Corrosion resistance of Nd–Fe–B magnets with PVD protecting coatings modified by pulsed plasma treatment

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The combination of PVD and pulsed plasma treatment has been applied to Nd–Fe–B based magnets to provide enhanced corrosion resistance. The corrosion behavior of plasma treated Nd–Fe–B sintered magnets with $Fe_{80}B_{20}$ film in naturally aerated sodium sulphate solutions have been studied. The corrosion behavior was estimated using electrochemical methods. It has been established that the sample corrosion resistance is influenced considerably by pre-treatment preceding the plasma treatment or $Fe_{80}B_{20}$ deposition.

Комбинация PVD технологии и импульсной плазменной обработки использована для повышения коррозионной стойкости магнитов Nd–Fe–B. Изучено коррозионное поведение магнитов Nd–Fe–B, покрытых пленкой $Fe_{80}B_{20}$ после плазменной обработки, в условиях природной аэрации в водных растворах сульфата натрия низкой концентрации. Оценку коррозионного поведения материалов проводили электрохимическими методами. Установлено, что на коррозионную стойкость образцов значительно влияет предварительная обработка исходной поверхности, выполненная до проведения обработки плазмой или до нанесения пленки феррробора $Fe_{80}B_{20}$.

The increasing use of rare-earth magnets in the micromagnetic devices (so called MAGMAS devices) makes ever tougher requirements to the magnet size, thus restricting somewhat the use of conventional methods for corrosion protecting of Nd–Fe–B rare-earth magnets. Because of low corrosion resistance, Nd–Fe–B magnets need corrosion control methods to improve their viability and to provide the use thereof as a construction material. Attempts were made to improve corrosion resistance of these magnets using metal and organic coatings [1–4] or alloying the initial materials [5–8]. While typical thickness of organic coatings can vary from 20 to 80 μm, this value for metallic coatings is restricted down to 7–19 μm for aluminum coatings and 10–30 μm for Ni and Zn ones. The phosphate conversion coating method was proposed, but the technology turned out to be too complicated for large-scale production [9].

Neodymium, being a basic component of rare-earth Nd–Fe–B magnets, is very reactive alloy element. Its fraction can vary between 30 and 36 wt. % which makes magnets highly susceptible to corrosion and corrosion attacks result in the of magnetic properties. At first, the corrosion attack results in degradation of magnetic properties (magnetic flux) and then to the partial or full failure of magnets.

It was shown previously that treatment of structural steels with high-intensity plasma flows (energy density 5–50 J/cm^2), generated by pulsed plasma accelerators, results in hardening of the surfaces and increasing the wear resistance [10–12]. Such surface modification is realized due to combination of the following physical processes: high speed cooling-quenching (10^7–10^8 K/s), structural-phase transformation in solid state, decay of solid solutions, melting, and diffusion of the plasma stream atoms into the material. As a result of these processes, a solid layer with increased hardness and excellent adhesion is formed on the sample surface. That is why one of the alternatives is expected to be plasma treatment of easily amorphizing coatings. The ferroboron coating Fe$_{80}$B$_{20}$ can be one of the potential candidates, which was proved in the laser treatment applications [15]. According to SEM and X-ray analyses, an amorphous layer was easily formed on the surface of ferroboron coated alloys after laser treatment. The modified layer microhardness reached its highest value of 17000 MPa at the depth of 20 μm underneath the surface. Moreover, a satisfactory adhesion of amorphous layers to the substrate was observed under bending and compression loadings. Thus, the high-speed crystallization under pulsed plasma treatment in near-surface region, causing the formation of amorphous or finely dispersed structure of strengthened phases, will define the high performance of near-surface layer [10].

The experiments were carried out using a pulsed plasma accelerator (PPA). The PPA device consists of coaxial set of electrodes with anode of 14 cm diameter and cathode of 5 cm diameter and vacuum chamber of 120 cm length and 100 cm diameter. The power supply system is a capacitor bank with stored energy of 60 kJ (at 35 kV). The discharge current amplitude is 400 kA, the plasma stream duration 3–6 μs. The pulsed plasma accelerator generates plasma streams with ion energy up to 2 keV, plasma density 2·10^{14} cm^{-3}, average specific power 10 MW/cm^2 and plasma energy density in the range of 5 to 40 J/cm^2. Nitrogen, helium, hydrogen, and other gases can be used as working media. The plasma treatment conditions were chosen by variation of both accelerator discharge voltage and the target surface distance from the PPA output.

The PVD deposition of ferroboron Fe$_{80}$B$_{20}$ (wt. %) coatings was carried out utilizing planar ECR plasma source [14]. The sputtered 5 μm thick amorphous Fe$_{80}$B$_{20}$ films with high adherence were formed on the surface of Nd–Fe–B sintered magnets. The initial Nd–Fe–B magnet samples were subjected to various pre-treatment procedures as shown in Table 1. Some samples were PVD coated with Fe$_{80}$B$_{20}$ and then plasma treated in various conditions (samples 3, 4, 7). Long plasma exposures at one and two-stage modes were applied to the initial surfaces of samples 5 and 6. Samples 4, 5, 6, and 7 were sealed with Fe$_{80}$B$_{20}$ coating after plasma irradiation. The microstructure of treated surfaces and cross-sections of samples were examined using a MMR-4 optical microscope.

The corrosion behavior of the magnets (see Table 1) was measured under complete immersion of samples in the naturally aerated sodium sulphate solutions. The electrodes were polarized using a PI-50-1 poten-

Table 1. Characteristics of the treated Nd–Fe–B magnets

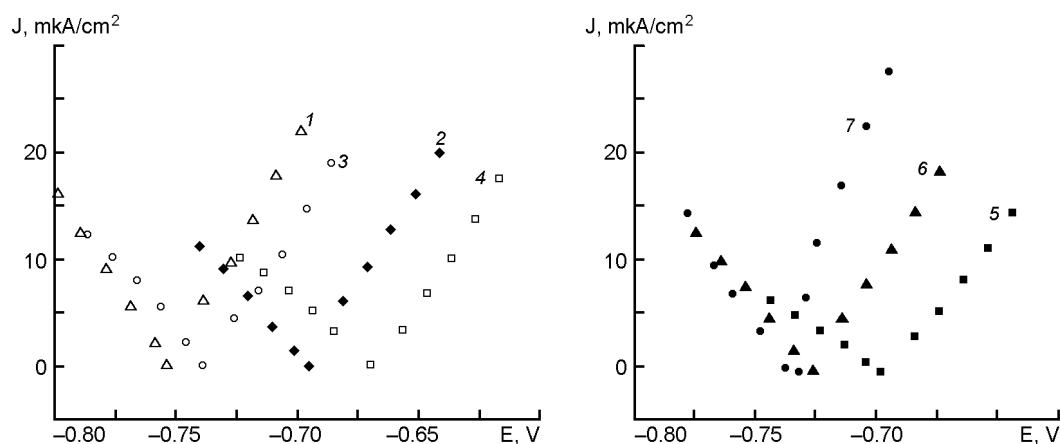| Sample	Pre-treatment procedure	1st protective coating ECR source	Plasma treatment conditions		2nd protective coating ECR source
			Energy density, J/cm^2	Number of pulses	
1	Polished	–	–	–	–
2	–	–	–	–	–
3	–	Fe$_{80}$B$_{20}$	20	5	–
4	Polished	Fe$_{80}$B$_{20}$	25	5	Fe$_{80}$B$_{20}$
5	Oxidized	–	21	20	Fe$_{80}$B$_{20}$
6	Polished	–	30	5	Fe$_{80}$B$_{20}$
			21	20	
7	–	Fe$_{80}$B$_{20}$	25	15	Fe$_{80}$B$_{20}$

Fig. 1. Polarization curves for the samples (see designations in Table 1).

tiostat and PR-8 programmer in the controlled potential conditions using a three-electrode scheme. The three-electrode cell arrangement was used for the electrochemical measurements, with platinum needle-like electrode as the auxiliary one and a remote saturated silver chloride half-cell with potential of 0.201 V as the reference electrode. The reference electrode was connected with the cell via electrolytic switch. The corrosion process was evaluated by polarization resistance R_p, which is equal to $(\Delta E/\Delta I)$.

Table 2 shows the corrosion characteristics of various samples in 1 % sodium sulphate solution. The results were obtained from the polarization data for the set of experiments with samples according to Table 1. The corrosion potential is scaled to standard hydrogen electrode. Fig. 1 presents examples of polarization curves for the untreated and plasma processed samples (see designation in Table 1). For the presented samples, the polarization curves are shifted. The corrosion current (I_c) as measured using Tafel constants and corrosion potential (E_{corr}) are shifted significantly. The highest and lowest I_c were observed for polished untreated sample and oxidized sample with $Fe_{80}B_{20}$ coating, respectively.

The polarization data show that the sample polishing results in a decreased corrosion resistance. For example, the unpolished sample 2 demonstrates an inhibition of both anodic and cathodic corrosion reactions as compared to the polished sample 1. Moreover, the inhibition of cathodic corrosion reaction near the corrosion potential is higher ($(dE/dI)_k = 3941$) than for anodic reaction ($(dE/dI)_a = 2901$). The values of Tafel constants for cathodic (b_k) and anodic (b_a) reactions for samples 1 and 2 point to the presence of a protective film of corrosion products on the sample surface which prevents oxygen supply and provides a barrier for depolarizer. Corrosion currents and corrosion coefficients are a strong evidence therefor (see Table 2).

Morphology of the polished sample 1 after corrosion test is presented in Fig. 2a. The examination of polished and unpolished

Table 2. The corrosion characteristics of various samples (see Table 1) in 1 % sodium sulphate solution

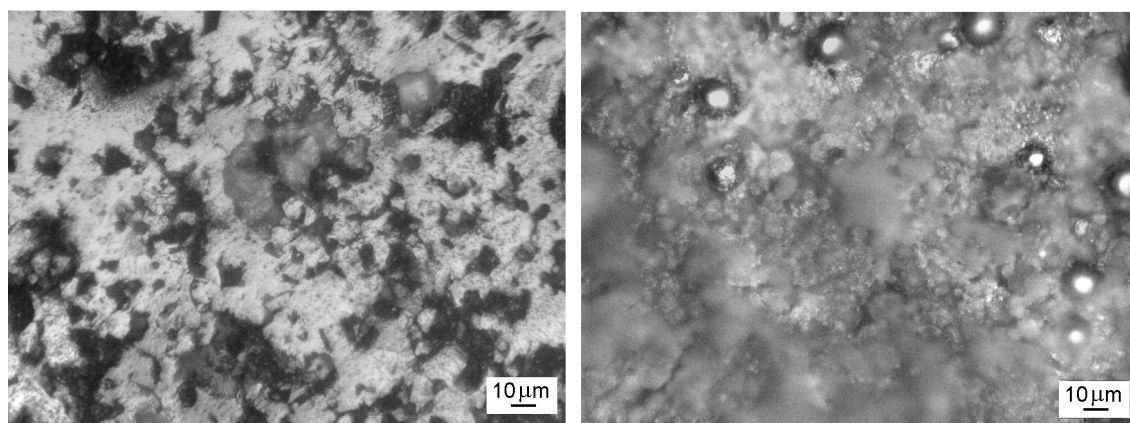| No.	E_{corr}, V	R_p, Om	Tafel constant, V		$I_{corr} \cdot 10^4$, A/dm^2	k_h, mm/year
			b_a	b_k		
1	−0.528	2574	0.073	0.046	10.4	0.121
2	−0.494	3421	0.065	0.051	7.2	0.085
3	−0.538	3341	0.065	0.065	7.8	0.090
4	−0.468	4184	0.061	0.068	6.8	0.079
5	−0.497	4497	0.058	0.063	5.2	0.060
6	−0.524	4281	0.059	0.055	5.9	0.069
7	−0.530	2169	0.071	0.051	7.8	0.090

Fig. 2. Surface of the Nd–Fe–B magnets after corrosion tests: (a) polished surface; (b) oxidized Nd–Fe–B magnets treated with helium plasma 21 J/cm^2 for 20 pulses coated with $Fe_{80}B_{20}$ film.

samples after anodic polarization allows to conclude that surfaces of both samples were coated with the corrosion spots. However, the polished sample 1 shows a higher level of failure with spots spread homogeneously over the surface, while the unpolished sample 2 is coated with oxides of red-brown color. It is supposed that the rough surface with large and reactive surface area generated by plasma treatment of oxidized surface or previously deposited ferroboron coating can result in continuous porous layer which could eventually increase the binding strength between the final ferroboron coating layer and the modified substrate.

The corrosion characteristics of plasma treated samples can be compared with unpolished sample 2. Consideration of Tafel constants demonstrates that inhibition of cathodic and anodic reactions for samples 3, 4, 5, and 6 is identical. While sample 5 shows a thick layer of corrosion products (see Fig. 2b), which block its surface and decreases the corrosion rate, such typical loose layer being absent on the surface of the sample 4.

Despite the halved R_p value for sample 7 as compared to that for 6, which points to lower corrosion resistance of the latter, the Tafel constants show the less hindrance of cathodic reactions and, as a result, an increased general corrosion rate. The polishing of the sample 6 prior to plasma treatment promotes an increased corrosion resistance as compared to sample 7 (See Table 2). The corrosion potential of these samples is more electronegative than the standard iron potential. This can be attributed to the formation of neodymium compounds in the near-surface layers, despite the presence of protective ferroboron layer.

The continuous efforts to enhance the surface properties of the rare-earth magnets have resulted in the development of various processing techniques. Utility of high power plasma modification to transform the easily amorphizing ferroboron coatings into durable and hard coating is demonstrated.

Alloys with lack of atomic long-range ordering are always of interest for their mechanical, chemical, optical, thermal, and electrical properties. Comparative analysis of various properties of crystalline and amorphous alloys shows that the latter have higher strength, corrosion resistance, ductility and radiation resistance [13, 15]. Despite high energy loads under plasma treatment and high-speed quenching of the modified layer, there is no desirable enhanced contact between liquid phase and the base of the sample and a thin layer of absorbed gas impurities is present, which also exists under conventional quenching techniques, resulting in destructive effects. Although cooling and heating rates of near-surface layers can be controlled by varying the plasma parameters, accumulated gases hinder amorphization and promote the formation of inhomogeneous modified layer including cracks, which may lead to the weak binding between the second ferroboron coating and the plasma modified substrate.

Thus, the corrosion properties of Nd–Fe–B magnets with $Fe_{80}B_{20}$ coatings vary depending on the pre-treatment procedure and plasma processing conditions. It has been revealed that polishing of the initial samples before plasma treatment does not provide a good binding with ferroboron coating. The sample surface roughness caused

by oxidation is among important factors to enhance the binding strength due to large and reactive surface area, which could result in a strong mechanical interlocking and chemical binding after the second ferroboron coating deposition. The plasma treatment increases the sample polarization ability that is a kinetic corrosion parameter. As to that parameter, the samples can be ranked as follows: 1, 7 < 2, 3 < 4, 6 < 5. Comparative analysis of the plasma treated samples under various polarization conditions allows to conclude that plasma treatment of Nd–Fe–B magnets does not significantly influence on their corrosion resistance.

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Корозійні властивості магнітів Nd–Fe–B з захисними покриттями нанесеними іонно-плазмовими методами та модифікованими імпульсною плазмовою обробкою

О.М.Бовда, В.О.Бовда, В.В.Чеботарев, В.Д.Федорченко, І.Є.Гаркуша, Л.В.Онищенко, М.Д.Сахненко, В.І.Терешин, О.С.Тортика, М.В.Ведь

Комбінацію PVD технології та імпульсної плазмової обробки застосовано для підвищення корозійної стійкості магнітів Nd–Fe–B. Вивчалася корозійна поведінка магнітів Nd–Fe–B, покритих ферробором $Fe_{80}B_{20}$ після плазмової обробки, в умовах природної аерації у водних розчинах сульфату натрію низької концентрації. Оцінку корозійної поведінки досліджували електрохімічними методами. Встановлено, що на корозійну стійкість зразків значно впливає попередня обробка вихідної поверхні, виконана до плазмової обробки або до нанесення плівки феробору $Fe_{80}B_{20}$.