CORROSION RESISTANCE OF NdFeB MAGNET TYPE WITH PROTECTIVE ZnAl COATING IN SELECTED ENVIRONMENTS

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Abstract

The problem of effective and powerful NdFeB type magnets is a lower corrosion resistance in many environments, a lower thermal stability of magnetic parameters in comparison with related permanent magnets and usually their brittleness. The results of corrosion tests and protective properties of layer ZnAl on NdFeB magnetic material are compared and evaluated in this contribution. The samples of as-received magnetic material NdFeB with special layer ZnAl and reference materials (Fe, Al, Zn, Zn/Fe) were used for corrosion tests in humid air (at temperature 65°C, during time 1200 hours) and salt spray test (35°C, 240 h.).

By means of the gravimetric method the time dependences of corrosion were found out. The corrosion resistance of ZnAl layer was much higher in comparison with Zn/Fe commercial one. Chemical composition of layers and materials (ZnAl/NdFeB) was determined by microanalysis, their structures and corrosion were studied by light microscopy.

The non-uniform thickness and corrosion of layers with two phase structure was observed in metallographic sections. On the basis of exposition tests the corrosion parameters of stated materials were determined and compared, especially with respect to uniform and pitting corrosion in water environments.

Key words:
NdFeB magnets, ZnAl coating, corrosion test, metallography, structure

1. INTRODUCTION

The effective, small and powerful magnets of type NdFeB can be applied in many devices (motors, computers, sensors) [1]. Their complex microstructure contains reactive components, like neodymium-rich phases, and this magnets exhibit a low corrosion resistance in humid atmospheres and water environments.

Neodymium is an active metal with a standard electrochemical potential $E_0 = -2.4$ V [2]. It has been also proved that Nd-rich phases and Nd$_2$Fe$_{14}$B matrix absorb hydrogen in humid environments leading to its degradation (decrepitation). In aqueous solutions, a preferential dissolution of the highly reactive intergranular Nd-rich phase occurs, which is strongly enhanced by the galvanic coupling of the Nd-rich phase to the much more noble ferromagnetic grains. The ferromagnetic grains on the bulk magnet surface loose adhesion and finally detach from the surface [3]. Thus, the Nd-Fe-B-based magnets cannot operate in technical devices with the absence of special anticorrosive coatings.

Secondary intergranular phases in new types of NdMeFeB magnets are composed of intermetallic compounds with better corrosion resistance than Nd rich phase. Corrosion resistance is enhanced for magnets with polymer (EP) binding of powder, but their magnetic properties and working temperatures are lowered.

The aim of the present work is to study the corrosion resistance of sintered NdFeB-based magnet material with the special protective coating (ZnAl) and to perform comparative investigations of corrosion resistance using reference metals and coatings.

2. METALS AND CORROSION TESTING

The powder mixture Al and Zn was applied on the magnet material (type NdFeB, dimensions 26x10x4.5 mm) surface by cold gas-dynamic sputtering (cold supersonic plating). The essence of the procedure consists in the fact that an applied material, which is present in the form of a powder and moves with inert gas flow, is...
accelerated to a supersonic speed, and fed to the deposition surface. Anticorrosive material particles are heated in striking against the material surface and, under the action of kinetic energy, and they fix firmly on the surface [4]. From selected sample the coating Al-Zn was removed by fine grinding in order to obtain base material (NdFeB) for testing. For comparative corrosion tests were used thin sheets of Al, Zn, Fe (non-alloyed low carbon steel with 0.2% C, CSN 41 1375) and commercially deposited layer of Zn on this steel (Zn/Fe). The thickness of metal sheets were in the range 0.6 - 0.9 mm.

Chemical microanalysis have revealed [4,5] that tested magnet NdFeB type consists of matrix of mean composition Fe69Nd25Dy4Co2AlB (wt. %, corresponding to (Nd,Dy)(Fe,Co)14B magnet, for simplicity these are written NdFe or NdFeB in this article) and secondary minor phase composed of Nd80Co9O8Fe2Dy1Si). Heterogeneous layer contains two phases rich in Zn and Al (Zn96Al2O2 and Al92Zn4O3Fe), surface analysis has revealed the average composition: 60% Al, 32% Zn, 8% O and 0.5% Fe (wt. %). The closed porosity was estimated by linear method and has the value around 25-30%.

Metallographic section of base material with the protective Al-Zn coating is shown in Fig. 1. A relatively large dispersion of the coating thickness was identified, in the range of 40-90 µm. The dark spots in Fig 1 are pores and/or secondary phases rich in Nd that partly dissolved during wet preparation of polished surface section. There is possibility of micro-galvanic action between Fe and Nd rich phases in water environment.

A relatively homogeneous protective Zn galvanic coating on steel has a thickness between 50-70 µm, Fig. 2.

Two corrosion tests were performed on these metals and coatings. The first group of samples were exposed in humid air at 65°C (100% relative humidity) during 1200 hours, with shutdowns for stereomicroscopy observation, photography and application of gravimetric method [6]. Second set of samples were exposed in neutral salt spray at 35°C according to standard [7]. Samples were tested in the vertical vertically or at the angle 20-30°C to the vertical direction. The small glass bowls were below the samples to capture some corrosion products (for more accurate weighting after water evaporation). After exposition from some samples were taken off smaller samples for metallography studies.

Fig. 1 As-received coating ZnAl on NdFeB. Markers of thickness measuring (polished section)

Fig. 2 Reference sample Zn/Fe (polished). Small inclusions or defects were found out.
3. RESULTS AND DISCUSSION

3.1 Corrosion tests

The mass gains of samples after certain time intervals were measured and average uniform corrosion was estimated. The corresponding time dependences of corrosion for tested metals and coatings are compared in Fig. 3 and 4. In humid air, the highest corrosion rates was confirmed on magnet material NdFeB, without coating, several times higher than in case of this magnet covered by special coating ZnAl. On the other hand, the lowest corrosion rate was measured on Al reference sheet. The ZnAl coating has a better corrosion resistance in both environment, but relative differences or ratios are smaller for longer time of exposition. Different corrosion behaviour were registered for iron, relatively small corrosion rate in clean humid air in comparison with high corrosion in salt spray with catalytic effect of chloride ions on iron.

The higher corrosion resistance of ZnAl layer in comparison with Zn can be explained by the positive influence of aluminium. The thick brown corrosion products (Nd(OH)$_3$, Fe(OH)$_2$, Fe(OH)$_3$) were formed of NdFe sample. The corrosion trend of pure Zn for longer time includes some corrosion losses.

![Fig. 3 Trends of corrosion mass gains on tested materials and coating after exposition in humid air (r.h. 100%, 800 hours at 65°C)](image)

![Fig. 4 Comparison of corrosion trends on tested metals and coatings after neutral salt spray test (240 hours).](image)
Zinc coatings can protect NdFeB magnets in similar way as low carbon steel, mainly by barriers effect and partly as sacrificial anode. Its protective properties determined by the difference of corrosion or equilibrium potentials between Zn and Nd rich phases. The life-time of zinc coatings is linear proportional to their mean thickness or weight per square meter and degree of the aggressiveness of atmosphere (C1 – C5) [8].

3.2 Light microscopy observations
In Fig. 5 are compared the surfaces of samples after exposition 800 hours in air at temperature 65°C and 100% relative humidity. The selected samples are placed from left to right – ZnAl/NdFe, NdFe, Zn/Fe, Zn and Fe (down). On the sample of aluminium the surface changes has not been observed and mass gain was negligible. A few spots (so called “red rust”) were formed on the Zn/Fe sheet and no dark spots on AlZn/FeNf samples, only light grey corrosion products, mainly Zn(OH)$_2$, in humid air at 65°C. Fig. 5. Dark small spots were found out on surface ZnAl/NdFe after 240 hours exposition in salt spray, many rust spots were formed on Zn/Fe sample under the same conditions, Fig. 6. On sample Zn/Fe approximately 5% of spots (relative surface) were observed at 120 hours exposition in salt spray. After 1200 hours exposure in humid air, the brown spots appeared on sample ZnAl/NdFe, preferably on edges in crevices between the sample and the pad and coating began lifting. The tests of ZnAl/FeAl in humid air at elevated temperature would continue up to time, when 5% rust spots would cover surface.

The example of corrosion attack of AlZn/NdFe system is documented in Fig. 7, where probably zinc corrosion products have grey shade (as islands in/on layer). The shallow pit on surface was also found out, mainly in the damaged layer, Fig. 8. Porosity of coating may reduce its corrosion resistance.
The metallographic section of Zn layer on steel (Zn/Fe) after long-time exposition in humid air is completed and compared in Fig. 9. Possibility of corrosion undermining of protective layer are also shown in Fig 10.

Comparative results can be used for evaluation of galvanic coating of zinc or zinc base coatings (ZnAl,ZnNi) for protection of magnetic materials of NdFeB type. The creation of two or three layers of different metals (Ni, Cu) in coating is another trend of protection of these magnets, as required for function and corrosion resistance of magnets.

CONCLUSION

Effective permanent NdFeB type magnets must be used in many fields of technology and equipment with protective coatings. Comparative corrosion tests (in humid air at 65°C and salt spray test) were performed with special coating ZnAl on magnetic material of NdFeB type, produced by powder metallurgy. For comparison purposes were used sheets of Al, Fe, Zn and coating Zn/Fe. Much higher corrosion rate was measured by gravimetric method on magnet NdFeB without coating in comparison with other tested metals and coatings. The corrosion resistance of special ZnAl layer was higher in comparison with Zn/Fe commercial one. The positive affect of Al on corrosion resistance of ZnAl coating has been proved.
Metallographic study confirmed closed porosity of ZnAl coating and base material NdFeB, non-uniform corrosion and rust spots after longer exposure time.

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