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Corrosion Properties of NdFeB Magnets Coated by a Ni/Cu/Ni Layer in Chloride and Sulfide Environments

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In this study, the corrosion behavior of a permanent magnetic alloy, Nd-Fe-B, coated by a triple layer of nickel-copper-nickel was studied. The corrosion resistance was investigated by (i) flux tests, carried out at 90 °C in an atmosphere containing chlorides or at 70 °C containing sulfides, (ii) electrochemical impedance spectroscopy (EIS), and (iii) potentiodynamic polarization tests, carried out in solution at different temperatures (0-90 °C) containing chlorides or sulfides. The morphology and the composition of the samples and the corrosion products were analysed by optical microscopy and scanning electron microscopy, equipped with an energy dispersive x-ray detector. The magnetic properties were characterized by magnetic flow measurements. The flux tests indicated that the triple layer of coating provided a greater corrosion resistance in atmosphere containing chlorides than the one with sulfides. The potentiodynamic and the EIS tests showed that the corrosion rate increased with temperature. The magnetic properties of the sample remained unchanged after exposure to the aggressive environment.

Keywords coated NdFeB, corrosion characteristics, electrochemical tests

1. Introduction

Sintered Nd-Fe-B permanent magnets possess excellent magnetic characteristics, such as high remanence (11 kG), high coercivity (13 kOe), and high energy product (>350 kJ/m^3) (Ref 1, 2). However, the corrosion resistance of Nd-Fe-B magnets is very poor and the high susceptibility to corrosion in common environments limits their life span (Ref 3-5). The poor corrosion resistance is due to the co-existence of multiple phases in the microstructure: the matrix phase $Nd_2Fe_{14}B$ (φ-phase), $Nd_{1+\varepsilon}Fe_4B_4$ (η-phase), and a Nd-rich phase (n-phase). The relative electro-negativity of these phases leads to the formation of an electrochemical couple between the η and n phases, which are anodic, and the cathodic φ-phase. The corrosion/oxidation process starts at the intergranular region of the φ-phase, where Nd-rich phase and B-rich phase are present. These phases then expand and cause a disintegration of the surface and, subsequently, the corrosion products as well as the φ grains break away from the bulk magnet (Ref 6). Aqueous corrosion is influenced by the existence of a magnetic field, i.e., the corrosion rates differ in the presence or absence of a magnetic field. It has been shown with potentiodynamic and impedance measurements in chloride solutions that nonmagnetized samples have a better corrosion resistance since they show a higher free corrosion potential and a lower corrosion rate than the magnetized ones (Ref 7). This is due to the paramagnetism of O_2 molecules that affects the oxygen transport when a magnetic field is present. It is supposed that a magnetic field facilitates the oxygen transport to the interface magnet/electrolyte, increasing the corrosion rate process. Previous studies investigated the corrosion behavior of Nd-Fe-B magnets in several environments: acidic solutions, humid and dry atmosphere, and nitrogen free atmosphere (Ref 8, 9): (i) the magnets showed a low corrosion resistance in acidic solutions since no protective oxide film formed on the surface; (ii) the humidity of the gas mixture affects the corrosion rate of Nd-Fe-B permanent magnets much more than the environment temperature; (iii) higher corrosion rates were measured in nitrogen free atmosphere than in air-water vapor mixtures at the same temperature, indicating that nitrogen inhibits corrosion, since a protective film formed on the surface.

To improve the corrosion resistance, the effect of adding alloying elements was studied, e.g., Co and N (Ref 10) or polymer addition (Ref 11). The beneficial effect of alloying addition was attributed to the reduction in the strength of galvanic coupling effect between ferromagnetic matrix and Nd-rich intergranular phases. Moreover, different coatings such as Zn, Au, Nickel, Ni/Cr, Ni/Cu, and Ni (10-30 μm)/TiN were studied to protect the surface of NdFeB magnets from corrosion (Ref 12-16).

This study investigates the corrosion behavior of Nd-Fe-B magnets, coated by Ni/Cu/Ni layers, by flux tests, electrochemical tests, and corrosion morphology observations. To simulate the storage in different environments, which can be found in industrial areas, and in different working conditions, the experiments were carried out, both, in environments containing chloride or sulfide, and in solution containing chloride or sulfide at different temperatures ranging between 0 and 90 °C.

2. Experimental

In the experiments were used round powder-sintered NdFeB permanent magnet samples, 5 mm thick, with an exterior

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diameter of 14.5 mm and an interior diameter of 3.5 mm. All specimens were coated by three distinct electrolytic layers: an internal of nickel, an intermediate of copper, and an external of nickel (Ref 17). The samples were magnetized.

The sections of the coatings of NdFeB magnets were analysed by scanning electron microscopy (SEM) to explore the morphology of the deposited layers and to obtain their qualitative composition. The flux corrosion experiments were carried out in an exposure chamber, a 5 L Pyrex vessel, which was fully isolated and heated by a hot plate. The samples were submitted for 96 h to a chloride atmosphere at 90 °C and to a sulfide atmosphere at 70 °C. The chloride atmosphere was obtained by heating a 3.5% NaCl and 1.4% Na_2SO_4 solution, and the sulfide atmosphere was prepared by heating at 70 °C a 3.75% CH_3CSNH_2 solution, leading by hydrolysis to the formation of sulfidric acid. This gas was injected into the bottom of the vessel and exhausted through the top, so that the natural convection effects counteracted any tendencies toward stratification or short circuiting of gas in the exposure chamber. Samples were hang in the chamber with a nylon string to expose them to the atmosphere. The temperature and the humidity were monitored by a thermo-hygrometer probe placed in the chamber.

Both untreated and scratched samples, in which the surface coating was removed in a limited area of the samples with 320 grit SiC abrasive paper until the exposure of the substrate, were submitted to the flux test. The sample weight was measured before the experiment and every 24 h during the experiment.

The anodic polarization curves were performed by an AMEL 551 potentiostat equipped with an AMEL 567 function generator using a scan rate of 0.5 mV/s, a saturated calomel one (SCE) as reference electrode and a platinum one as counter electrode. The EIS tests were carried out with a Solatron Schlumberger 1255 FRA spectrometer coupled with an EG&G 273 A potentiostat, at the open circuit potential of the samples and with a signal amplitude of 10 mV in the frequency range of 10^5 to 10^{-2} Hz. Both, anodic polarization and EIS tests, were carried out in solutions containing 3.5% NaCl and 1.4% Na_2SO_4 at three different temperatures (0, 20, and 90 °C). A potentiodynamic test was performed also in a H_2S saturated solution at 20 °C. The samples were encapsulated in epoxy resin, leaving exposed an unscratched face.

The measurements of the coated NdFeB magnetic flow were carried out by a MPS fluxmeter EF 5, equipped with a coil with a resistance of 37 Ω.

The surface morphology and the corrosion products were examined using optical microscopy (OM) and a Cambridge Stereoscan 440 SEM equipped with a Philips PV9800 EDS detector.

3. Results and Discussion

3.1 Microstructure of Magnets and Coating Characterization

Figure 1 shows the microstructure of NdFeB magnets obtained by SEM analysis. The $Nd_2Fe_{14}B$ matrix phase was surrounded by the Nd-rich phase, and a small amount of B-rich phase was located inside the Nd-rich phase.

The SEM-BSE cross section image of the coated NdFeB permanent magnet sample is shown in Fig. 2. The composition of the layers was examined by SEM-EDS analysis. The coating

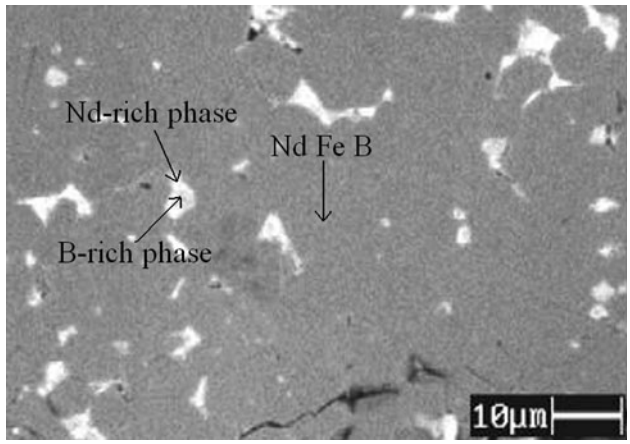

Fig. 1 Microstructure of NdFeB magnets, SEM image

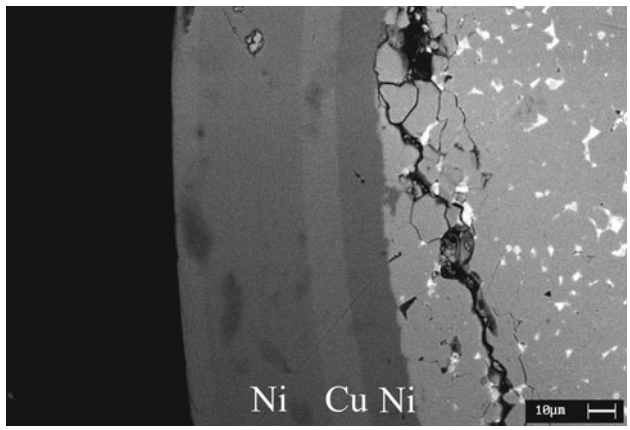

Fig. 2 SEM image of the triple layer coating

was constituted by an outer layer of nickel with a thickness of about 45 µm, an intermediate layer of copper of 12 µm, and an inner layer of nickel of about 12 µm.

3.2 Flux Test

In order to determine the coating corrosion resistance, a series of tests with exposure time of 96 h each, were performed at high temperature in different environments with high humidity (water saturated), both, on the unscratched and the scratched samples.

The unscratched samples exhibited good corrosion resistance in the atmosphere containing chloride at 90 °C. After 96 h the surface was undamaged, the coating remained adherent and no evidence of peeling-off was revealed (Fig. 3a). The weight, measured before and after the flux tests, was almost unchanged. In fact the average weight change recorded on the tested samples was 0.14%. The behavior of the scratched samples was different (Fig. 3b): the surface of scratched samples, unlike that of the unscratched ones, was partially corroded, indicating that, when the coating layers were removed, the magnets exhibited poor resistance corrosion in an environment containing chloride and humidity. The corrosion products were analysed by EDS, and they resulted iron and/or copper oxides.

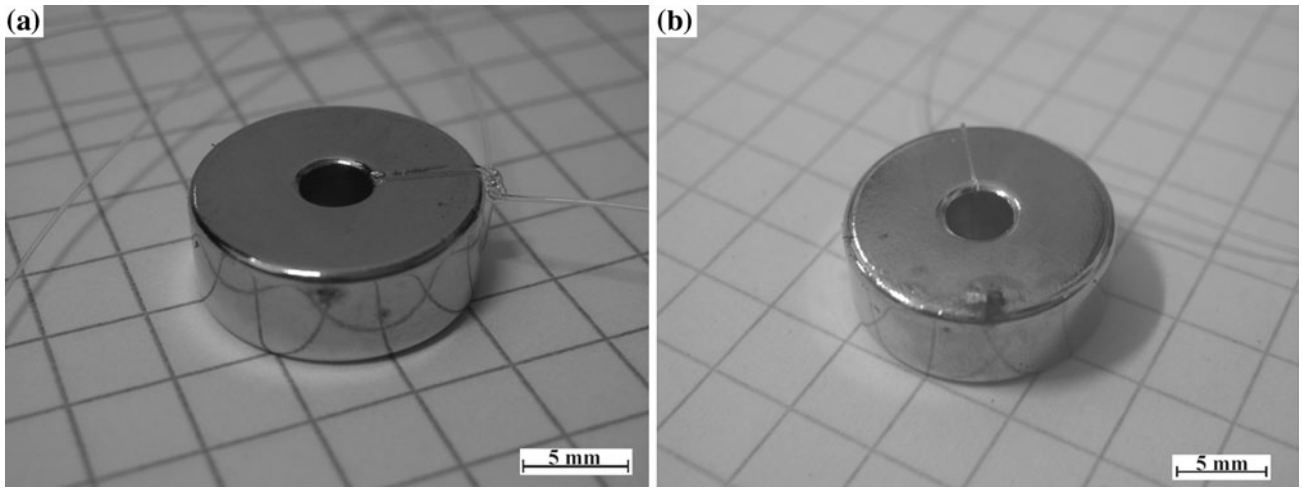

Fig. 3 Image of a sample submitted to chloride atmosphere at 90 °C for 96 h: (a) unscratched sample and (b) scratched sample

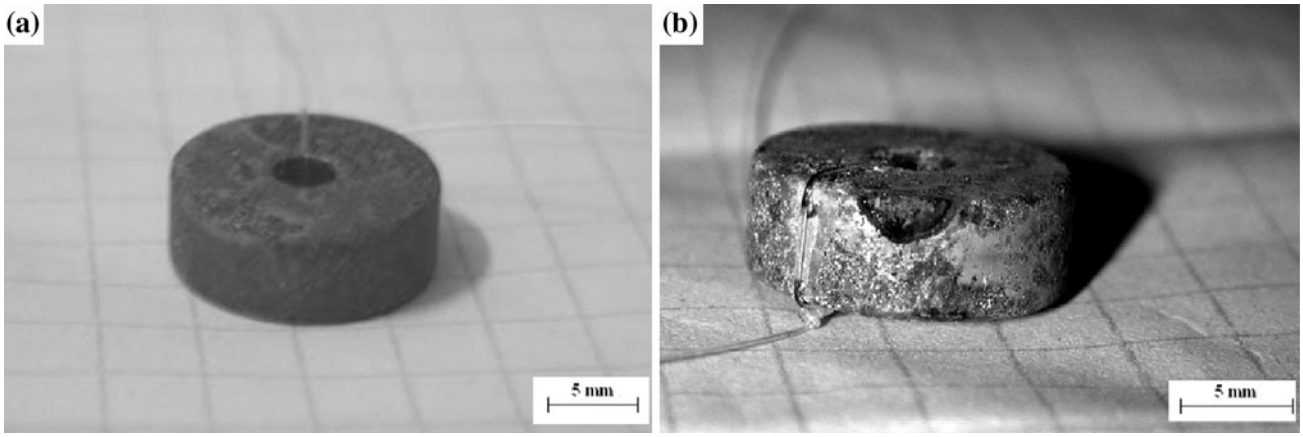

Fig. 4 Sample submitted to a sulfuric flux at 70 °C: (a) unscratched sample and (b) scratched sample

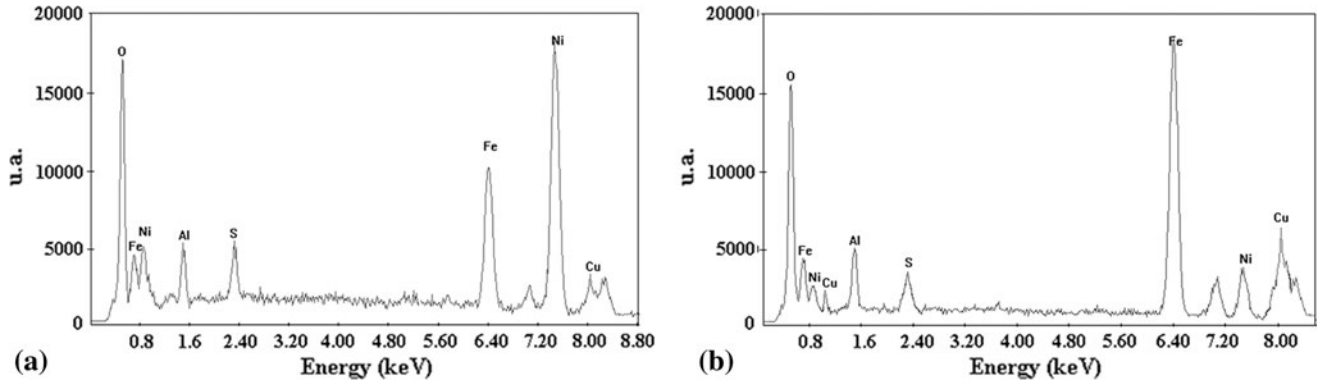

Fig. 5 EDS spectra of corrosion products on (a) unscratched sample and (b) scratched sample

Flux tests were performed also with sulfide atmosphere at 70 °C. The formation of corrosion products was evident by a visual inspection, both, on unscratched and scratched samples (Fig. 4a, b). The composition of the corrosion products was studied by EDS analysis (Fig. 5a, b). On the unscratched samples surface, a high amount of oxygen, sulfur, nickel, and a small amount of iron and copper were detected. This could be due to the formation of copper and iron oxides and sulfur compounds, in addition to nickel corrosion products on the sample surface. This can be explained by the ability of the sulfide atmosphere to remove the Ni coating and, in many surface zones, the triple layer. So, the exposition to this atmosphere of the copper layer and even of the substrate caused the formation of copper and iron corrosion products. This was

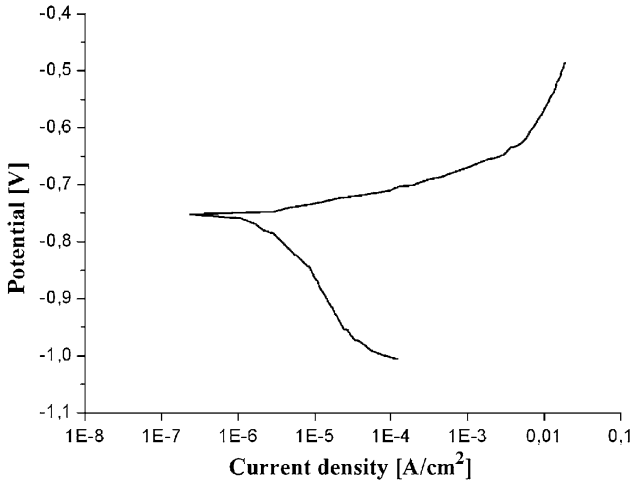

Fig. 6 Potentiodynamic curve of uncoated NdFeB magnets in 3.5% NaCl and 1.4% Na_2SO_4 aqueous solution

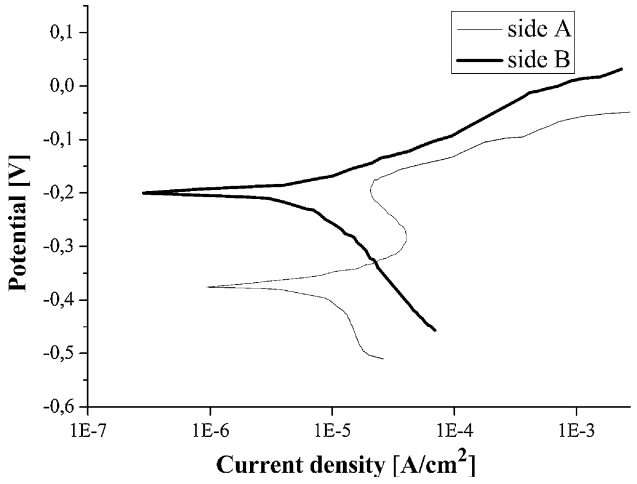

Fig. 7 Potentiodynamic curves on two different sides of coated magnets in 3.5% NaCl and 1.4% Na_2SO_4 aqueous solution

Table 1 Magnetic induction values of NdFeB samples before and after flux tests (1,2,3 chloride environment; 4,5,6 sulfide environment)

Sample	B (mT) before	B (mT) after
1	1050	1027
2	1051	1043
3	1053	1036
4	1040	1027
5	1053	1036
6	1050	1039

more evident in the scratched samples: the amount of copper and iron corrosion products was higher near and inside the scratched area, indicating that an environment containing S^{2-} ions is more aggressive than an environment containing chloride ions.

Table 1 reports the measures of the magnetic induction obtained before and after the flux tests. It is evident that the prolonged staying, both, in the sulfide environment and in the chloride atmosphere, at high temperatures, did not influence the magnetic properties of the NdFeB magnets (three samples for each flux test were analyzed).

3.3 Electrochemical Behavior

The NdFeB magnets without coating were analyzed in 3.5% NaCl and 1.4% Na_2SO_4 aqueous solution at 20 °C. The corrosion potential was 750 mV, and the corrosion current density was about 3×10^{-6} A/cm^2, as it is shown in Fig. 6.

The NdFeB magnets coated with Ni-Cu-Ni were initially tested at room temperature on both sides of the sample (side A, side B). The results of these tests were very different due to the different polarity of the two faces studied. The polarity influences the measurements because the oxygen transport is affected by the magnetic field on account of the paramagnetism of O_2 molecules. Figure 7 shows that the corrosion potential for the two sides analysed varied between −200 and −400 mV, depending on the polarity of the magnet's surface exposed to the environment, while the values of the corrosion current density were about the same (1×10^{-5} A/cm^2). The values of corrosion potential were higher than the ones of uncoated sample (750 mV), indicating the good corrosion protection of the coatings.

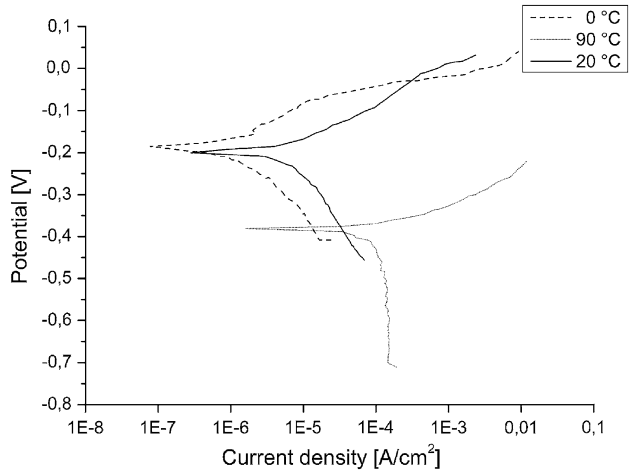

Fig. 8 Potentiodynamic curves of coated magnets in 3.5% NaCl and 1.4% Na_2SO_4 solution at different temperatures

Table 2 Values of corrosion potential and current density

	E_{corr}, mV	I_{corr}, A/cm^2
0 °C	−187	1.18×10^{-6}
20 °C	−200	5.74×10^{-6}
90 °C	−385	1.24×10^{-4}

In Fig. 8, the potentiodynamic curves obtained at three different temperatures are compared, and in Table 2 the values of the corrosion current density and corrosion potential are reported. At 90 °C, the samples tested showed the highest values of current density (about 1×10^{-6} A/cm^2) because the high temperature promotes the oxygen transport and, as a consequence, the corrosion rate. At 0 °C, the curves obtained are very similar to the ones performed at room temperature, but show higher values of corrosion potential (about −180 mV). In Fig. 9, the surface of a sample after potentiodynamic tests was

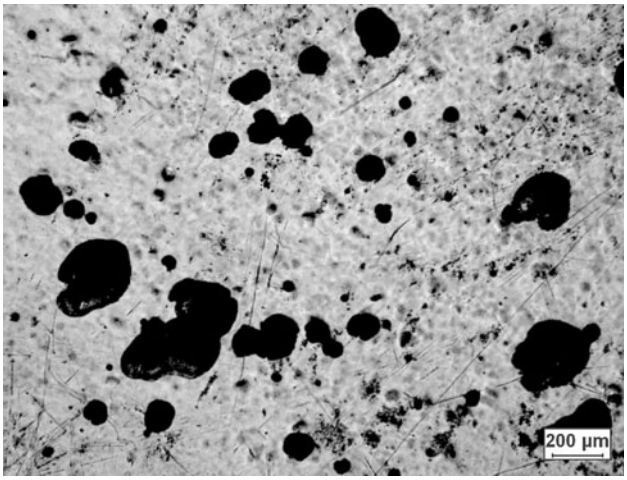

Fig. 9 Optical microscope image of NdFeB magnet after the potentiodynamic test in salt solution at 20 °C

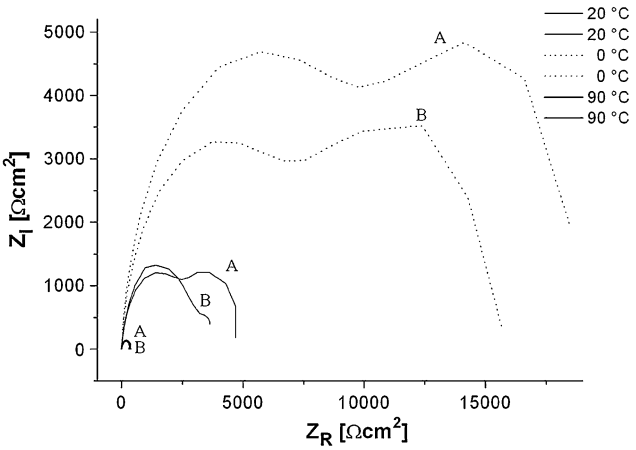

Fig. 10 Impedance curves at different temperatures in 3.5% NaCl and 1.4% Na_2SO_4 aqueous solution

shown. The black holes are the product of the pitting corrosion of nickel layer which induces the exposure of the below copper layer. This is more evident on the samples submitted to corrosion test at the highest temperature, while on the samples submitted to corrosion test at 0 °C the pitting corrosion of Ni layer was not recorded. This confirms that the environment temperature affects the corrosion resistance of the magnets and at higher temperature the materials are less resistant to corrosion.

The EIS results obtained by the NdFeB magnets coated by Ni-Cu-Ni in solution with 3.5% NaCl and 1.4% Na_2SO_4, at different temperatures, are reported in Fig. 10. The Nyquist plots were fitted by the equivalent circuit reported in Fig. 11. In this circuit, the resistance R_1 represents the solution resistance, R_2 the resistance of Ni outer surface, R_3 the interface between Ni and Cu layers, and R_4 the resistance of Cu layer. The elements C_2 and C_4 stand for the capacitance of Ni layer and Cu layer, respectively.

As shown in Fig. 10, the amplitude of circles decreases with increasing of temperature. The calculated data of the different resistances, reported in Table 3, are in agreement with the results of the potentiodynamic tests. The samples at the lowest

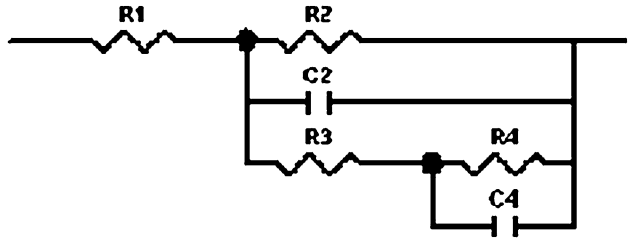

Fig. 11 Equivalent circuit developed for the study of NdFeB magnets coated by Ni-Cu-Ni

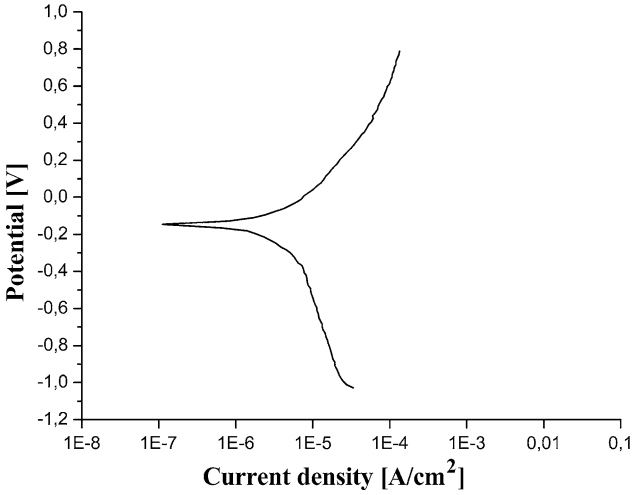

Fig. 12 Potentiodynamic curve in H_2S saturated solution

Table 3 Values of resistances in the equivalent circuit for EIS measurement

	20-25 °C	85-90 °C	0-5 °C
R2, Ω	6,300	2000	23,700
R3, Ω	3,000	250	19,100
R4, Ω	138,000	760	4.6×10^6

temperature showed a resistance of Ni layer (R_2) one order of magnitude higher, and a resistance of Cu layer (R_4) four orders of magnitude higher than those recorded at the highest temperature. This indicates that the Ni layer is less resistant than the Cu layer, as resulted from the potentiodynamic tests. In fact, the samples submitted to the test at 90 °C showed a localized corrosion on the external Ni layer unlike the lower layer of copper, where no corrosion was detected.

The effect of magnetic field on the corrosion process was also evidenced by EIS measurements. In fact, the Nyquist plots of the same sample recorded on opposite surfaces were different, as shown in Fig. 10. These differences are more pronounced at lower temperature. This is due to the fact that the mobility of oxygen molecules decreases with temperature, and the effect of magnetic field is higher when the mobility is lower.

Potentiodynamic tests were performed also in sulfide solution. Figure 12 reports the potentiodynamic curve obtained at 20 °C: the corrosion current density is about 4.2×10^{-6} A/cm^2 and the corrosion potential is −146 mV. Comparing these values with the data obtained in solution containing 3.5% NaCl and 1.4% Na_2SO_4, it comes up that the corrosion potential is

higher in sulfide solution and the current density is almost of the same value. This is in agreement with the results obtained by flux tests. However, the samples submitted to a flux test showed a heavily damaged surface, while the surface of samples submitted to electrochemical tests the surface appeared unaffected. This is probably due to (i) the different severity of the test and (ii) the different corrosion mechanism. Moreover, the length of time is different. The polarization tests lasted about 2 h whereas the flux test lasted 96 h.

4. Conclusions

The corrosion behavior of NdFeB permanent magnets coated by Ni/Cu/Ni layers was studied using flux tests, electrochemical techniques, OM investigations, and SEM-EDS analysis.

Flux tests showed that coated magnets have excellent corrosion resistance in environment containing chloride, certainly superior to uncoated magnets. The nickel coating is sensitive to the exposition to sulfuric atmosphere. In fact, the external nickel layer was completely removed during the exposition, and corrosion products of copper and iron were observed on the surface.

The results obtained by potentiodynamic polarization curves and EIS tests indicated the dependence of the corrosion rates on the temperature. The corrosion potential shifted to less noble values with increasing temperature. Samples tested at 90 °C showed a corrosion rate three orders of magnitude higher than those tested at 20 °C. The Nyquist plots indicated that the resistance of the layers decreased with increasing temperature.

The magnetic properties of the tested samples were unaffected after protracted exposition to the atmospheres and solutions used in the several tests.

In this study, the influence of the polarity of the magnetic field on the corrosion behavior was confirmed, due to the paramagnetism of O_2 molecules which are the main responsible cause of the corrosion in neutral environments.

Acknowledgments

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