

Corrosion tests on alloys and permanent magnets based on NdFeB, used in aerospace industry

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For special applications like aerospace field, the NdFeB permanent magnets must work in different aggressive conditions: extreme temperatures (very high or very low), very high humidity media, etc. The paper presents the results of experimental researches performed in order to determine the behaviour against corrosion of Nd-Fe-B permanent sintered magnets, with different chemical composition.

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1. Introduction

The industrial development stage imposes the realization of new materials in order to improve the quality of products and the economic efficiency. The last category includes also the coating of NdFeB magnets by electrochemical deposition of protective metallic layers or resins [1-3]. The NdFeB magnets are high performance products and they have a large utilization in industry. The NdFeB permanent magnets imposed because of their remarkable magnetic properties: $B_r \geq 12$ kGs, $H_{c_j} \geq 26$ kOe, $(BH)_{max} \geq 34$ MGOe. For all that, they present some disadvantages: low temperature and reduced corrosion stability [4-6]. The coated NdFeB permanent magnets have high corrosion resistance, without mechanical deterioration, so that they have high working reliability.

The NdFeB permanent magnets have low chemical stability at surfaces, the Nd-rich phases oxidizes and one produces material losses and broken parts, that signify increased flux losses. The low chemical stability relative to the corrosion is based on the microstructure: the Nd-Fe-B alloys show a three-phase microstructure consisting of $Nd_2Fe_{14}B$ phase (Φ), the $NdFe_4B_4$ phase and the Nd-rich binder phase. In order to improve the corrosion stability of NdFeB based permanent magnets, there are two possibilities: to modify the magnet microstructure using different adding elements [7-10], as well as using coatings with metallic or nonmetallic layers [11].

The particularity of sintered NdFeB magnets is that they present an adherent layer of oxides resulted after the thermomagnetic treatments, the essential condition for the realization of coatings is the removing of this adherent layer of oxides. Because of the high sensitivity of NdFeB alloys to oxidant inorganic acids, especially of the Nd-rich phase, it is imposed a rapid chemical cleaning. This work presents the improvement of corrosion stability using different adding elements for the sintered permanent magnets based on NdFeB and the corrosion tests

performed on these permanent magnets with various type of coating layers.

2. Experimental

The NdFeB permanent magnets are realised using methods specific of powder metallurgy. The $Nd_{15}Fe_{77}B_8$, $Nd_{13.5}Dy_{1.5}Fe_{73}V_4B_8$, $Nd_{15}Fe_{74}Co_2Al_1B_8$ alloys were prepared by induction melting and then the cast ingots were decrepitated in H_2 , milled in balls mill and the obtained hydrogenated powders were compacted (at 2 tf/cm² pressure) in presence of external magnetic field (12 kOe). The green-compacts were sintered (at 1100 °C for 2-3 hours) and annealed (at 600-660 °C for 2-3 hours).

After the experiments, we established the specific operations for the preparation of the NdFeB magnets surfaces:

- surface grinding and polishing;
- degreasing in organic solvent and after that in alkaline solvent;
- chemical attack in diluted in alcohol HNO_3 solutions and chemical cleaning in organic acids.

After surface preparation, the NdFeB can be protected. Function of the medium where they will be used and atmosphere corrosion agents, will be established the type of corresponding coating by:

- a) coating with metallic micron layers of Zn, Ni, Ag;
- b) nonmetallic coating, using paints and epoxy resins.

The metallic micron coating with Zn, Ni, Ag is realized by electrochemical deposition [12,13], the methods are described below.

3. Coatings

3.1 Coating using Zn Layer

An essential condition to realize a technology for anticorrosive coating is to use ecological coating methods, competitive from the economic point of view and taking

into account the corrosion sensibility of NdFeB magnets. After experiments it was established the zinc coating medium from an electrolyte low acid [2] that presents a high penetration power, one can apply high currents density to realize a deposition velocity of 1 - 2 mm/min., resulting a high and economic productivity. The zinc coating bath is: electrolyte - KCl + ZnCl₂; 120 g/l Cl and 25 g/l Zn; additives - H₃BO₃, polishing agents, equalizers, urging pH 5.6 - 5.8; temperature 20 - 50 °C; current density 1 - 10 A/dm²; voltage 5 - 10 V.

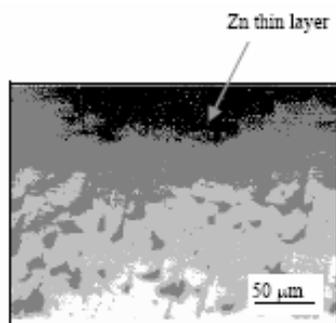


Fig. 1. Transversal microstructure of the Zn deposition layer of a NdFeB magnet.

The obtained depositions can be easy passive rendered, so that the corrosion resistance is improved. The layer is uniform, without porosity, with a good adherence and high corrosion resistant. The thickness of the Zn layer is correlated with the working conditions of the magnets. In figure 1 is presented the microstructure of the transversal Zn layer.

3.2 Coatings using Ni layer

The Ni deposition are applied of satisfy some special applications [14]. The Ni protections are used for small pieces of NdFeB magnets, magnets that are used in miniaturized circuits and also for decorative objects. The depositions are realized in acid coating bath, such as: electrolyte - Ni sulfate and Ni chloride; additives - H₃BO₃, polishing and nickel agents; pH: 4.5 - 4.8; temperature: 35 - 50°C; current density: 2 - 6 A/dm²; voltage: 4 - 8 V.

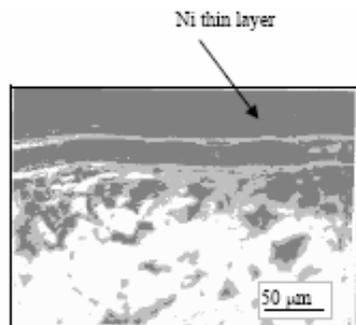


Fig. 2. Transversal microstructure of the Ni layer deposition on a NdFeB magnet.

3.3 Coating using Ag layer

The Ag layers were done for small pieces of NdFeB magnets, used in medical applications.

The deposition of silver is realized on a layer of Cu, and the silver coating is realized from cyanide electrolytes. The cyanide bath has the following technological parameters: cyanide electrolyte based on Ag and K; additives - K₂CO₃; current density: 0.5 - 1 A/dm²; pH: 12; temperature: 20 - 30 °C; voltage: 1 - 1.5 V.

The obtained layers are of high quality with good adherence and uniform, the transversal microstructure is presented in Fig. 3.

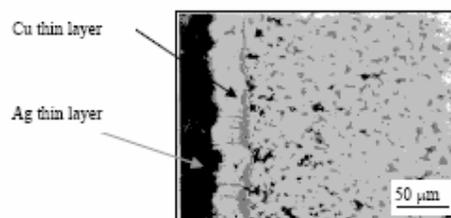


Fig. 3. Transversal microstructure of the Ag and Cu layer deposition on a NdFeB magnet.

3.4 Coatings using non-metallic layers

For the nonmetallic layers on the NdFeB permanent magnets we used epoxy resins and paints. Coatings with epoxy resins [15] have a high corrosion resistance during time. Because of their disadvantage of porosity and hygroscopy of these layers, it is imposed the realization of layers with a thickness of 50 - 60 μm.

The layers can be obtained by different methods: using specific paint, by sputtering, by immersing, by electrostatic deposition followed by a drying treatments, polymerization. One can obtain relative resistant layers, adherents, with high mechanical resistance and remarkable commercial properties at corrosion.

The composition of the layer, the application mode and the metallic surface preparation are essentials factors to obtain a high quality of protection layers. The obtained layers are uniform, adherents, with high resistance at wet and drying corrosion agents, having insignificant magnetic fluxes or dimensions variations, a layer of 5 - 10 μm can ensure an efficient protection. The polished Ni deposition for decorative purposes increases in the same time the magnets mechanical resistance. The microstructure of the Ni deposition is presented in Fig. 2.

4. Corrosion tests

In order to study the behaviour of the corrosion resistance for the prepared uncoated and coated NdFeB sintered magnets, were performed different tests:

- in humid heat: 45°C, 95% RH for 100 - 800 hours;
- in dried heat: 120°C, for 100 - 500 hours;

- in salt spray: NaCl 5% continuous spraying, 200 hours (only for coated magnets);
 - in sulphured hydrogen: 400 hours (only for coated magnets).

In the case of humid heat, after 100 hours of investigations, we didn't observe a weight loss for all

studied samples: (table 1). After 300 hours, we have obtained a good corrosion resistance for the samples with additions based on Dy-V and Dy-Co (see Table 1).

Table 1. Results of corrosion test of NdFeB magnets at 45°C and 95 % RH.

Time (h)	Nd ₁₅ Fe ₇₇ B ₈ (at. %)		Nd _{13.5} Dy _{1.5} Fe ₇₃ V ₄ B ₈ (at. %)		Nd ₁₅ Fe ₇₄ Co ₂ Al ₁ B ₈ + 3 % Dy ₂ O ₃ (at. %)	
	Δm/m ₀ •10 ⁻⁴	Aspect	Δm/m ₀ •10 ⁻⁴	Aspect	Δm/m ₀ •10 ⁻⁴	Aspect
100	9	rust points	9	rust points	10	-
300	22	rusted	17	rusted	11	rusted
500	26	rusted	17	rusted	25	rusted

For the same samples like in the case of the humid heat investigations (Nd₁₅Fe₇₇B₈, Nd_{13.5}Dy_{1.5}Fe₇₃V₄B₈, Nd₁₅Fe₇₄Co₂Al₁B₈+3%Dy₂O₃ and Nd₁₅Fe₇₄Co₂Al₁B₈+5 % Dy₂O₃, coated with a 10 μm Zn or Ni layer or noncoated), after 100 hours, 300 hours and 500 hours at 120°C/dry heat, we hadn't weight losses or modifications of the magnets surfaces.

In order to study the efficiency of different protections against corrosion of sintered NdFeB permanent magnets we have used the next coverings:

- galvanic depositions of Zn (A) and Ni (B), thickness of about 5-20 μm;
- (C) PPCE-epoxy resin by electrostatic painting, thickness of about 40-100 μm;
- epoxy resin layer with different additions of Zn

(D) and Al (E) powders by electrostatic painting, thickness of about 40-100 μm;

- (F) PEP-G type epoxy resin layer by electrostatic painting, thickness of about 40-100 μm;
- thin layer with Zn (G) and Al (H) spray, thickness of about 3-15 μm;
- (I) thin layer with Varnish spray, thickness of about 3-15 μm;
- (K) thin layer with PTFE-epoxy resin, thickness of about 3-15 μm.

From the Table 2, with the next codifications, we can observe the best behaviour for the coated magnets by electrostatic painting, with epoxy resin layer with additions of Zn.

Table 2. Aspects of the covered surfaces after different periods, and environments.

Layer type	Aspects after different periods of salt spray environment					Aspects after different periods of humid heat environment				
	24 h	96 h	144 h	19 h	200 h	144 h	200 h	400 h	600 h	800 h
(A)	CC 80%	CC 90%	CC100% CM 10%	-	-	NM	NM	CM0.5% CC	CM 1% CC	CM 3% CC
(B)	CM 30%	-	-	-	-	CC	CM1.5%	CM3%	CM7%	CM10%
(C)	NM	NM	E	-	-	NM	E*	E	-	-
(D)	NM	NM	NM	NM	E	NM	NM	NM	NM	NM
(E)	NM	NM	E*	E	-	NM	CC	CM0.5%	-	-
(F)	NM	NM	NM	E	-	NM	NM	DS+E*	CM	-
(G)						NM	NM	CC1.5%	CC 6% CB 2%	CC 6% CB 5%
(H)						NM	CC	CC	CM 1%	CM 8%
(I)						NM	NM	NM	CC	CM 2%
(K)						NM	NM	NM	CC	CM 2%

NM - without modifications of the covering aspect
 CC - corrosion of the covering
 CM - corrosion of the magnet

E - exfoliation of the covering
 E* - exfoliation, especially at the edges

After 800 hours of dry heat at 120 °C we didn't observe any deterioration of the covering layer (we have used the same coverings like in the case of the above environments).

For the sulphured hydrogen corrosion test, in the case of the Zn spray layer, after 300 hours, the covering is not

deteriorated and after 400 hours the layer colour is little modified. After 300 hours, in the case of the Al spray layer we had few corroded points of the magnet and after 400 hours 2 % of the surface is corroded. In the other coatings, we didn't observe changes in the covering aspect.

5. Conclusions

The experiments done were aimed to establish the most efficient methods for the protection against corrosion of the NdFeB permanent magnets. The coatings have to be resistant at different type of corrosion agents. It was established that the optimum protection is by using the electrochemical deposition, method that has a very good stability at corrosion tests. Correlated with the working medium of the NdFeB magnets, the protection by electrochemical painting and organic epoxy resins ensure the maximum corrosion resistance, without altering the magnetic properties of the magnets.

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