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## THE EFFECT OF CONSOLIDATION METHOD ON ELCTROCHEMICAL CORROSION OF POLYMER BONDED Nd-Fe-B TYPE MAGNETIC MATERIAL

### WPLYW METODY I PARAMETRÓW KONSOLIDACJI NA WŁAŚCIWOŚCI MAGNETYCZNE I ODPORNOŚĆ KOROZYJNĄ MAGNESÓW TYPU Nd-Fe-B

Effect of the consolidation parameters of the powdered rapid quenched Nd Fe-B based strip (MQP-B type, Magnequench) on magnetic properties and corrosion behaviour has been investigated. Bonded magnets were prepared from single-phase, nanocrystalline magnetic powder and polymer binder, followed by their isostatic compression. The mixtures were uniaxially pressed at room temperature under the pressure ranging 700 – 1000 MPa. For consolidation of magnetic strip the epoxy-resin both in powdered solid state and as acetone solution has been applied. It has been established that acetone solution of chemical setting epoxy-resin satisfactorily micro encapsulates individual particles of the powder and, consequently, significantly inhibits corrosion processes of the final material. Additionally, it was found that magnets made of powder particles preliminary covered by the binder film were very sensitive to compaction pressure during magnets preparation.

*Keywords:* Nd Fe-B bonded magnets, nanocrystalline powder, corrosion

Oceniono wpływ parametrów konsolidacji proszków magnetycznych typu Nd-(Fe, Co)-B na własności magnetyczne oraz odporność korozyjną magnesów. Magneszy wykorzystane do badań zostały wykonane z jednofazowego, nanokrystalicznego proszku MQP-B (Magnequench) Kompozycję proszku magnetycznego oraz żywicy epoksydowej poddano prasowaniu z zastosowaniem nacisków z przedziału 700 – 1000 MPa. Oprócz powszechnie stosowanej metody konsolidacji sproszkowaną termoutwardzalną żywicą epoksydową wykorzystano również acetonowe roztwory zarówno termo- jak i chemoutwardzalnej żywicy w celu równomiernego pokrycia ziaren proszku magnetycznego przed procesem prasowania. Badania dowiodły, że mikro-enkapsulacja ziaren proszku chemoutwardzalnego żywicą epoksydową korzystnie wpływa zarówno na charakterystyki korozyjne jak i właściwości magnetyczne typu Nd-(Fe, Co)-B.

## 1. Introduction

Hard magnetic materials based on rare earth elements (RE) and transition metals (M) are increasingly used 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, so 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 (so 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]. The hard magnetic powders can be obtained, among others, by the hydrogenation/decrepitation/desorption/recombination (HDDR), hydrogenation/decrepitation (HD), mechanical alloying (MA), and melt quenching (MQ) methods [1,2]. Magnets produced from powdered rapid quenched strips characterize with single-phase structure of randomly oriented Nd<sub>2</sub>Fe<sub>14</sub>B grains with high uniaxial anisotropy. 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]. The binder dielectric properties also give the ability to use them in direct neighborhood of the fast changing magnetic

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fields [2]. Additionally, technology of bonded magnets production makes it possible to produce small elements with complicated shape without expensive mechanical work and without material losses. The properties of Nd-Fe-B dielectromagnets depend mainly on their composition: amount of high coercivity powder and epoxy resin concentration as well as manufacturing technology [7].

Significant problem with Nd-Fe-B magnets during their manufacturing process and application 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.  $E_{Nd^{3+}/Nd}^{\circ} = -2.43$  V) [4,10]. As many authors indicate [4,11-14], 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 [8,11,15]. 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 [11,16-19]. 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]. Thus, organic micro encapsulation of nanocrystalline powder grains seems to be a promising method in protection of bonded magnets against corrosion in the environments containing moisture [8,21]. The purpose of present paper is to evaluate the effect of consolidation parameters on the magnetic properties and on corrosion resistance of Nd Fe B magnets bonded with thermo and chemical setting epoxy resin.

## 2. Experimental

The experiments were made with the use of polymer-bonded magnetic material based on nanocrystalline powdered rapid quenched Nd-Fe-B strip MQP-B type made by Magnequench ( $Nd_{14.8}Fe_{76}Co_{4.95}B_{4.25}$  – where subscripts denote atomic percentages). In order to evaluate the effectiveness of powder coatings three kinds of samples consolidation method were used. All samples based on *as received* MQP-B powder, for which strip particles morphology and their size distribution are presented in Fig. 1.

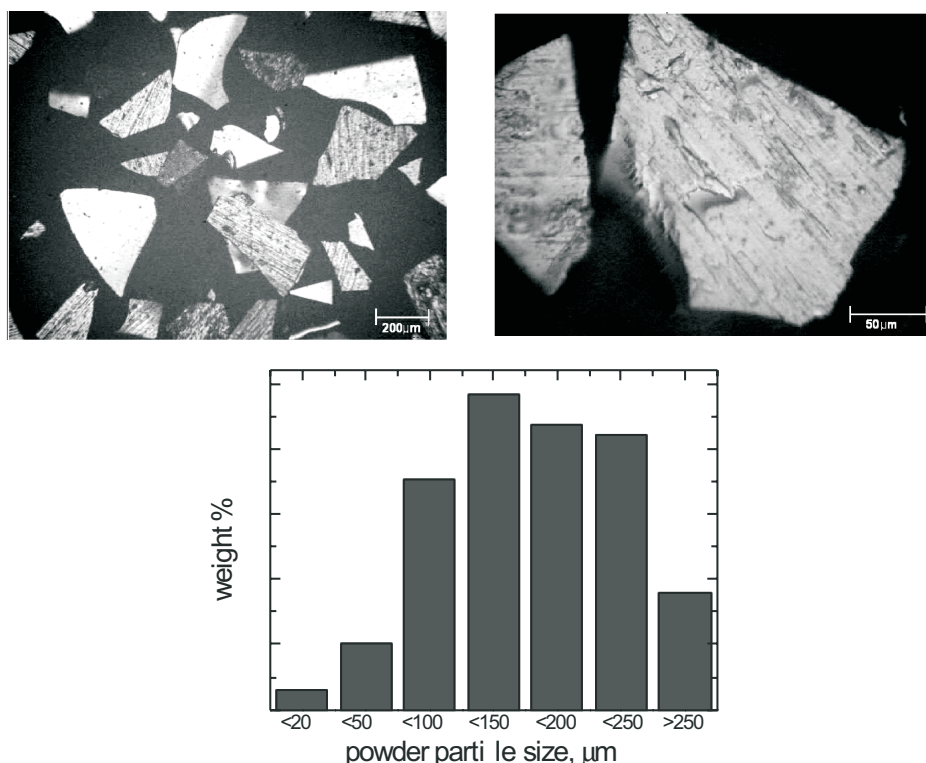


Fig. 1. Morphology and distribution of powder particle size of MQP-B material

The differences between tested samples consisted in technique applied for magnetic powder consolidation i.e. A – consolidation with powdered (dry) thermo-setting epoxy resin, B – preliminary micro encapsulation of powder particles using 5 wt.% solution in acetone of thermo-setting epoxy resin, and C – as previously but using 10 wt.% solution in acetone of chemical setting epoxy resin (additions of epoxy resin were equal 2.5% in all types of samples). After treatment of B and C type, powders were dried in cold air stream to constant mass and then pressed under the pressure ranged between 700 1000 MPa (step 100 MPa).

The influence of consolidation parameters on corrosion behaviour has been evaluated according to:

- i. The potentiokinetic polarization curves measured in 0.5 M sulphate solution acidified to  $\text{pH} = 2$  and in phosphate ( $\text{pH} = 3$ ) solutions containing 0.1 M of chloride ions. Potentiokinetic tests have been carried out in temperature of  $20^\circ\text{C}$  and the disk electrode rotation speed equal to 21 rps., with potential change from cathodic to anodic direction, ranging from  $-1.5\text{V}$  to  $+2.0\text{V}$  with a scan rate of  $10\text{ mV} \cdot \text{s}^{-1}$ . All potentials are expressed vs. Ag/AgCl auxiliary electrode.
- ii. Accelerated gravimetric tests in an artificial industrial atmosphere: aerosol produced from aqueous solution of  $3\text{ mg} \cdot \text{dm}^{-3}$   $\text{SO}_2$ , at temperature of  $40^\circ\text{C}$  – five 10 hour's exposure cycles. 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.

Magnetic properties of obtained cylindrical shaped samples ( $\phi = 10\text{ mm}$ ,  $h = 4\text{ mm}$ ) were evaluated using BELL 5070 gaussmeter in temperature of  $20^\circ\text{C}$ .

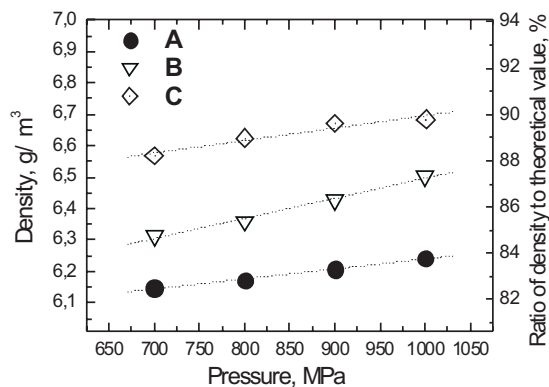


Fig. 2. Samples density: A – magnetic powder consolidated with powdered (dry) thermo-setting epoxy resin, B – powder preliminary micro encapsulated with thermo-setting epoxy resin and C – powder micro encapsulated with chemical-setting epoxy-resin

### 3. Results and discussion

In Fig. 3 potentiokinetic polarization curves of the tested as received MQP-B epoxy resin bonded material (at four different pressure values) measured in acidified, 0.5 M sulphate solution with  $\text{pH} = 2$  are presented.

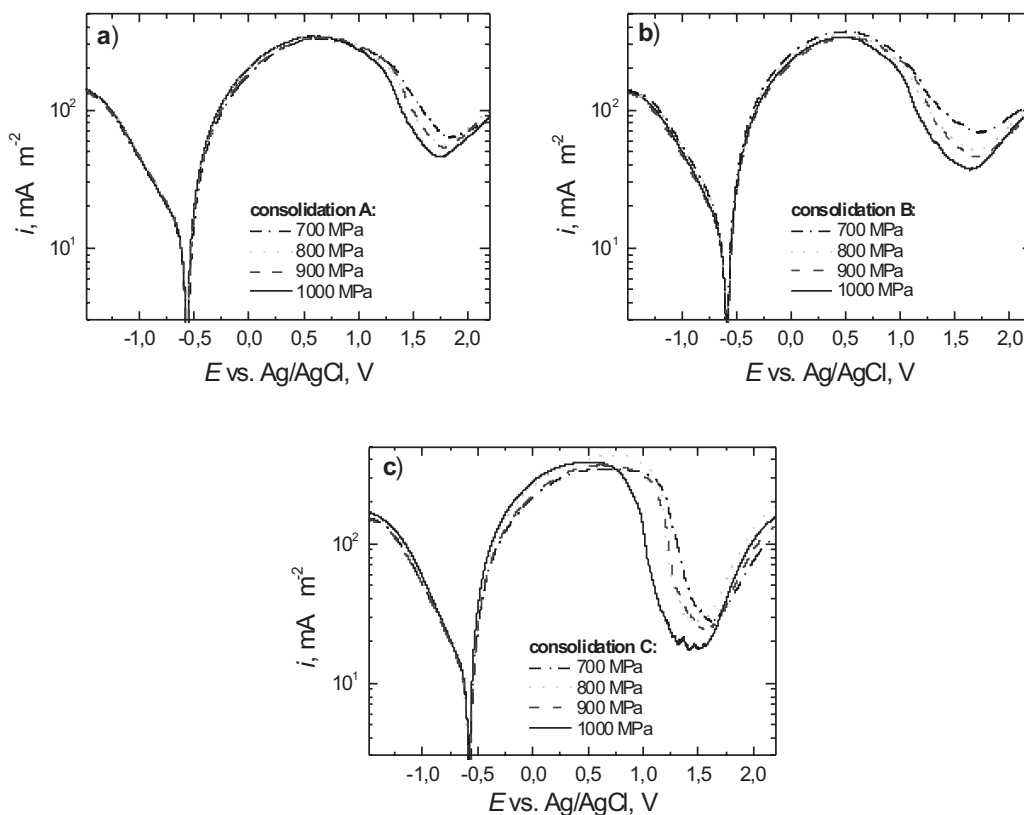


Fig. 3. Potentiokinetic polarization curves of MQP-B epoxy resin bonded magnetic material a) magnetic powder consolidated with powdered (dry) thermo-setting epoxy resin, b) powder preliminary micro encapsulated with thermo-setting epoxy resin and c) powder micro encapsulated with chemical-setting epoxy-resin. Experimental conditions: 0.5 M sulphate solutions, 20°C, potential scan rate: 10 mV · s<sup>-1</sup>, disk rotation speed: 21 rps

Shape of cathodic and anodic curves indicates that in the applied solution (pH = 2) the corrosion process occurs with activation control at  $E_{cor} = -0.55$  V. For more positive potentials (above 1.0 V) there appears a certain tendency to passivation. There is practically no difference between corrosion potential as well as cathodic and anodic plots in active region obtained for the as received MQP-B powder consolidated with epoxy resin bonded with three methods. The differences appear in the passive range. The composite materials produced from the powder preliminary micro encapsulated with epoxy-resin show generally lower values of minimal current in passive range ( $i_{min,p}$ ) the higher compaction pressure. The strongest tendency to passivation is observed for material consolidated with method C. The ranges of  $i_{min,p}$  value for samples compacted with A, B and C method are: 45 ÷ 64 mA · cm<sup>-2</sup>, 37 ÷ 70 mA · cm<sup>-2</sup>, 18 ÷ 29 mA · cm<sup>-2</sup>, respectively (where the lower value corresponds to the pressure 1000 MPa and the greater one – 700 MPa).

In Fig. 4 dependencies of  $\Delta E$  vs.  $\Delta i$  are presented. According to Stern Hoar [22] equation in the vicinity of

$E_{cor}$ , the external current density is a linear function of electrode potential:

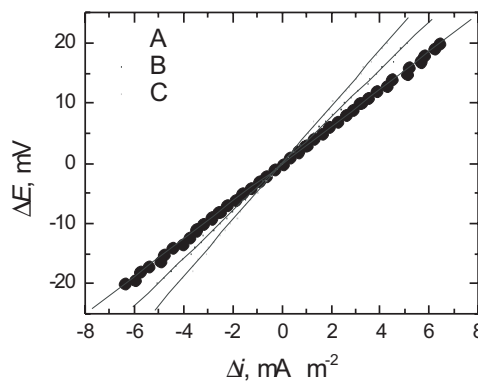


Fig. 4. Dependencies of external currents vs. electrode potential in the range of  $E_{cor} \pm 20$  mV for MQP B epoxy resin bonded magnetic material in 0.5 M sulphate solution with pH = 2. A – magnetic powder consolidated with powdered (dry) thermo-setting epoxy resin, B –

powder preliminary micro encapsulated with thermo-setting epoxy resin and C – powder micro encapsulated with chemical-setting epoxy-resin (compaction pressure 800 MPa)

$$R_p = (\Delta E / \Delta i)_{E_{\text{cor}} \pm 20 \text{mV}}$$

The slope of  $\Delta E / \Delta i$  straight lines allows to evaluate corrosion currents for the tested samples. In Table 1

values of  $R_p$  and calculated values of corresponding corrosion currents for all samples compacted at different pressures are presented. Assuming that Tafel slopes are analogous as for iron in sulphate solutions i.e.  $b_a = 0.04$  and  $b_c = 0.12$  V) [23] one can find that  $i_{\text{cor}} [\text{A} \cdot \text{cm}^{-2}] = 0.013 R_p^{-1} [\Omega \cdot \text{cm}^2]$ .

TABLE 1

Values of polarization resistance ( $R_p$ ) and corrosion current density ( $i_{\text{cor}}$ ) of MQP-B magnetic material bonded with tree methods and compacted at four different pressures

Sample	Pressure [MPa]			
	700	800	900	1000
$R_p [\Omega \cdot \text{cm}^2]$				
A	2.98	3.12	3.20	3.21
B	3.78	3.94	4.01	3.37
C	4.22	4.68	4.70	3.89
$i_{\text{cor}} [\text{mA} \cdot \text{cm}^{-2}]$				
A	4.36	4.16	4.06	4.05
B	3.44	3.29	3.18	3.49
C	3.08	2.78	2.77	3.34

In Fig. 5 the polarization behaviour of the tested samples in 0.5 M phosphate solution containing 0.1 M chloride ions is 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  $10^{-1} \text{mA} \cdot \text{cm}^{-2}$ . As its results from Fig. 5, 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 [24]. However, it should be stressed that in phosphate solutions the anodic currents in passive range are two orders of magnitude smaller than those for sulphate solution (compare Fig. 2). In order to evaluate the resistance of the tested samples against pitting corrosion addition of 0.1 M of  $\text{Cl}^-$  ions into 0.5 M phosphate solution (pH = 3) has been applied in our experiments.

In presence of  $\text{Cl}^-$  ions the breakdown of the passive layer is observed for all types of samples. The range of passive state depends not only on consolidation method but also on the compaction pressure (mainly in method A and C) as well. The pit nucleation potential ( $E_{\text{pit}}$ ) increases with an increase of compaction pressure for MQP-B bonded with powdered thermo setting epoxy resin (A); this way, pressure increase (and consequently decrease of sample porosity) is advantageous from local corrosion limiting point of view. Contrary to samples obtained with method C the values of  $E_{\text{pit}}$  are more positive with decrease of compaction pressure. It is possible, that pressure increase favours additional stress in magnet particles which increases number of surfacial active sites and facilitates pitting corrosion. On the other hand, the slope of anodic curves directly above  $E_{\text{pit}}$  is more steep for samples bonded with thermo setting epoxy resin (A and B) than those for samples bonded with chemical setting epoxy resin (C), which indicates more rapid pits development for samples A and B.

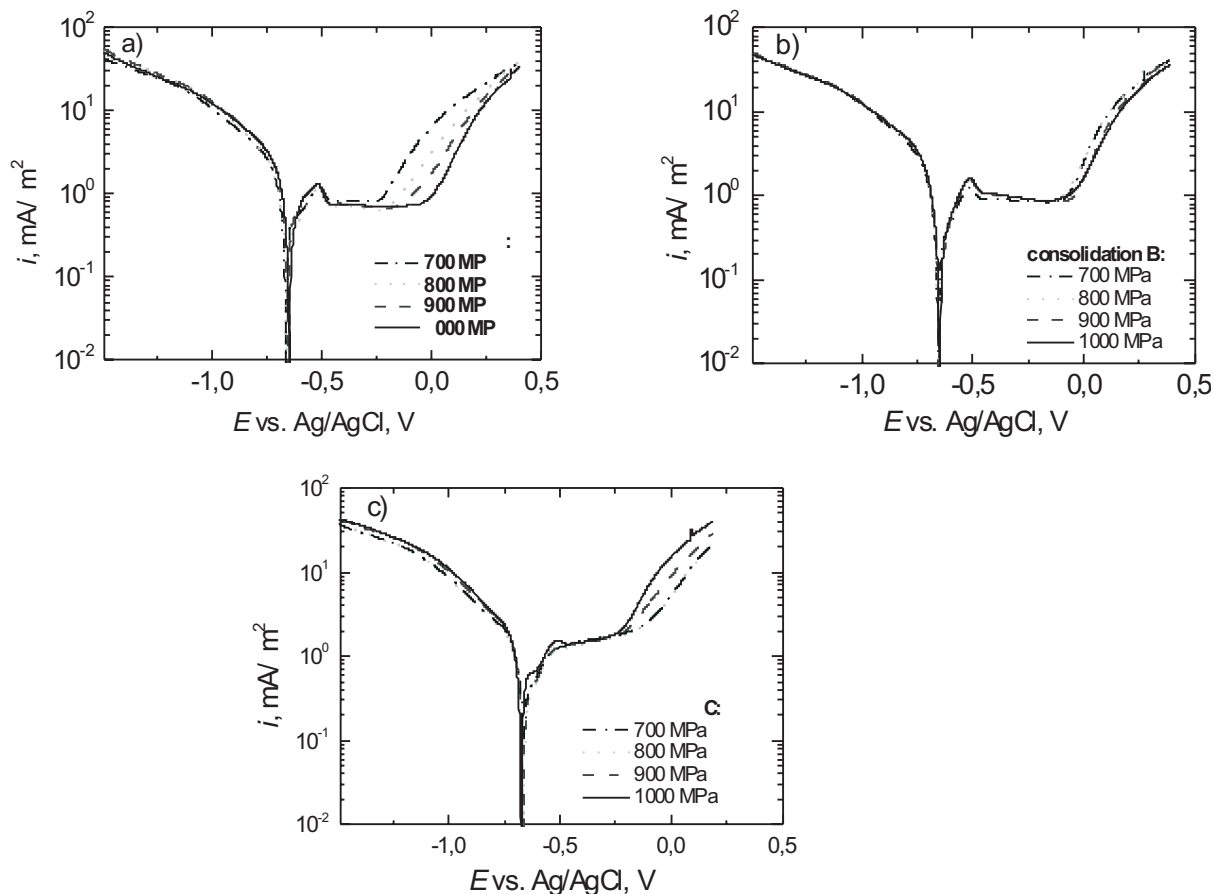


Fig. 5. Potentiokinetic polarization curves of MQP B epoxy resin bonded magnetic material a) magnetic powder consolidated with powdered (dry) thermo-setting epoxy resin, b) powder preliminary micro encapsulated with thermo-setting epoxy resin and c) powder micro encapsulated with chemical-setting epoxy-resin. Experimental conditions: 0.5 M phosphate solution with 0.1 M  $\text{Cl}^-$  addition, 20°C, potential scan rate:  $10 \text{ mV} \cdot \text{s}^{-1}$ , disk rotation speed: 21 rps

In Fig. 6 the exemplary results of accelerated atmospheric corrosion tests for MQP-B magnets bonded with the applied techniques (compacting pressure 800 MPa) are presented. The mass of the particular samples linearly increases with exposure time in artificial industrial environment. The slopes of respective straight lines are the measure of atmospheric corrosion rate. The corrosion rates are practically constant with time for all the tested samples, however, atmospheric corrosion behaviour clearly depends on magnet preparation method. The powder encapsulation with chemical setting epoxy resin (sample C) is the most advantageous for atmospheric corrosion inhibition. The appearance of magnet surface (sample C compacted with pressure 800 MPa) before and after its 50h exposure in artificial industrial atmosphere is presented in Fig. 7.

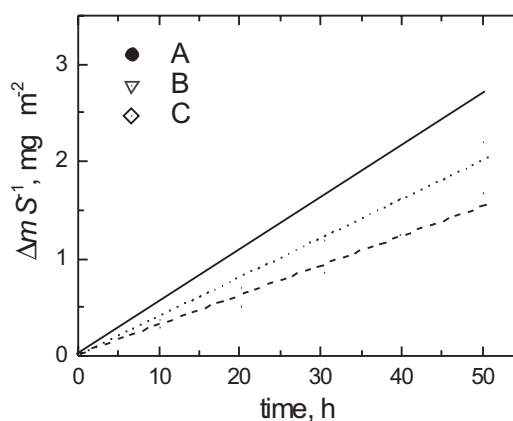


Fig. 6. Mass growth as a function of time during exposure of MQP-B epoxy resin bonded magnetic material in industrial atmosphere. A – magnetic powder consolidated with powdered (dry) thermo-setting epoxy resin, B – powder preliminary micro encapsulated with thermo-setting epoxy resin and C – powder micro en-

capsulated with chemical-setting epoxy-resin (compaction pressure 800 MPa)

As it results from the literature data, the main atmospheric corrosion products of Nd-Fe-B type mag-

nets are: white  $\text{Nd}(\text{OH})_3$  and “brown rust”  $\text{Fe}(\text{OH})_2$  and  $\text{FeO}(\text{OH})$  compounds [15–17]. According to most of authors,  $\text{Nd}(\text{OH})_3$  predominates in corrosion products. Simplifying the problem, the main reaction responsible for the atmospheric corrosion process is:

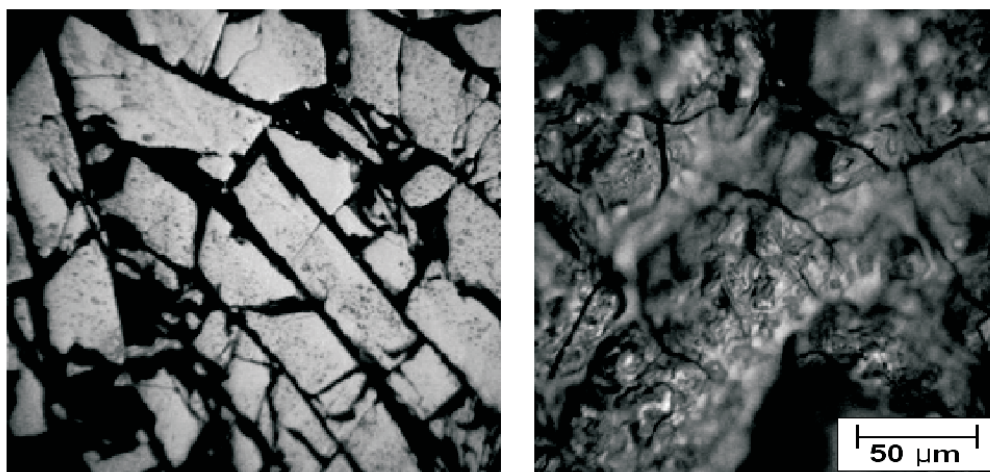
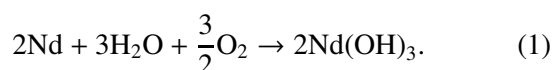


Fig. 7. Surface of MQP B epoxy resin bonded magnetic material (sample C compacted with pressure 800 MPa): a) before exposition, b) after 50 h exposure in artificial industry atmosphere



The mass gain during atmospheric corrosion process is equal to mass of  $\text{OH}^-$  groups in corrosion products. Assuming that measured  $\Delta m$  value is equal to mass of  $\text{OH}^-$  groups, one can calculate that the real corrosion rate is:

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

Where  $M_{\text{Nd}(\text{OH})_3}$  and  $M_{\text{OH}^-}$  are molar masses of  $\text{Nd}(\text{OH})_3$  and  $\text{OH}^-$ , respectively. The slopes of straight lines allow to determine magnets atmospheric corrosion rate for all tested samples on the basis of the following equation:

$$r_{\text{cor}} = \text{slope} \times 3.83. \quad (2a)$$

The calculated values of atmospheric corrosion rate for four applied compaction pressure are presented in Table 2.

TABLE 2  
Corrosion rates [ $\text{mg} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ ] of MQP-B epoxy resin bonded magnetic material (samples A, B and C) in artificial industrial atmosphere at different pressures of powder compaction

Sample	Pressure [MPa]			
	700	800	900	1000
A	5.2	5.1	5.0	5.0
B	3.8	3.5	3.7	3.9
C	2.8	2.8	2.8	3.0

Comparison of results presented in Table 2 allows to conclude that the applied micro encapsulation of MQP-B particles with chemical setting binder inhibits atmospheric corrosion process nearly two times more effectively as compared to common consolidation method with the use of thermo setting epoxy powder.

In Fig. 8 the example of demagnetization curves of the tested samples based on nanocrystalline MQP B powder prepared in three different methods A, B and C compacted under pressure of 800 MPa are presented. The magnetic properties all of tested samples are compared in Table 3.



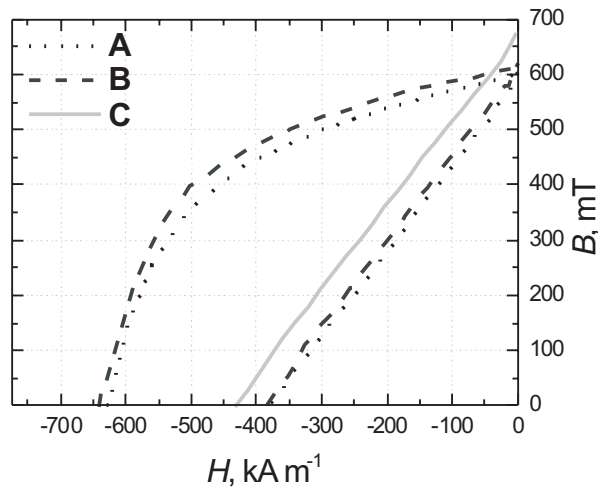


Fig. 8. Demagnetization curves of MQP B epoxy resin bonded magnetic material. A – magnetic powder consolidated with powdered (dry) thermo-setting epoxy resin, B – powder preliminary micro encapsulated with thermo-setting epoxy resin solution in acetone and C – powder micro encapsulated with chemical-setting epoxy-resin solution in acetone

TABLE 3

Magnetic properties of MQP B epoxy resin bonded samples (A, B and C) at four different compaction pressures

Samples	Preassure [MPa]			
	700	800	900	1000
Residual induction $B_r$ [T]				
A	0.62	0.61	0.63	0.64
B	0.60	0.61	0.61	0.61
C	0.64	0.66	0.68	0.66
Intrinsic coercivity ${}_cH_j$ [kA/m]				
A	644	640	659	666
B	639	640	634	631
C	715	711	707	701
Coercive force ${}_cH_B$ [kA/m]				
A	386	379	387	393
B	377	382	380	378
C	418	430	436	426
Energy product $(BH)_{max}$ [kJ/m <sup>3</sup> ]				
A	59.8	57.5	60.5	62.4
B	56.4	58.6	58.3	57.9
C	67.9	73.0	75.0	71.0

As it results from Table 3, magnetic parameters of the individual samples mainly depend on bonding method then compaction pressure. One can notice that among of three applied methods of powder bonding the best magnetic properties were obtained for chemical setting epoxy resin (sample C) and compaction pressure do not affect distinctly on these parameters. The differences between corrosion resistance of the samples produced in all applied methods can be explained in some extend on

account of partial cracking of strip particles during samples compaction. Consequently, the greater compaction pressure, the stronger splitting of strip particles, which is confirmed by particle size distribution for final samples obtained at different compaction pressure – Fig. 8. For example, contribution of the smallest particles ( $< 25\mu\text{m}$ ) after compaction at 700 MPa is 21% whereas after compaction at 1000 MPa it increases to 46% (compare Figs. 9(a) and (d)).



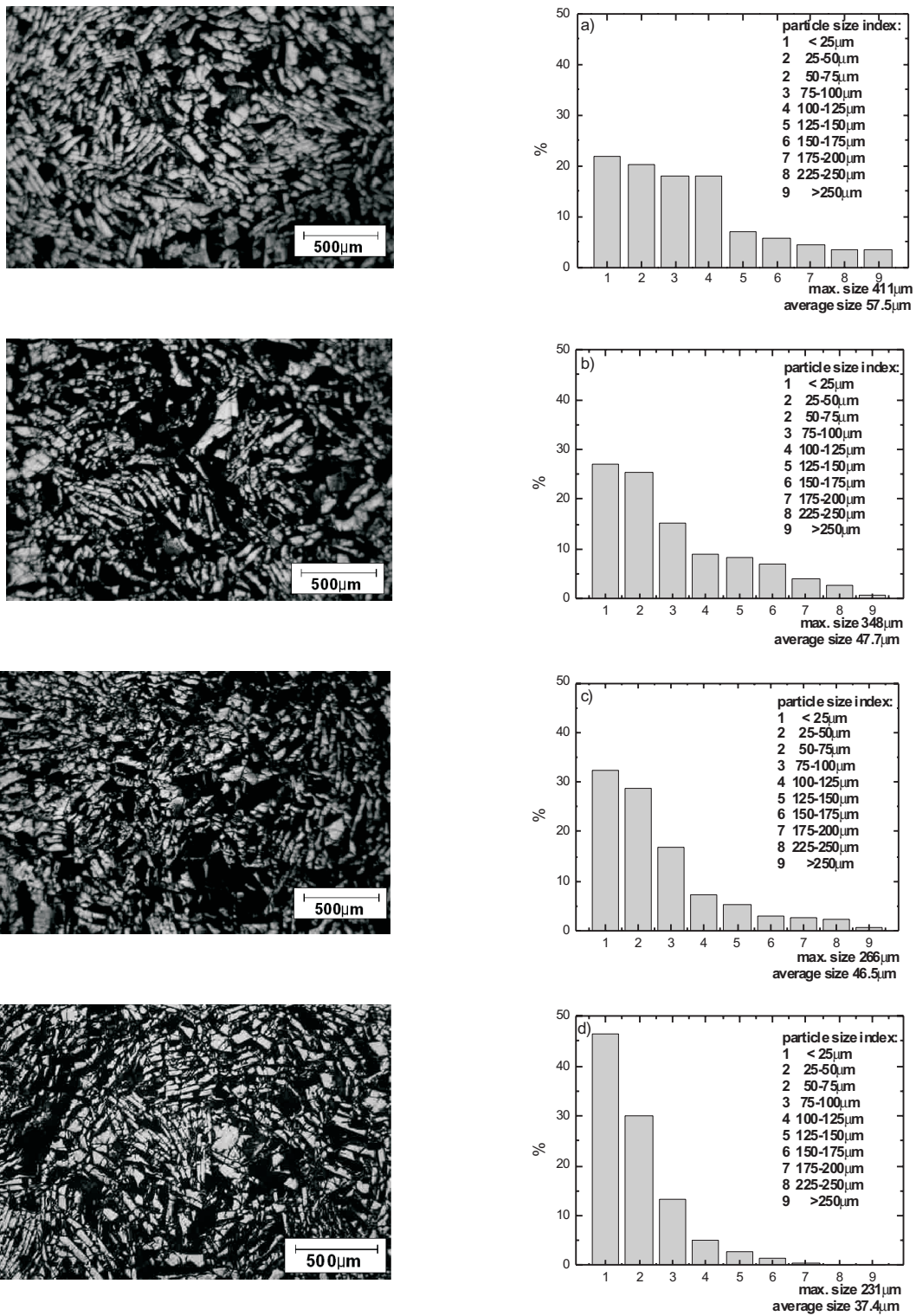


Fig. 9. Microstructure and grain size distribution of MQP-B epoxy resin bonded magnetic material(sample C) pressed with different pressure a) 700 MPa, b) 800 MPa, c) 900 MPa, d) 1000 MPa. The grain size has been determined using Met-Ilo program

Particles with initial size  $> 150\mu\text{m}$  after splitting cannot be effectively bonded with polymer binder because the binder is not able to fill all created cracks. In material structure there appear additional gaps with uncovered parts of powder, which are particularly sensitive to attack by aggressive environments and clearly manifest as local corrosion phenomena.

#### 4. Conclusion

Compaction pressure applied during magnets preparation strongly affects the corrosion behaviour of MQP-B bonded magnets. Especially disadvantageous are compaction pressures greater than 800 MPa because of particles splitting and cracking which is prone to local corrosion development. At low pressure (700 MPa) micro encapsulation of magnet particles with chemical setting epoxy resin solution in acetone is very promising from the magnet corrosion resistance point of view.

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