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Multilayer ceramic coating for impeding corrosion of sintered NdFeB magnets

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Abstract: Sintered NdFeB magnets have complex microstructure that makes them susceptible to corrosion in active environments. The current paper evaluated the anticorrosion characteristics of multilayer titanium nitride ceramic coating applied through cathodic arc physical vapour deposition (CAPVD) for protection of sintered NdFeB permanent magnets. The performance of ceramic coating was compared to the electrodeposited nickel coating having a copper interlayer. Electrochemical impedance spectroscopy (EIS) and cyclic polarization in simulated marine environment were employed to determine the rates of coatings degradation and passivation behaviour respectively. The coating morphologies and surface chemistry were studied with scanning electron microscope (SEM). X-ray diffraction (XRD) was used for identification of component phases in the coatings and the substrate. The results showed that the polarization resistance of ceramic coating increased with the exposure time. The rate of degradation of R_p for the ceramic coating had an extraordinary negative slope followed by a stable duration, before declining towards the coating failure. In comparison the nickel coating with copper interlayer degraded sharply. The vapour deposited ceramic coating was found to have permeable defects that tended to "re-passivate" during exposure providing prolonged corrosion protection to the NdFeB substrate. The magnetic properties were unaffected and remained at par with the nickel coating having copper interlayer.

Keywords: sintered NdFeB magnets; multilayer ceramic coating; permeable defects; rare earths

The NdFeB permanent magnets have become important technological materials due to the exceptionally advantageous magnetic properties since their discovery in 1983[1–3]. At ambient temperature, neo magnets have highest energy product and thus known for the efficient utilization of electrical energy. Over the years, neo magnets have occupied a leading position among the strong permanent magnetic materials for variety of engineering applications, namely computer peripherals, automation, automobile, aerodynamic, magnetic resonance, biomedical, acoustics and consumer electronics[4,5]. However, the presence of electrochemically active phases in the microstructure of the sintered NdFeB magnets[6] deteriorate their efficiency as they corrode during exposure to various environments[7,8].

Efforts have been made to control the corrosion of sintered neo magnets either by alloying additions to alter the electrochemical potential of active microstructural phases[9–12] or by tailoring the surface to incorporate mechanical barrier coatings like epoxy, metallic or alloy coatings[13–15]. Improving corrosion resistance by alloying additions did not serve the purpose as only a few alloying elements marginally improved the corrosion resistance at a substantial compromise of magnetic properties[16–18]. The surface treatments such as electrodeposited nickel or zinc, electroless nickel, electroless nickel-phosphide or nickel- cobalt-phosphide, hot dip zinc, aluminizing, electrophoresis, chromate passivated aluminium coating are known corrosion-proofs for neo magnets but each has its own limitations. So, new developments are always on cards. Currently, the cathodic arc physical vapour deposited transition metal nitride coating has been reported to cater the corrosion protection of sintered neo magnets[19]. In CAPVD process the plasma assisted high energy cathodic arc ejects the metal vapours from the solid metal at ambient temperature in an evacuated chamber. The applied potential gradient accelerates the metallic ions in the vapour flux towards the substrate with kinetic energies in the range of 10–100 eV. The metallic ions encounter the methane or nitrogen gas introduced in the chamber, before their impact to the substrate surface. The vapour deposited transition metal nitride coatings normally have microscopic defects such as pores, pin holes and/or voids[20,21] that provide path for the environmental species to access the substrate surface. Such permeable defects can not be completely eliminated but their size and density can be reduced by depositing thicker coatings[22,23], by incorporating noble and dense interlayer[24], by interrupting columnar

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growth with multilayered coatings[25] or by post deposition sealing of defects with polymeric deposits[26].

The present work aims at depositing the multilayered titanium nitride coating by CAPVD process to impede the corrosion of sintered neo magnets. It also aims at studying the degradation mechanism of the coating//substrate system during exposure to simulated marine environment by electrochemical impedance spectroscopy (EIS). The properties of the titanium-nitride//neo-magnet system were compared to Ni-Cu-Ni//neo-magnet system.

1 Experimental

1.1 Materials

Sintered NdFeB magnets, commercially produced through powder metallurgical route were used as substrate material in this study. The neo magnets had the hydrostatic density of 7.58 g/cm^3, while their theoretical density is 7.60 g/cm^3. The chemical composition of the magnets (Table 1), was determined through wet analysis since low atomic number elements like boron having low electronic transition energies can not be detected by commercially available EDX analyser.

Table 1 Chemical composition of sintered NdFeB permanent magnets

Elements	B	Nd	Fe
w/wt.%	1.26 ±0.15	32.90 ±0.33	Balance
x/at.%	8.0	15.0	77.0

1.2 Specimen preparation

Disc shaped neo magnets with 12 mm diameter and 2.5 mm thickness were polished metallographically to 1.0 μm alumina suspension and ultrasonically cleaned in ultrasonic soap solution at ambient temperature. To reveal the microstructure the specimens were etched in 2% Nital.

1.3 Coating set up for CAPVD

The prepared substrates were mounted on a rotary sample holder at an angle of 30° with the normal to the cathode. The coating set up had a disc shaped cathode (titanium target) mounted on water cooled copper stage. The anode was also a disc, fixed at a perpendicular distance of 300 mm on top of the cathode. A double walled stainless steel jacket was used to enclose the whole assembly. The hollow cathode argon plasma discharge was used to clean the chamber after evacuation. Ground copper wire was used to trigger the arc. Automatic microprocessor controlled feeding system was used to introduce nitrogen into the chamber with controlled partial pressure. Keeping other parameters constant as reported earlier[19], three coating cycles of 40 min each were run to deposit the multilayer ceramic coating in an attempt to deposit a thick and dense coating with low density of permeable defects.

1.4 Electrodeposition of nickel with copper interlayer

Electrodeposition of nickel and copper was carried out with the Watt's solution and copper sulphate bath respectively. The bath composition and coating parameters have already been reported[19]. A nickel strike layer was deposited followed by the copper interlayer and again nickel layer above all. The coated surfaces were buffed before intermediate shifting between the baths and after final layer of nickel.

1.5 Characterization

After gently cleaning with muslin cloth the coated specimens were fixed in the specimen holder for exposure to aerated aqueous solution containing 3.5% NaCl. The neo substrate was made working electrode where as graphite rod was used as counter electrode. The Ag/AgCl electrode was used as a reference. The EIS measurements were carried out at ambient temperature from high frequency to low frequency i.e. from 10^5 to 10^{-2} Hz. The amplitude of ac potential was 10 mV. The EG&G Potentiostat 273A was employed for DC cyclic polarization measurements. The range of potential scan was –250 to +250 mV with respect to open circuit potential (OCP). The potential scan rate was 5 mV/s. Gamry Potentiostat and Echem Analyst software was used to measure and plot the AC impedance of the coating//substrate systems. The qualitative phase analyses were carried out with Siemens D-500 X-ray diffractometer using Fe filtered Co Kα radiations and Origin-5 graphic software. Jeol scanning electron microscope (SEM) equipped with EDS analyzer was used to study the back scattered electron images. The magnetic properties were measured with the help of Riken Denshi B-H curve tracer. The experimental measurements were repeated three times to verify the reproducibility and consistency of results.

2 Results and discussion

The chemical composition of the NdFeB magnet is given in Table 1. The comparison of phase components and sectioned views of coating//substrate systems is shown in Fig. 1.

The diffraction pattern of the substrate had the signatures of $Nd_2Fe_{14}B$ tetragonal phase while the CAPVD coating had a single reflection at 42.34º Bragg's angle corresponding to Ti_2N tetragonal phase. The titanium nitride ceramic coating