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Investigation of the inherent magnetic field influence on corrosion resistance of Nd – Fe – B permanent magnets

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Nowadays permanent magnets of Nd - Fe - B system are widely used in various branches of production. The trend has been toward increase of the world consumption of the magnets in the making of advanced technology gadgets (smartphones, navigators, television sets, and computers). However, this magnet material can not be always applied in the special-purpose devices because of its low corrosion resistance and poor temperature stability. To elongate service life of the magnets it is necessary to deposit a protective coating based on nickel, zinc, copper as well as on the combination of other substances (phosphate, epoxy resin).

The given paper is dedicated to the results of implemented comparative research of corrosion resistance of permanent magnets made of magnetically hard material based on Nd – Fe – B alloy both with metallic anticorrosive coat and without it in a magnetized and non-magnetized state.

It has been found that the inherent magnetization influence on the corrosion resistance of PM made of Nd – Fe – B MHM both with metallic anticorrosive coat and without it are of an opposite nature. The corrosion resistance of the samples without coating in the magnetized state has increased by 12%. At the same time, the corrosion resistance of Zn- and Ni-coated samples in the magnetized state has decreased by 40–45%. It is determined that the coating-free magnets are better to be stored and transported in the magnetized condition while the magnets protected by metallic anticorrosive coats need to be stored in the non-magnetized condition.

Key words: rare-earth elements, permanent magnets, corrosion resistance, anticorrosive coat, magnetization, magnetic field

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Introduction

s it is known, high-performance magnetically hard materials (MHM) based on Nd - Fe - B alloy are characterized by low resistance to corrosion [1–2]. It is one of their main imperfections along with poor temperature stability [3–4]. Therefore, vari-

ous anticorrosive coats are used to elongate service life of permanent magnets (PM) made of the above mentioned materials [5–6].

For the most part, different metals (Ni, Zn, Al, etc.) are used as a material of anticorrosive coats, being deposited by galvanic or another method [7].

Currently, there are several works [8–9], in which the rare-earth PM corrosion resistance with different coatings have been studied, but all of them have been carried out with the use of non-magnetized PM, but for all that, the latter are used in the magnetized state only.

Now, the magnetic fields effect on corrosion processes is not adequately explored, and information from different sources varies.

For example, in the paper [2] there is presented a study on corrosion resistance of steel samples. The results of experiments have shown that exposure of external magnetic field has increased corrosion resistance of the samples by the factor 2.1, in comparison with the samples under conditions of terrestrial magnetic field only.

In the works [10-11], on the contrary, it is determined that magnetic filed influence intensifies corrosion of aluminium and steel.

The presented paper is focused on comparative study of corrosion resistance of PM made of MHM based on Nd - Fe - B alloy with different anticorrosive coats in the magnetized and non-magnetized conditions.

Materials and research procedure

Melting of the $\mathrm{Nd}_{15}\mathrm{B}_{7,5}\mathrm{Fe}_{\mathrm{res}}$ ($\mathrm{Nd}_{15}\mathrm{B}_{7,5}\mathrm{Fe}_{\mathrm{ocr}}$) MHM alloy has been fulfilled out of pure source materials in inert atmosphere in a vacuum-induction furnace in a boron nitride crucible. Homogenization of the ingots has been fulfilled during 12 hours at 1100 °C and residual pressure no more than 0.001 Pa.

Following dressing, the ingots have been grinded in three stages. In the first stage coarse grinding of ingots into the particles of size up to 4 mm took place in a jaw-breaker. In the second stage fine mechanical grinding into the particles of size up to 0.8 mm has been fulfilled in a cone-inertial crusher in argon medium. Thereafter the powder fraction with the particles of size $50-300~\mu m$ has been separated by sieve selection.

Final grinding has been carried out in a ball vibratory mill in an isopropyl alcohol medium during 180 minutes until achieving an average particle size of 3.1–3.3 μ m. At this stage 2 wt.% of a Dy₂Al alloying addition powder has been added to Nd₁₅B_{7,5}Fe_{res} alloy powder in order to increase magnetic characteristics.

Pressing of the powder billets has been implemented in magnetic field with magnetizing force more than 2500 kA/m at the pressing specific pressure of 45–50 MPa.

Sintering of the samples after pressing has been carried out in vacuum furnaces at 1120-1130 °C during 40 minutes at residual pressure no more than 0.001 Pa. The sintered samples have been mechanically treated to put into a washer shape with $D20\times D6\times 2$ mm dimensions.

All in all, there were prepared 45 samples for investigation. 20 µm thick coatings have been deposited on 30 samples evenly divided between the nickel and zinc ones.

Corrosion testing of all the samples has been carried out in a KTK-800 climatic chamber by holding in humid

air (98%) at 55 °C. In the course of testing, relative mass variation of the samples $E = (\Delta m/m)100\%$ have been fixed on an HT84RCE analytical balance. In addition to the samples with coating, the samples without that have been also tested.

All the samples have been tested in three states: non-magnetized, partly magnetized and completely magnetized. The samples magnetization up to the state of technical saturation (residual induction $Br = 1.32-1.35\ T$) has been implemented on an EX-25/50-30 pulse setting. Partly magnetized samples (up to 0.5 Br) have been obtained by demagnetization of completely magnetized samples on a Permagraph C-300 hysteresisograph.

For each magnetization condition, 5 samples were tested with each coating type and without coating.

Results of investigation

The corrosion testing results averaged over 5 samples are presented in the Table 1 and in Fig.1.

As it is evident from the testing results, the inherent magnetization influence on the corrosion resistance of PM made of Nd - Fe - B MHM with metallic anticor-

Table 1

Relative mass variation after 600 hours of testing

Coating	Relative mass variation E, %		
	Magnetization-free	Partial magnetization	Total magnetization
No coating	0.75	0.69	0.64
Zn	0.17	0.21	0.24
Ni	0.09	0.11	0.13

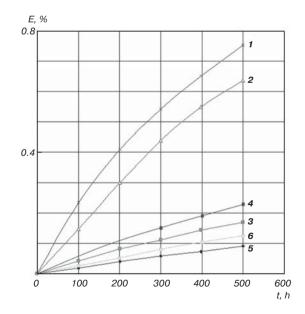


Fig. 1. Relative mass change of the samples in the course of testing: 1, 2 — without coating; 3, 4 — with a Zn coating; 5, 6 — with a Ni coating; 1, 3, 5 — non-magnetized samples; 2, 4, 6 — magnetized samples

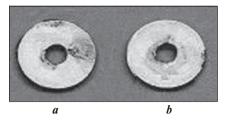


Fig. 2. An outward appearance of the samples without coating after the tests: a — non-magnetized sample; b — magnetized sample



Fig. 3. An outward appearance of the samples with a Zn coating after the tests: a — non-magnetized sample; b — magnetized sample

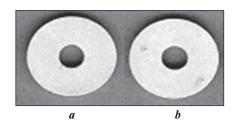


Fig. 4. An outward appearance of the samples with a Ni coating after the tests: a — non-magnetized sample; b — magnetized sample

rosive coat and that without it are of an opposite nature. So, corrosion resistance of the samples without coating in the magnetized state has increased by 12%. Photograph of the coating-free samples after the tests is depicted in Fig. 2.

At the same time, the corrosion resistance of Zn- and Ni-coated samples in the magnetized state has decreased by 40–45%. Photographs of the samples with an anticorrosive coat after the tests are given in Figs. 3 and 4.

Starting from results of testing one can suppose that mechanism of the magnet field influencing on the rate of corrosion processes proposed in [10], is due to be corrected. In fact, the process of metal corrosion in electrolytes is most often electrochemical because the metal surface consists of multitude of microcells (microanodes and microcathodes) and serves as a multielectrode galvanic cell. Such a structure stipulates an occurance (both on macroand microlevel) of galvanic current between the parts with different electrochemical potentials.

At that, electrolyte ions in the magnet field are affected by the Lorentz force, which twist their trajectory, forming microvortexes in electrolyte, thus leading to increase of some effective resistance of electrolyte itself. In the light of this fact the magnetic field, by [10], may weaken the corrosion process.

Notwithstanding, such a mechanism would only matter for those materials, specific electrical resistance of which is lower than that of electrolyte. For metals with their specific resistance essentially smaller as compared with electrolyte, transfer of charges will be realized predominantly over their volume. At the same time, main corrosion process will take place at the electrolyte — MHM interface, and therefore will lead to accelerated corrosion of the metal.

In this case, the Nd – Fe – B MHM specific resistance (1.44 Ω ·m [12]) is much above the specific resistance of zinc (5.9×10⁻⁸ Ω ·m) and nickel (4.5×10^K Ω ·m), which probably causes such a difference in behaviour of the samples without coat and with metallic coat.

Besides, the observable effect is probably connected with the fact that in case of ferromagnetic corrosion products (for example, ferric oxides and hydrated ferric oxides), their lesser amount will slip away from the sample surface and pass into electrolyte. At that, they are themselves able to protect the sample surface to some extent

and serve a nucleus of center for the salts contained in the solution, assisting by this in formation of different salt films on the sample surface, which in its turn allows to still more decrease the corrosion rate [13].

As for now, a unique explanation of the reasons of a positive or negative magnetic field effect on corrosion resistance of materials is not yet in hand. However, the obtained results allow to draw a conclusion of weighty practical significance. Storage and transportation of Nd — Fe — B MHM PM without coating should be better implemented in the magnetized condition. On the other hand, the PM, protected by metallic anticorrosive coats should be stored in the non- magnetized condition to elongate their service life.

Conclusion

- 1. Corrosion resistance of PM samples of the coating-free Nd Fe B MHM in the magnetized state increases by 12%.
- 2. Corrosion resistance of the Zn- and Ni-coated samples in the magnetized state decreases by 40-45%.

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Investigation of the structure and properties of eutectic alloys of the AI – Ca – Ni system containing REM

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This study investigated the eutectic alloys based on aluminum containing small amount of rare earth metals (REM): Al - 6Ca - 3Ni - 2Ce; Al - 6Ca - 3Ni - 2La; Al - 6Ca - 3Ni - 2Pr. The compositions of the alloys were selected on the basis of previous studies of ternary Al - Ca - Ni and Al - Ni - Ce systems, taking into account the similarity of the structure of the AI - REM binary systems. Melting was carried out in an induction furnace by RELTEC. Alloys were prepared on the basis of aluminum A99. Annealing of the samples at 550 °C for three hours was carried out in SNOL 8.2/1100 and SNOL 58/350 muffle electric furnaces. Calculation of Al - Ca - Ni - Ce systems at 6% Ca by means of Thermo-Calc (databases TTAL5, TCAL4), showed that primary crystals of the Al₃Ni phase should be formed in the alloys of the selected compositions, however these crystals were not present. Using optical and scanning electron microscopy, the structure of alloys in the as-cast and heat-treated states was studied. It is established that in the process of non-equilibrium crystallization, the boundary of the phase region of existence of the aluminum solid solution significantly expands. Using micro-X-ray spectral analysis (MRSA), it was determined that during the equilibrium crystallization conditions in the Al - Ca - Ni - Ce system, rather than the binary Al₃Ni the ternary Al_aNi₂Ca phase is formed. The possibility of applying hot rolling to Al - Ca - Ni based alloys additionally alloyed with Ce, La and Pr has been established, and the mechanical properties of hot-rolled samples have been obtained. Hot rolling was carried out at 500 °C. Rolling was carried out in five passes, the total degree of deformation in all cases was about 70%. Samples of the AI - 6Ca - 3Ni - 2Ce alloy were additionally rolled at a temperature of 550 °C. On the basis of a comparison of the mechanical properties and the microstructure of rolled products, it is assumed that the best mechanical properties are possessed by the samples of those alloys in which intermetallics have the smallest dimensions and are most evenly distributed in an aluminum solid solution. In particular, this demonstrates the AI - 6Ca - 3Ni - 2La alloy rolled at 500 °C and the Al – 6Ca – 3Ni – 2Ce alloy rolled at 550 °C.

Key words: eutectic alloys, rare earth metals, ternary Al_gNi_2Ca phase, intermetallics, microstructure, hot rolling, mechanical properties

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