

Evaluation of the corrosion behaviour for the permanent magnets based on rare earths, used in aeronautical industry

W. KAPPEL^{*}, M. M. CODESCU, N. STANCU, D. POPA[†]

R&D National Institute for Electrical Engineering ICPE Advanced Research, 313 Splaiul Unirii, Bucharest, Romania

[†]South Airport Otopeni, Romania

Applications with permanent magnets need to know the optimum solution between price and quality. In the case of the aeronautical industry applications of the permanent magnets based on rare earths (RE), we need to know where is the best solution for our application and for that we make a comparison between the corrosion behaviour of different type of permanent magnets in various aggressive media. For the optimum performance of a permanent magnet in special devices must know the work conditions: pressure, temperature, vibration, demagnetizing field, other perturbation, and consequently their behavior in these conditions. The paper presents the evaluation of the corrosion behaviour of different permanent magnets or alloys, based on RE and transition metal (MT).

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1. Introduction

Despite their outstanding magnetic properties at room temperature, the use of the Nd-Fe-B permanent magnets has been limited due to essential reasons:

- the low temperature coefficient of the intrinsic coercivity leads to quite low maximum operating temperatures (around 150 °C) and
- the oxidation of the unavoidable Nd-rich phase, which plays a great role in the coercive mechanism, leads to a bad corrosion resistance of these magnets.

Overcoming these features is of great scientific and economic interests, and therefore a lot of works have carried out in this field mainly concentrated an Al /1-3/, heavy rare earth's /4/ or Co /5/ substitutions. Unfortunately, too low maximum use temperature and poor corrosion resistance remains.

The NdFeB permanent magnets have low chemical stability at surfaces, the Nd-rich phase oxidizes and one produces material losses and broken parts, that signify increased flux losses. The low chemical stability relative the corrosion is based on the microstructure: the Nd-Fe-B alloys show a three-phase microstructure consisting of Nd₂Fe₁₄B phase (Φ), the NdFe₂B₄ 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 as well as using coatings with metallic or nonmetallic layers.

2. Experimental

The cast ingots were prepared, by melting in the induction furnace, form different industrial ferroalloys

(Nd84-Fe16, Fe80-B20) and from pure dysprosium, aluminum, gallium, silver, copper and/or technical iron. The chemical compositions of the cast alloys and the thermal treatments (the annealing temperature range was: 630 – 750 °C) were presented in the Table 1. The permanent magnets were prepared by the conventional powder metallurgy route, using the “single alloy” method or the “two alloys” method and including decrepitation of the ingots, ball-milling, compaction, with the pressure ($p = 2 \text{ tf/cm}^2$) axis perpendicularly to the field axis ($H_{\text{magn}} = 12 \text{ kOe}$), liquid phase sintering (1050 – 1100 °C/2 –3 h) and annealing (600 – 660 °C/2-3 h). The potential measurement were performed by the Gerischer - Vielstich method, using the potentiostat type PG 201, with H₂O + 3 % NaCl electrolyte and with potentiodynamic regime, the scanning speed was 50 mV/min.

Table 1. Chemical composition of the alloys used as intergranular phase (δ -phases).

Alloys code	Chemical composition (weight %)						Annealing temperature (°C)
	Nd	Fe	Al	Ga	Cu	Ag	
O ₁	55.45	39.36	5.19	-	-	-	630
O ₂	56.50	36.45	7.05	-	-	-	700
O ₃	57.14	34.66	8.20	-	-	-	750
O ₄	52.10	43.70	-	4.20	-	-	650
O ₅	51.84	41.48	-	6.68	-	-	650
O ₆	69.40	-	-	-	30.60	-	650
O ₇	53.16	-	-	-	46.84	-	650
O ₈	53.50	43.16	-	-	-	3.34	650
O ₉	51.83	38.48	-	-	-	9.69	650

3. Results and discussions

The corrosion tests performed on different alloys, cast or annealed, and also on magnetic samples, prepared by various routes, aim (i) to establish the influences of different adding elements on the chemical stability of the Nd-Fe-B alloys, and also (ii) to identify new phases, in order to replace the intergranular Nd-rich phase.

The investigation of the corrosion behaviour have been made by the plotting of the polarization curves (overtoltage / current densities), which show the dependence of the corrosion current on the overvoltage applied to the electrode.

We continued the started researches [6] to find corrosion resistant phases in order to replace the unstable Nd-rich intergranular phase in NdFeB permanent magnets. We have investigated different alloys and compounds: Nd-Fe-Al, Nd-Fe-Ga, NdCu, NdCu₂ and Nd-Fe-Ag, in accordance with Table 1.

Using this alloys and Nd₂Fe₁₄B compound, we have prepared magnets with different amounts of additives.

The investigations used to determine the corrosion resistance behaviour, are the same, for the magnetic samples and for the alloys based on Nd: corrosion potential measurements with PG 201 type potentiostat, 3 % NaCl water solution, 50 mV/min scanning speed.

In Table 2 were presented the values of the electrochemical potentials for an alloys based on the Nd-Fe-B system, for the hard magnetic phase (Φ -phase) and for the Nd-rich phase (measured for an alloy with 84 % weight Nd, Fe, balance). Comparatively, were presented also the potentials of different metals, usually used as surfaces coatings.

Table 2. The values of the electrochemical potentials for an alloy based on Nd-Fe-B ternary system, for Φ and Nd-rich phases, and for Al, Zn, Mg.

Material	Mg	Nd-rich phase	Zn	Nd-Fe-B alloy	Al	Nd ₂ Fe ₁₄ B
Electrochemical potential, (mV)	- 1590	- 1163	- 980	- 717	- 710	- 680

We can observe from the values presented in the Table 2, that the Nd-rich phase has the lower chemical stability, in comparison with the Φ -phase and with the Nd-Fe-B alloy. In the presence of an electrolyte, the electrochemical reaction is started in the magnet microstructure between these phases, because of their different electrochemical potentials. If the electrolyte don't exists and in low humidity conditions, this permanent magnets can be used uncoated.

Table 3 presents the corrosion potentials determined by potentiostatic measurements, together with the corrosion rates, calculated for different types of RE permanent magnets and alloys used as intergranular phase (δ -phases), including also the prepared magnets, between the mixing of the Φ -phase with different amounts of δ -phases.

Table 3. Corrosion potential, corrosion speed and corrosion rate of used alloys and compounds (after Table 1).

Pos.	Composition	Corrosion potential E ₀ (mV)	Corrosion speed I _{corr} (10 ⁻³ mA/cm ²)	Corrosion rate Corr (mm/year)
1	Permanent magnets (50-x) Nd ₂₄ Dy ₅ Al _{0.4} B ₁ Fe _{rest} + 50 Nd _{28.5} Dy ₅ Al _{0.4} B ₁ Fe _{rest} + x-Dy ₂ O ₃ (x = 1 ... 2,5)	- 744 - 716	50 - 60	0.600 – 0.700
2	Nd _{28.5} Dy ₅ Co _{2.5} Al _{0.4} B ₁ Fe _{62.6}	- 716	20	0.23
3	Nd ₂ Fe ₁₄ B (cast)	- 681	70	0.09
4	Nd ₂ Fe ₁₄ B (annealed)	- 178	1,3	0.015
5	Nd ₃₂ Fe ₅₅ Al ₁₃ (cast)	- 1137	332	7.46
6	Nd ₃₂ Fe ₅₅ Al ₁₃ (annealed)	- 711	29.6	0.66
7	δ - Nd ₃₀ Fe ₅₅ Al ₁₀ (annealed)	- 644	7.7	0.105
8	δ - Nd ₃₀ Fe ₅₅ Al ₁₀ (annealed)	- 680	20.2	0.281
9	δ - Nd ₃₀ Fe ₄₇ Al ₂₃ (annealed)	- 970	11.9	0.172
10	δ - Nd ₃₀ Fe ₆₅ Ga ₅ (annealed)	- 734	6.4	0.082
11	δ - Nd ₃₀ Fe ₆₂ Ga ₈ (annealed)	- 655	7.9	0.098
12	SmCo ₅ permanent magnets	- 592	25.2	0.27
13	Nd ₂₄ Dy ₅ Al _{0.4} B ₁ Fe _{rest} alloy (cast)	- 753	29.5	0.35
14	Nd _{28.5} Dy ₅ Al _{0.4} B ₁ Fe _{65.1} alloy (cast)	- 966	52.3	0.61
15	Nd _{30.5} Dy _{2.5} Co _{1.2} Cu _{0.2} B ₁ Fe _{64.6} magnet	- 693	10.9	0.13
16	Nd _{30.5} Dy _{2.5} Co _{2.5} Cu _{0.2} B ₁ Fe _{63.3} magnet	- 709	22.2	0.28
17	Nd ₅₀ Cu ₅₀ (NdCu)	- 836	53.9	1.163
18	Nd ₃₅ Cu ₆₅ (NdCu ₂)	- 766	45.5	0.918
19	Nd _{31.5} Fe ₆₆ Ag _{2.5}	- 1157	331.6	7.010
20	Nd _{31.5} Fe ₆₀ Ag ₈	- 1023	6.8	0.142
21	Φ + 5 % O ₁	- 750	15.3	0.200
22	Φ + 10 % O ₁	- 732	9.2	0.126
23	Φ + 15 % O ₁	- 734	7.5	0.101
24	Φ + 5 % O ₂	- 780	0.1	0.001
25	Φ + 10 % O ₂	- 743	0.6	0.009
26	Φ + 15 % O ₂	- 740	0.06	0.001
27	Φ + 5 % O ₃	- 707	60.2	0.799
28	Φ + 10 % O ₃	- 704	9.5	0.128
29	Φ + 5 % O ₄	- 718	68.1	0.866
30	Φ + 10 % O ₄	- 725	12.9	0.185
31	Φ + 15 % O ₄	- 721	165.3	2.263
32	Φ + 5 % O ₅	- 724	23.1	0.321
33	Φ + 10 % O ₅	- 737	14.6	0.196
34	Φ + 15 % O ₅	- 705	0.1	0.001

Fig. 1 shows the polarization curves for different samples, according to the positions 1 - 14 from the Table 3.

From the informations presented in the Table 3 and from the Fig. 1, we can observe that the magnets from the Nd-Fe-B system (pos. 1, table 3) have a lower chemical stability as the SmCo₅ permanent magnets.

We can observe also, that the Co adding increases the corrosion resistance, especially when the cobalt is added together with copper. At the same amount of Cu, 0.2 weight % (pos. 16, Table 3), an addition of 1.2 weight % of Co, leads to an increased chemical stability of the alloy, comparatively with an addition of 2.5 weight % Co.

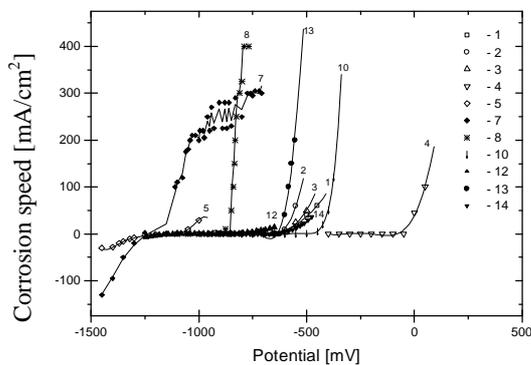


Fig. 1. Polarization curves of different magnetic samples and alloys, according to the positions 1 - 14 from table 3.

For the cast alloys, (pos. 13 – 14) we can observe that the stability is better for a lower amount of RE.

Other observation refers to the intergranular δ -phases and to the permanent magnets prepared using this new intergranular phases. We can see that the corrosion resistance of the prepared magnets increases together with the amount of the intergranular phase, based on Al or Ga. The lower corrosion speed (0,008 ... 0,002 mm/an) was obtained for all magnets with 20 % at. Al intergranular phase.

In the case of the magnets prepared using intergranular phase based on Ag we can observe the increase of the corrosion resistance with the intergranular phase amount, but this magnets have an corrosion potential (- 890 ... - 760 mV) lower than of the magnets prepared with the intergranular phase based on Al. For the magnets based on δ -phase with Al, the corrosion rate is higher: 0.001 – 0.002 mm/year, due to the better pasivant character of the Al.

From the Table 3 result that the alloys containing Ag have the highest corrosion potentials, and the δ -phases containing Ga (for 8 atomic %) and Al have the lowest corrosion potentials (for 15, respectively 20 atomic %).

4. Conclusions

In order to increase the chemical stability, the intergranular Nd-rich phase must be replaced with more chemical stable phases, like δ -phases from the systems: Nd-Fe-Al, Nd-Fe-Ga, intermetallic compounds: NdCu₂ or NdCu.

The most stable additives are those based on Ga (samples O₄ and O₅) and with Al (sample O₁).

For the same prepared magnets which use Al - based additives, the good resistance against corrosion is obtained only with higher concentration of low Al content additive (see samples 21, 22, 23). Very good stability is obtained with medium level of Al concentration in the additive (see samples 24, 25, 26).

The Ag - based additives seems to have not the expected behaviour in the improvement of the corrosion resistance (sample O₈, Table 3).

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*Corresponding author: kappel@icpe-ca.ro