EFFECT OF SELECTED PARAMETERS ON THE CORROSION BEHAVIOUR OF Nd-Fe-B/BIOTOLERABLE ACRYLATE POLYMER COMPOSITES

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ABSTRACT

The properties of bonded magnets depend not only on the magnetic properties of Nd-Fe-B powder, but also on the parameters of the consolidation process and the type of binder. Increasing the binder content in magnetic composites is desirable from the point of view of corrosion resistance, but it is not desirable due to its magnetic properties. A compromise between the two trends is necessary to obtain a material with adequate corrosion resistance with an acceptable decrease in magnetic properties.

In the paper the corrosive characteristics of the magnetic composite in aggressive environments with different acidity, in the presence of chloride ions and at different temperatures are presented. The composite based on Nd-(Fe,Co)-B powder consolidated with biocompatible polymer, where the binder content is about 10 % by mass. The composite has been found to be less sensitive to the presence of chloride ions than the composites with a lower binder content. However, the decrease in pH, especially in the environment of artificial saliva and the increase in temperature cause its strong degradation. Thus, in contact with physiological fluids (at high temperature, chloride ion content, pH decrease), additional protection in the form of biencapsulation of powder particles is necessary.

Keywords: magnetic composite, Nd-Fe-B, bonded magnets, corrosion behaviour.

INTRODUCTION

Magnetic materials, based on rare earth metals (RE) and transition metals (M), are used because of the strong ferromagnetic properties of $RE_2M_{14}B$ intermetallic phase are used because of the strong ferromagnetic properties of $RE_2M_{14}B$ intermetallic phase [1 - 2]. That kind of materials are currently used in sintered or bonded composites form. The method of obtaining magnetic materials and its chemical composition affect not only the magnetic properties, but also their corrosion resistance [3 - 9].

In sintered materials a higher content of the highly electrochemically active rare earth element is required - most often Nd (the value of the standard potential is $E_{Nd^{3+}/Nd} = -2.43$ V) [4, 5] which, together with the multiphase structure, promotes the susceptibility to corrosion of these materials in many aggressive environments [6 - 9]. However, to obtain powder composites it is possible to use alloy powders with a limited content of rare earths. The limited content of rare earths and the appropriate production technology (rapid casting) promote the creation of a metastable single-phase structure. The single-phase structure is conducive to reducing the corrosion rate, and in addition, plastic powder binding isolates individual powder particles [7 - 10]. An additional advantage of that type of consolidation is the simplicity of the technological process. In the art, for magnetic powder consolidation, chemo- or thermosetting epoxy and polyester resins are most often used. Such a binder is beneficial from the point of view of the material's corrosion resistance and ensures adequate material consistency. In resin-consolidated materials, the cured binder, which is highly resistant to acid corrosion, insulates powder particles. This allows for a significant reduction (advantage over sintering) of the risk of selective corrosion occurring as a result of rapid digestion of the neodymium phase (presents at the boundaries of sintered magnet grains) [8 - 13].

However, the presence of toxic epoxy resin eliminates them from medical applications - such materials cannot be used within organic tissues [9]. In view of the prospects for using bonded magnets in prosthetics, the binder must be changed. Such an adhesive is acrylic material used in dentistry, which harmonizes with the surrounding tissues of the body. It was found [10], that 10 % content of such biocompatible polymer provides good strength and magnetic properties.

The aim of this work is to characterize the corrosion resistance of Nd-Fe-B/biotolerable polymer (content 10 % in mass of polymer) in various aggressive environments.

EXPERIMETAL

Commercial magnetic powder (Magnequench) with the chemical formula $Nd_{12}Fe_{77}Co_5B_6$ (subscripts represent the percentage of atoms) has been used in the research. That type of powder is obtained from tapes cast by the method of rapid cooling of an alloy from a liquid state. The obtained tapes are mechanically crushed and subjected to heat treatment (heating at 600°C). When choosing acrylic material for the consolidation of magnetic powder particles, the type of material, product availability, price and usability have been taken into account. Consolidation with the help of commercial acrylate mixture have been used - Duracryl - the mixture includes: polymer and additional substances such as softeners, fillers and coloring agents. The binder content was 10 % by weight. The polymerization process has been carried out at ≈ 90°C for 1 hour. In further part of the paper the composite is calld Nd-Fe-B/10BP.

The corrosion resistance tests have been carried out:

- in sulfate solutions with different acidity - 0.5 M Na_2SO_4 was used as the base working solution for potentiokinetic studies. In order to obtain sulfate solutions with pH = 2, 4 and 6, appropriate amounts of 0.5 M H_2SO_4 were added to the solution;
- in phosphate solutions with the addition of chloride ions;
- in Ringer's solution at pH = 6 (8.6 $g{\cdot}L^{-1}$ NaCl; 0.30 $g{\cdot}L^{-1}$ KCl; 0.48 $g{\cdot}L^{-1}$ $CaCl_2{\cdot}6H_2O$);
- in a solution of artificial saliva at pH = 6.7 (0.7 $g{\cdot}dm^{-3}$ NaCl; 1.7 $g{\cdot}dm^{-3}$ KCl; 0.2 $g{\cdot}dm^{-3}$ KH_2PO_4; 1.5 $g{\cdot}dm^{-3}$ $NaHCO_3$; 0.2 $g{\cdot}dm^{-3}$ Na_2HPO_4; 0.33 $g{\cdot}dm^{-3}$ KSCN);
- in artificial saliva solution at pH = 2.7 (0.4 $g{\cdot}dm^{-3}$ NaCl; 0.4 $g{\cdot}dm^{-3}$KCl; 0.005 $g{\cdot}dm^{-3}$ Na_2S; 0.61 $g{\cdot}dm^{-3}$ anhydrous Na_2HPO_4; 0.795 $g{\cdot}dm^{-3}$$CaCl_2{\cdot}2H_2O$; 1.0 $g{\cdot}dm^{-3}$ $(NH_2)_2CO_3$; 80 % lactic acid).

RESULTS AND DISCUSSION

The effect of pH

The Nd-Fe-B/10BP composite material has been tested in sulphate solutions with variable acidity. It was found that as the acidity decreases, the corrosion potential of E_{corr} shifts towards negative values (Table 1), and the recording of polarization curves in a slightly acidic environment, especially neutral, is encountered as a result of corrosion deposits forming. The corrosion rate has been measured by the polarization resistance method. After reaching the corrosion potential, the potential was swept at a sweep rate of 0,001 V s^{-1} in the range E_{corr} to E_{corr} + 10 mV. Directional coefficient of the E = f (i) line defines the value of polarization resistance (in $\Omega{\cdot}cm^2$). It was found that the increase in the pH of the sulfate solution causes an increase (3 to 5 times) in the polarization resistance for the Nd-Fe-B/10BP composite (Table 1, Fig.1). As it is well known, environments with reduced acidity cause rapid degradation of Nd-Fe-B magnetic materials, especially sintered materials. For Nd-Fe-B/BP composites, this trend is also noticeable, but to a lesser extent.

The composite material under study is dedicated for use in restorative medicine, including dentistry, for overdenture dentures. For this reason, the behavior of the composite in environments imitating human body fluids has been investigated. The tests have been performed

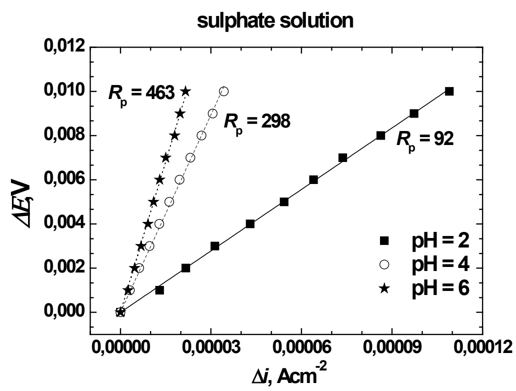

Fig. 1. Changes in external current when the potential changes in the range E_{corr} +0,01 V in 0,5 M sulfate solutions at pH = 2, 4 and 6 (20°C, 0,001 $V{\cdot}s^{-1}$, 16 rps) for Nd-Fe-B/10BP composite - $Nd_{12}Fe_{77}Co_5B_6$ powder consolidated with 10 wt. % acrylate mixture, (rps - rotation per second).

Table 1. Values of parameters determining the resistance in sulfate solutions (pH = 2; 4; 6) of Nd-Fe-B/10BP composite - $Nd_{12}Fe_{77}Co_5B_6$ powder consolidated with 10 wt. % acrylate mixture.

0. 5 M sulfate solutions	E_{corr} [V]	R_p [$\Omega \cdot cm^2$]
pH = 2	−0.68	92 ± 27.93
pH = 4	−0.78	298 ± 27.07
pH = 6	−0.73	463 ± 10.00

Table 2. Values of parameters determining resistance in artificial saliva solution, pH = 2.7 and 6.7 of Nd-Fe-B/10BP composite - $Nd_{12}Fe_{77}Co_5B_6$ powder consolidated with 10 wt. % acrylate mixture.

Artificial saliva	E_{corr} [V]	R_p [$\Omega \cdot cm^2$]
pH = 2.7	−0.66	284 ± 1.41
pH = 6.7	−0.55	669 ± 36.17

in artificial saliva with different acidity. Human saliva is an aggressive environment with high salinity and wide pH range (depending on the type of meals taken and possible inflammation and temperature [11]). The average saliva should have a pH of 6.7, while inflammation in surrounding tissues can increase its acidity to 2.7 [12 - 14]. Fig. 2 presents the effect of the pH of the artificial saliva solution on the polarization resistance of the Nd-Fe-B/10BP magnetic composite (Fig. 2, Table 1). In the sulfate environment, a decrease in pH by 4 units caused a decrease in polarization resistance by about 35 %, and in artificial saliva by as much as about 48 %. However, despite the greater sensitivity due to the change in acidity, the composite material tested exhibits greater resistance to degradation in the aggressive environment of artificial saliva than in the neutral sulphate environment.

An effect of the temperature

Assessment of the temperature effect on the corrosive behavior of the Nd-Fe-B/10BP magnetic composite has also been carried out in a solution imitating physiological fluids. The resistance of polarization of the material in Ringer's solution (pH = 6) has been examined by changing the temperature from room temperature (20°C) to the temperature of the inflamed human body (37°C). The increase in temperature caused the corrosion potential of the Nd-Fe-B/10BP composite to shift

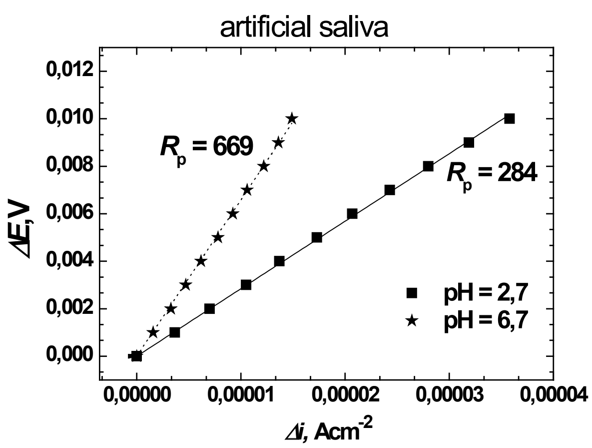

Fig. 2. Changes in external current when the potential changes in the range E_{corr} + 0,01 V in artificial saliva solution, pH = 2.7 and 6.7 (20°C, 0.001 $V \cdot s^{-1}$, 16 rps) for Nd-Fe-B/10BP composite - $Nd_{12}Fe_{77}Co_5B_6$ powder consolidated with 10 wt. % acrylate mixture.

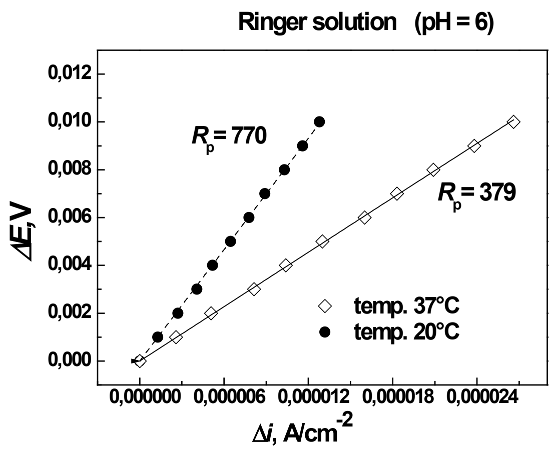

Fig. 3. Changes in external current when the potential changes in the range E_{corr} +0,01 V in Ringer solution, pH = 6.0 (20°C, 0.001 $V \cdot s^{-1}$, 16 rps) for Nd-Fe-B/10BP composite - $Nd_{12}Fe_{77}Co_5B_6$ powder consolidated with 10 wt. % acrylate mixture.

Table 3. Values of parameters determining resistance in Ringer solution, pH = 6.0 of Nd-Fe-B/10BP composite - $Nd_{12}Fe_{77}Co_5B_6$ powder consolidated with 10 % wt. acrylate mixture.

20°C		37°C	
E_{corr} [V]	R_p [Ω·cm²]	E_{corr} [V]	R_p [Ω·cm²]
−0.66	770 ± 14.14	−0.73	379 ± 19.14

Table 4. Breakthrough potential values (E_{pit}) of Nd-Fe-B/10BP composite determined in 0,5M phosphate solution with pH = 3 and variable concentration of chlorides.

concentration of chloride ions	E_{pit} [V]
0.5M Cl^-	−0.35
0.1M Cl^-	−0.02
0.05M Cl^-	+0.05
0.03M Cl^-	+0.30

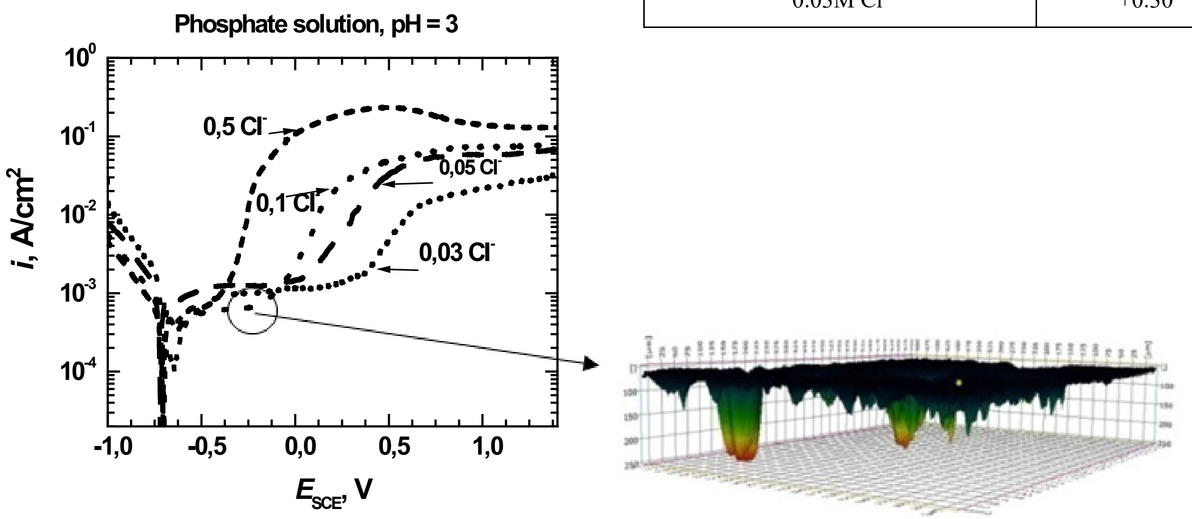

Fig. 4. Potentokinetic polarization curves of Nd-Fe-B/10BP composite determined in phosphate solution with pH = 3 and variable concentration of chloride ions (10 mV · s^{-1}, 16 rps, 20 °C).

towards negative potentials with a simultaneous decrease in polarization resistance (Fig. 3, Table 3).

As the temperature increased the material resistance was doubled.

An effect of the chloride ions (Cl^-) concentration

Discontinuities occurring in the material structure in the presence of ions Cl^-, Br^- I^- and CN^-, may lead to the initiation and development of pitting corrosion. The body fluid environment of the human body is an electrolyte about high chloride ion content. For this reason, the composite behavior of Nd-Fe-B/10BP composite have been conducted in solutions containing Cl^- ions. The tests have been carried out in a phosphate solution in which the tested materials passivate in a wide range of potentials. The effect of chloride ion concentration on the polarization curves of the Nd-Fe-B/10BP composite is shown in Fig. 4, which also shows the image of the surface (image obtained using an optical microscope with EPI overlay). The image shows pits formed on the sample surface after exposure to a corrosive medium at the potential of $E > E_{pit}$ in an acidified phosphate solution with 0.1M Cl^-.

With the increase of chloride ions concentration 0.03 - 0.5 M Cl^- the passivation efficiency in the phosphate solution (pH = 3) is gradually reduced (Table 4) which illustrates the decreasing E_{pit} breakthrough potential.

Fig. 5 shows the $E_{pit} = f(\log[Cl^-])$ function. In the

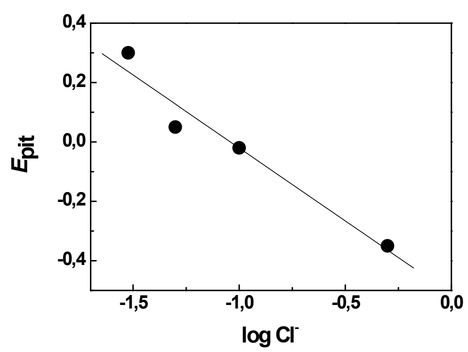

Fig. 5. Dependence of the Epit value on the content of chloride ions in the acidified phosphate solution (pH = 3) of Nd-Fe-B/10BP composite.

range of 0.03 - 0.5 M Cl^- the pitting nucleation potential decreases linearly with the logarithm of chloride concentration. Linear function, E_{pit} = f (log[Cl^-]), for the tested material in this range has a slope about - 0.5. Comparison of this result with literature data [13, 14] indicates a lower sensitivity to the presence of chloride ions, initiating pitting corrosion in the area of contact of powder particles with a botolerable polymer than epoxy resin.

CONCLUSIONS

Replacement of the binder used in NdFeB magnetic bonded materials may allow the use of these composites in restorative medicine.

Based on the conducted tests, it was found that the tested material is less sensitive to the presence of chloride ions, initiating pitting corrosion in the area of contact of powder particles with the biotolerable polymer, than epoxy resin. However, external conditions, and such include an increase in acidity, temperature, and Cl^- aggressive ion concentration, can significantly accelerate the degradation of the NdFeB composite bound with a biotolerable polymer. Physiological fluids (high temperature, chloride ion content, pH decrease) are aggressive environments, and the material in contact with them requires additional protection in the form of an additional biopolymer layer or the use of a biencapsulation process of magnetic powder particles.

The next stage of research is determining the optimal parameters for coating powder particles with layers that will positively affect the applicability of these materials in medicine.

REFERENCES

1. L.H. Lewis, Effect of the boron:rare-earth ratio on metastable phase formation in Nd2Fe14B-based nanocomposites, J.Appl.Phys., 85, 1999, 4883-4888.
2. G. Woodcock, Y. Zhang, G. Hrkac, G. Ciuta, N.M. Dempsey, T. Schrefl, O. Gutfleisch, D. Givord, Understanding the microstructure and coercivity of high performance NdFeB-based magnets, Scr. Mater., 67, 6, 2012, 536-541
3. G. Pawłowska, Corrosion processes of magnetic materials RE-Fe-B type obtained by various method (Procesy korozyjne materiałów magnetycznych typu RE-Fe-B otrzymanych różnymi metodami), Częstochowa, wyd. Politechnik Częstochowskiej, 2011.
4. M. Pourbaix M, Atlas of electrochemical equilibria in aqueus solutions, New York, Pergamon Press, Oxford, 1966.
5. L.-X. Luo, Y.-L. Liu, N. Liu, L. Wang, L-Y. Yuan, Z-F. Chai, W-Q. Shi, Electrochemical and thermodynamic properties of Nd (III)/Nd (0) couple at liquid Zn electrode in LiCl-KCl melt, Electrochim. Acta, 191, 2016, 1026-1036.
6. M. Rada, S. Kardelky., I. Mazilu, A. Kirchner, A. Gebert, O. Gutfleich, I. Schultz., Corrosion behaviour of polimer bonded Nd-Fe-B based nanocrystalline magnets, IEEE Trans. Magn., 40, 4, 2004, 2864- 2866
7. G. Pawłowska, Corrosion of nanocrystalline magnetic RE-M-B-type materials, Ochr. przed Korozją, 4-5, 2008, 144-148.
8. J. Ni, X. Cui, X. Liu, H. Cui, Z. Xue, Z. Jia, Ch. Wang, J. Ma, S.Gong, Corrosion behavior of NdFeB sintered magnets in HNO_3-HF acid mixture solution, Mater. Chem. Phys., 162 , 2015, 518-524.
9. W. Domański, Dian epoxy resins - the dangers of chemical agents (Dianowe żywice epoksydowe – zagrożenia czynnikami chemicznymi), Bezpieczeństwo Pracy, 9, 2004, 16-20.
10. G. Pawłowska, K. Radomska, D. Klimecka – Tatar, Effect of the powder consolidation with biopolymer on the corrosion characteristics of bonded magnets based on Nd-(Fe,Co)-B, Ochr. przed Korozją, 04,2016, 128-131.
11. H. Chang, S. Tomoda, C. J. L.Silwood, E. Lynch, M. Grootveld, Iinvestigations of the molecular nature of cobalt (II) ions in human saliva, Arch. Biochem. Biophys., 520, 1, 2012, 51-65.
12. J. Choi, K. Lyons, J. Kieser, et al., Diurnal variation of intraoral pH and temperature, BDJ Open 3, 2017, 17015.
13. D. Klimecka-Tatar, Modification of physicochemical properties of magnets by chemical treatment of nanocrystalline powder based on Nd-Fe-B (Modyfikowanie właściwości fizykochemicznych magnesów poprzez chemiczną obróbkę nanokrystalicznego proszku na bazie Nd-Fe-B), Częstochowa, wyd. Politechniki Częstochowskiej, 2009.
14. D. Klimecka-Tatar, G. Pawłowska, K. Radomska, Preliminary Quality Control of Magnetic Materials for applications in Restorative Medicine - Quantitative Analysis of Structural Homogeneity of RE-M-B /Polymer Composites , Manufacturing Technology, 20,1, 2020, 49-54.