0.02 M Cl<sup>-</sup> addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps.

Source: own study



**Fig. 2.3.** Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Cu/epoxy resin)  $Nd_{12}Fe_{77}Co_5B_6$  powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0.5 M Cl<sup>-</sup> addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps.

Source: own study



**Fig. 2.4.** Potentiokinetic polarization curves of magnetic material based on encapsulated and biencapsulated (Cu/epoxy resin)  $Nd_{12}Fe_{77}Co_5B_6$  powder. Experimental conditions: 0.5 M phosphate solutions (pH = 3) with 0.1 M Cl<sup>-</sup> addition, 20°C, potential scan rate: 10 mV/s, disk rotation speed 21 rps.

Source: own study

In Fig. 2.1-2.4 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  $10^{-1}$  mA/cm<sup>2</sup>. 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.

From the course of curves shows that the applied powder coating technologies (biencapsulation with Cu/epoxy resin) have not substantial effect on the cathode curves course and the value of the corrosion potential varies in the range of -0.66 V to -0.69 V (Fig.2.1-2.4). Shape of cathodic curves indicates that corrosion process in acidified phosphate solution (pH = 3) occurs with activation control.

The differences are observed after crossing the corrosion potential ( $E_{\text{corr}} = -0.66 \div -0.69$  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/cm<sup>2</sup>.

In all solutions materials produced from powder biencapsulated with Cu and epoxy resin shows distinctly higher value of current in anodic curves. As there is no significant passive range ( $i_{\text{min,p}}$ ) (as in reference sample), the range of potential within the material cover with passive layer. In this range the anodic dissolution is inhibited by layer created mainly of Nd phosphate. This shape of cathodic curves determined for magnetic materials obtained from powder preliminary isolated with thin layer of Cu (encapsulation) and with epoxy resin (biencapsulation) that the passive is not continuous and does not cover the entire surface of the composite material against chloride ions.



Further increase in the concentration of chloride ion results in more negative values of pitting potential for the reference sample (encapsulation with epoxy resin) but curves determined for materials produced from powder biencapsulated with Cu and epoxy resin shows different slope and the break of the passive layer potential (pitting potential,  $E_{\text{pit}}$ ) correctly it is difficult to determine.

## 2.4. Summary

Application of the powder particles biencapsulation before their bonding process greatly affects on corrosion resistance. But it is very imported to apply the right kind of protective layer during the biencapsulation. In some cases, the applied layer may limited in some extent resistance to corrosion of bonded magnets. However, in certain cases (biencapsulation of Cu/epoxy resin) the effect of improvement in corrosion resistance is not achieved. The reasons for the lack of improvement in corrosion resistance may result from the thickness of layer created during encapsulation (Cu coating application time 5 minutes, may be too long).

## Acknowledgments

*This research was supported by funds for education in the years 2010-2013 by Ministry of Science and Higher Education (Republic of Poland) as a research project No. N N507 616838.*

## Bibliography

1. BALA H., SZYMURA S. 1995. *Inż. Materialowa*.3, 119.
2. BALA H., TREPAK N.M., SZYMURA S., LUKIN A.A., GAUDYN V.A., ISAICHEVA L.A., PAWŁOWSKA G., ILINA L.A. 2001. *Intermetallics*. 9, 515.
3. DOBRZAŃSKI L.A., DRAK M., TRZASKA J. 2005. *J. Mater. Proc. Tech.* 164, 795.
4. EDGLEY D.S., LE BRETON J.M., STEYAERT S., AHMED F.M., HARRIS I.R., TEILLET J. 1997. *J.Magn.Magn.Mater.* 173, 29.

5. EL-MONEIMA A.A., GEBERT A., SCHNEIDER F., GUTFLEISH O., F.SHULTZ, 2002. *Corros. Sci.* 44, 1097.
6. EL-MONEIMA A.A., GUTFLEISH O., PLOTNIKOV A., GEBERT A. 2002. *J.Magn.Magn. Mater.*, 248, 121.
7. KLIMECKA-TATAR D. 2009. Praca doktorska. Politechnika Częstochowska. Częstochowa.
8. KLIMECKA-TATAR D. 2011. *The Production Process of Bonded Magnets Based on Microencapsulated Nd<sub>14.8</sub>Fe<sub>76</sub>Co<sub>4.95</sub>B<sub>4.25</sub> Powder*. Chapter 10. In: Toyotarity. Heijunka. Monography. Editing and Scientific Elaboration Stanisław Borkowski, Robert Ulewicz s.155-170 Dnipropetrovsk.
9. KLIMECKA-TATAR D., PAWŁOWSKA G., RADOMSKA K. 2013. *Ochr Przed Koroz*, 56/5, pp. 187-190.
10. KLIMECKA-TATAR D., PAWŁOWSKA G., SZYMURA S., BALA H. 2003 *Ochr. przed Korozjq.* 11s/A, 187
11. KLIMECKA-TATAR D., ŚLUSAREK B., BALA H., GĘSIARZ K. 2005. *Ochr. przed Korozjq.* 11s/A, 93.
12. LEONOWICZ M., WOJCIECHOWSKI S. 1988. *Archiwum Nauki o Materiałach.* 9, 263.
13. LEONOWICZ M., WYSŁOCKI J.J. 2005. *Współczesne magnesy*. WNT. Warszawa.
14. PAWŁOWSKA G. 2005. *Inż. Materialowa.* 5, 558.
15. PAWŁOWSKA G., KLIMECKA-TATAR D., MAZIK A. 2013. *Ochr Przed Koroz* 56/4, pp. 174-176.
16. RADA M., LYUBINA J., GEBERT A., GUTFLEISCH O., SCHULTZ L. 2005. *J. Magn. Magn. Mater.*, 290, 1251.
17. SKULJ I., DOUVALIS A.P., HARRIS I.R. 2006. *J.Alloy.Compnd*, 407, 304.
18. SZKLARSKA-SMIALOWSKA Z. 2005. *Pitting and Crevice Corrosion*. NACE, Huston.
19. ŚLUSAREK B. 2001. *Dielektromagnets Nd-Fe-B*. Oficyna Wyd. Politechniki Wrocławskiej. Wrocław.