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Corrosion resistance of the polymer matrix hard magnetic composite materials Nd-Fe-B

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Abstract: The paper presents the corrosive wear of the hard magnetic composite materials with the polymer matrix, reinforced with the Nd-Fe-B particles from the rapid quenched strip, sintered Nd-Fe-B magnets, and composite materials coated with the protective polymer, lacquer, and metal coatings. The corrosive resistance values in the water environment and in the 5% NaCl solution environment were determined. The neural network model for evaluation of the rate of corrosive wear of the polymer matrix hard magnetic composite materials with addition of metallic powder was established based on the research results from the investigations carried out in two corrosive environments.

Keywords: Protective coatings, Permanent magnets; Nd-Fe-B; Composite materials, Corrosive wear, Neural network,

1. INTRODUCTION

The dynamic development in the engineering and technology domains gives the reason to increase the requirements posed to various engineering materials, also to those used for hard magnets. They should have not only the advantageous magnetic properties but also the required mechanical properties and resistance to the corrosive environment. [1-3] The neodymium magnets of the Nd-Fe-B type reveal a poor corrosion resistance in the moisture environment, which greatly limits their applicability. [4] The significant susceptibility to corrosion of the neodymium magnets calls for using the protective coatings that safeguard them from corrosion during their operation in the devices. The neodymium magnets are coated with the protective coatings, whose task is to protect them from fast wearing out due to action of the corrosive environment. Both single component metal coatings are used, like nickel, chromium, aluminium, zinc, tin, silver, gold, as well as the multi-component, multilayer ones like Ni-Cr or Ni-Cu. [5,6] Putting down the protective paints and lacquers, as well as resins resistant to moisture, acids, and alkalies, onto the neodymium magnets, is a method making it possible to protect them from corrosion in an simple way.

The goal of the work is to determining the corrosion resistance of the neodymium magnets with the polymer matrix, reinforced with the Nd-Fe-B particles, sintered magnets, and magnets coated with the protective polymer, lacquer, and metal coatings. Artificial neural networks were used to establish the rate of corrosive wear of Nd-Fe-B hard magnetic composite materials.

2. EXPERIMENTAL

The examinations were carried out on the polymer matrix hard magnetic composite materials reinforced with particles of the powdered rapid quenched Nd-Fe-B strip MQP-B type made by Magnequench ($Nd_{14,8}Fe_{76}Co_{4,95}B_{4,25}$), sintered magnets and composite materials covered by polyurethane, phtal-uretane and epoxy lacquer (sprayed under pressure), polymer epoxide, poliester, poliester-epoxy (electrostatic painted), zinc, nickel, cooper, chromium coatings (galvanic method).

Coating adherence evaluation was made with the stamp tear off test. Hardness tests of the lacquer and polymer coatings were made using the Persoz pendulum damping test, in which the basis of the measurement is counting the time (in seconds) of damping the pendulum from the 12° swing to 4° one. Metal coatings thickness tests were made with the "calotest" method, and for the polymer and lacquer ones the wedge-shaped slanted incision method was used and the slanted incision projection width was measured with the microscope.

The samples were placed in a corrosive environment and two tests were made: Test No.1 – at the temperature of 40°C, relative humidity of 93%, time of 96h for magnets, 240h – magnets covered by protective coatings, Test No. 2 – at the temperature of 35°C, 5% solution of NaCl, time of 6h for magnet, 72h - magnets covered by protective coatings. The character of the developed failure was evaluated basing on observations on the LEICA MEF4A light microscope. The surface damage extent during the corrosion test and after its completion was evaluated using the computer image analysis system. Observations of the magnets surfaces were carried out. Corrosion resistance tests were also made on magnets covered with the protective coatings. The character of the developed failure was evaluated basing on observations of the scratched and non-scratched coatings on the light microscope.

A series of observation of uncoated composite materials surfaces were made after the periods of time: Test No.1 – 24h, 48h, 96h, respectively, Test No.2 - 1h, 2h, 6h, respectively. Then, the area of corrosion wear area was measured by the computer-assisted colour-based image analysis system and the results were referred to the total observation area. Corrosive wear was defined as:

$$Z = \frac{P_{cor}}{P_{tot}} \tag{1}$$

where: Z – corrosive wear [%], P_{cor} – corrosive wear area [mm^2], P_{tot} – total area [mm^2]

In order to quantify the relationship between the mass contribution of the powdered additions and the corrosive wear rate, artificial neural networks were employed. Three types of input data were used in the investigation: the contribution of the added powder, the nominal variable that defined the corrosive environment and the time duration of the test. The corrosive wear of the surface expressed in terms of the percentage ratio between the corrosive wear area and the total area was the output produced from such input data. A multilayer perceptron (MLP) network with a single hidden layer composed of three neurons (a logistic activation function). The neural network was trained using the Lavenberg-Marquardt algorithm for the next 160 training epochs.

3. RESULTS AND DISCUSSION

Employing the natural differentiation of the corrosion products and specimen material the colour metallography methods were used to evaluate the corrosion wear of the magnet surface. It was found out that the corrosion wear of the surface grows quickly at the beginning, and the decrease of its growth rate is observed with time. Corrosion wear of the composite material surface after the test in the water environment is 72%; whereas, after the test in the NaCl environment is 99.4%. The sintered magnet gets destroyed after 96 h in the water environment and after 2 h in the NaCl environment. The surface of the sintered magnet is getting destroyed at a uniform rate. In case of the composite materials development of the corrosion centres and their further growth were revealed (Fig.1.)

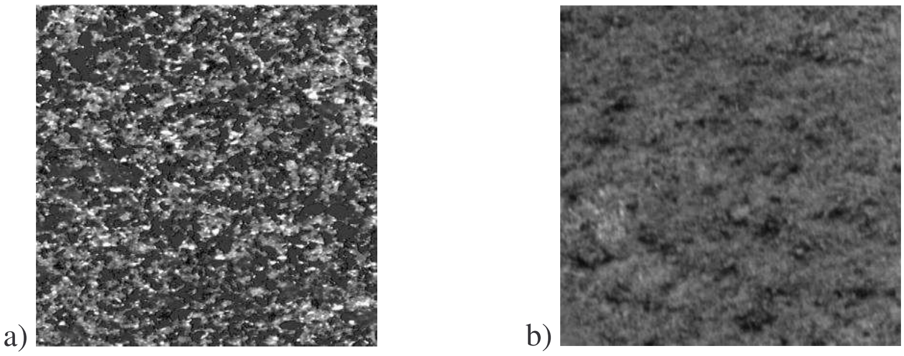

Figure 1. Corrosive wear of surface after corrosion test in water environment of a) composite materials, b) sintered magnets

The use of powdered metallic additions brings benefits in terms of reduced corrosion rate of composite materials. The findings of the water corrosion test indicate that the best corrosive behaviour is attributed to aluminium powder added composites. Also cast copper and tin alloy powders and those of high alloy steel contribute to better corrosion resistance of composite materials. The lowest values of corrosion resistance were obtained in powdered iron-added composites. In case of the NaCl test, the lowest corrosive wear was observed in aluminium powder added composites, whilst those with addition of iron powder revealed the highest corrosion intensity (Table 1.)

Table 1.
Corrosive wear of composite materials in water test and 5% NaCl solution

Kind of addition	Amount of addition [% wt.]	Test 1 [h]				Test 2 [h]			
		12	24	48	96	1	2	4	6
No addition	-	18,6	38,7	56,9	72	80	95	98,7	99,4
Iron	5	21	42	60	78,8	82	93,1	95,5	95,7
	10	26	52	67,6	86	87,6	95,7	97,4	97,9
	15	29,2	55	70,4	89,6	93	98,6	100	99,8
Aluminum	5	8	16	25,2	33,6	30	38	40,6	41,7
	10	6,2	12,4	20	26	22	30	32	34,3
	15	3,6	7,2	12,4	15,2	18	25	26,8	28,2
CuSn10	5	17,5	35	42	50	65	79,1	82,5	84,4
	10	15	30	36	44	58	69	72	75
	15	13,5	27	32	35	45	59,5	63	64,5
X2CrNiMo17-12-2	5	13	32	39	46	67	75	77,8	80
	10	16	26	30	33	55	64	68	69,8
	15	13	18	26	30	43	53	56	59

It was found out, basing on the investigation results, that the protective coatings put down on the substrate from the hard magnetic composite material with the polymer matrix reinforced with the Nd-Fe-B particles with the metal additions are characteristic of the uniform deposition on the entire surface and of the same thickness all over their area. These coatings are characterised by a compact structure with no visible delaminations and defects. Polymer coatings demonstrate higher hardness compared to the lacquer ones. The highest hardness of 350 s is characteristic of the polyester polymer coating. It was found that the highest adherence of 8.4 MPa is characteristic of the polyester-epoxy coating; whereas, the lowest adherence is displayed by the phthal-urethane coating – 5.0 MPa (Table 2.).

Table 2.
Thickness, hardness and adherence of protective coatings

Coating	Thickness [μm]	Hardness[s]	Adherence[MPa]
Polyurethane lacquer	45	300	7,3
Phtal-uretane lacquer	60	195	5,0
Epoxy lacquer 1	45	168	5,6
Epoxy lacquer 2	55	175	7,1
Polymer epoxide	80	350	6,4
Polymer poliester	80	310	7,9
Polymer poliester-epoxy	80	292	8,4
Zinc	45	-	8,4
Nickel	38	-	6,8
Cooper	20	-	5,2
Chromium	15	-	7,4

It was found out that the composite materials made from the powder from the rapid quenched strip bound with the polymer material are less susceptible to the corrosive environment than the sintered magnets. Polymer coatings demonstrate the best resistance in both corrosion tests. The lacquer coatings are resistant in the water environment; whereas, in the 5% NaCl solution environment they get locally blistered and are torn away from the substrate. Metal coatings demonstrate a lower corrosion resistance compared to the polymer and lacquer ones in both corrosive environments. The best resistance among the metal coatings is characteristic of the zinc coating, a good resistance is characteristic of the chromium one; whereas the nickel and copper coatings get blistered and are spalling (Fig. 2.).

Based on the investigation findings of corrosive wear of composite materials a model of neural network was developed. This model allows to quantify the relationship between the mass contribution of the powdered additions and the corrosive wear rate. Three types of input data were used in the investigation: the contribution of the added powder, the nominal variable that defined the corrosive environment and the time duration of the test. The corrosive wear of the surface expressed in terms of the percentage ratio between the corrosive wear area and the total area was the output produced from such input data.

Based on the developed neural network model, there was possible to carry out a computer simulation of the role of metallic powder as an additions and/or the influence of the duration of the corrosion test time on the corrosive wear. Table 3 presents the results of the quality evaluation for the optimised neural network model. These results, namely the low value of the error-mean square, close to zero standard error deviation ratio for errors and data and Person's correlation coefficient close to 1 confirm the validity of the neural network-based mapping approach. Merely the same coefficients for the sets: training, validation and test ones indicate that the developed neural network is able to generalize. Figure 3 illustrates a comparison between real and calculated values of corrosive wear in composite materials.

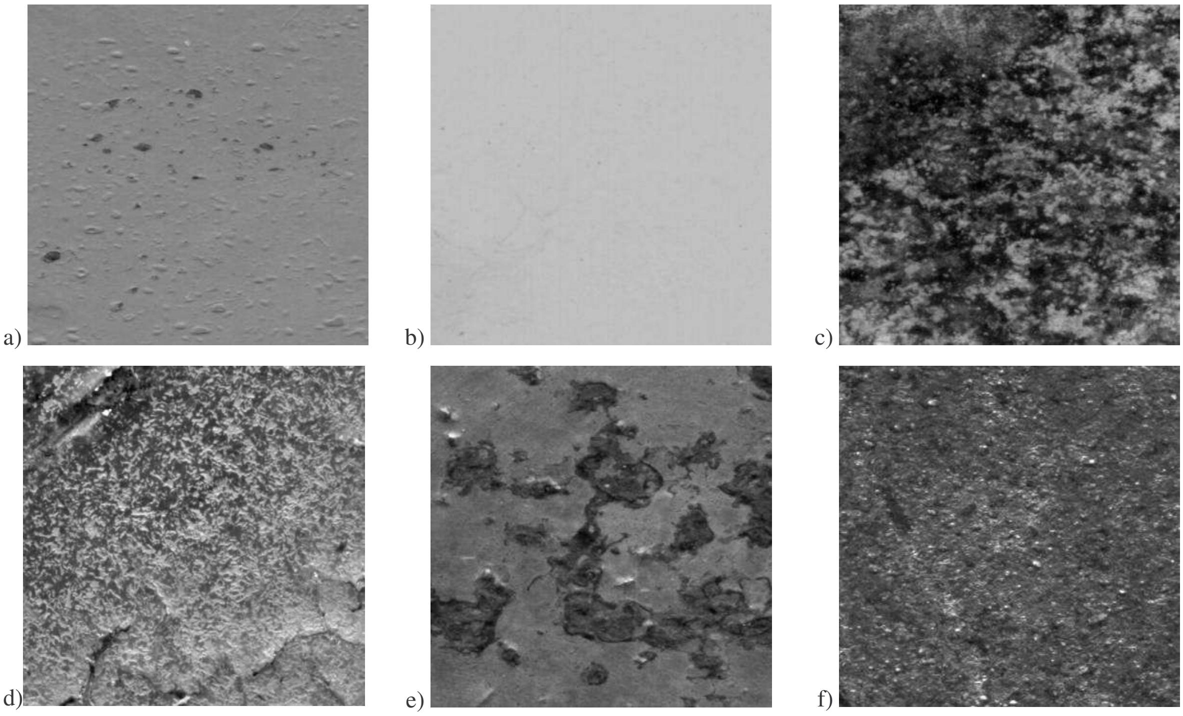

Figure 2. Corrosive wear of protective coatings after 72h corrosive test in 5% NaCl solution : a) epoxy lacquer 2, b) polymer poliester-epoxy, c) zinc, d) nickel, e) cooper, f) chromium

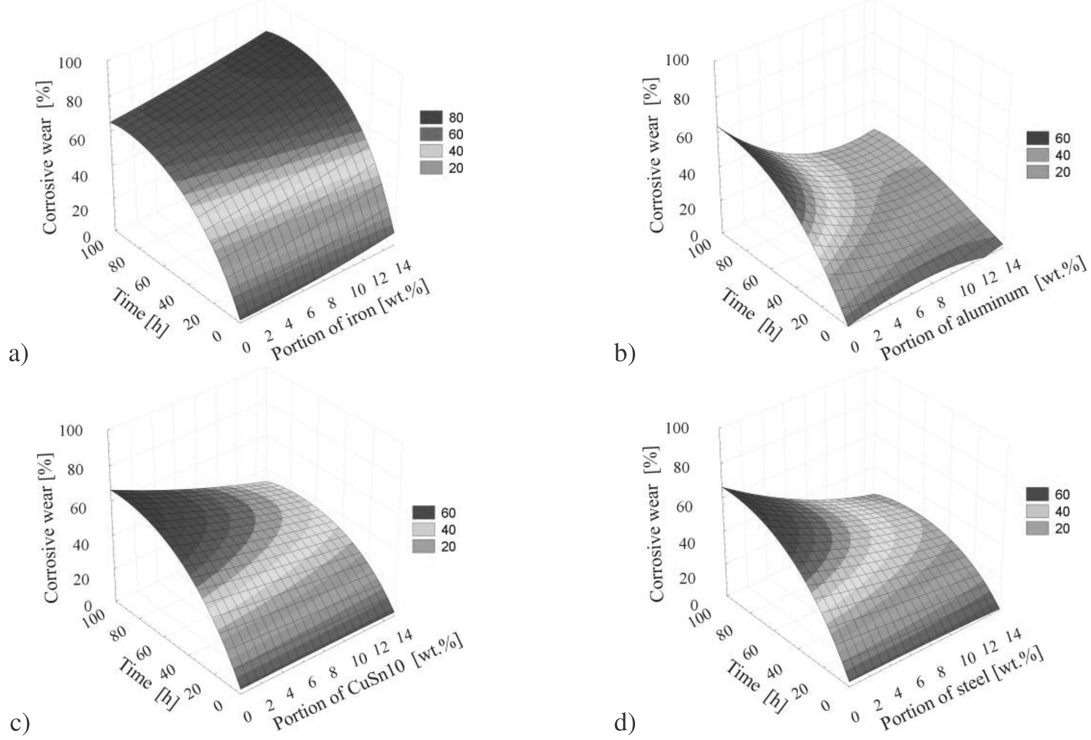

Figure 3. The relationship between the corrosive wear in composite materials during corrosion test No. 1 with addition of powder: a) iron, b) aluminum, c) CuSn10 type cast copper-tin alloy, d) X2CrNiMo17-12-2 high-alloy steel

Table 3.
Quality assessment coefficients for neural networks

Quality assessment	Set		
	Training	Validating	Testing
Standard error deviation	1.94	3.38	3.74
Mean error	1.36	2.80	2.93
Ratio of standard deviations	0.08	0.09	0.12
Pearson's correlation coefficient R	0.99	0.99	0.99

4. CONCLUSION

The corrosive environment resistance tests carried out made it possible to determine the corrosive wear of the hard magnetic Nd-Fe-B composite materials with the polymer matrix and sintered Nd-Fe-B magnets. It was found that composite materials shows higher corrosion resistance than sintered magnets in both corrosive environment. The best corrosion resistance show composite materials with aluminum powder addition. Corrosive wear of magnets surface is the smallest and decrease with the growth of portion of metallic powder.

The protective coatings put down on the substrate from the hard magnetic composite materials are characteristic of the uniform deposition on the entire surface and of the same thickness all over their area. These coatings are characterised by a compact structure with no visible delaminations and defects. Polymer coatings demonstrate the best resistance in both corrosion tests. The lacquer coatings are resistant in the water environment; whereas, in the 5% NaCl solution environment they get locally blistered and are torn away from the substrate. Metal coatings demonstrate a lower corrosion resistance compared to the polymer and lacquer ones in both corrosive environments.

Moreover, there was proposed a simulation approach to model the corrosive wear in metallic powder added polymer-matrix composite materials filled with magnetically hard Nd-Fe-B particles in function of the chemical composition, nature of the corrosive environment and the test duration, employing a neural network technique. The obtained results indicate that the developed neural network is able to generalize that justify using this model to the simulation of corrosive wear of hard magnetic composite materials.

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