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The properties of chromium oxide coatings on NdFeB magnets by magnetron sputtering with ion beam assisted deposition

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ABSTRACT

The coatings of Cr_2O_3 were deposited on sintered NdFeB magnets by direct current (DC) pulse magnetron sputtering with and without ion beam at different O_2 pressures. The coatings were compact and had a thickness of 1.8–2.2 μm. The coatings achieved a hardness up to 29 GPa and a wear rate of 1.78×10^{-7} mm^3/Nm when ion-beam-assisted-deposition (IBAD) was used. Excellent anti-corrosion properties were obtained in the coating prepared by IBAD while the good magnetic properties of NdFeB substrate were retained. Electrochemical measurements revealed that the corrosion current density of the sample decreased from 4.66×10^{-6} A/cm^2 (bare NdFeB) to 2.87×10^{-7} A/cm^2 when O_2 flux was 17 sccm during IBAD process.

1. Introduction

Sintered NdFeB has excellent magnetic properties, such as large energy product [$(BH)_{max} > 450$ kJ/m^3], high saturation magnetization (1.6 T), and high coercivity ($1.2–2.08 \times 10^6$ A/m) [1], and has been widely used in electronic vehicles, medical devices, energy applications, computer drives and other fields [2,3]. However, NdFeB is susceptible to severe corrosion attack in many environments, such as acids, harmful gases, which subsequently leads to deterioration of the magnetic properties [4]. Its poor corrosion resistance is due to the co-existence of multiple phases in the microstructure: the matrix phase $Nd_2Fe_{14}B$, $Nd_{1+\varepsilon}Fe_4B_4$, and a Nd-rich phase [5–7]. Among these intermetallic phases, Nd-rich phase has the most active electrochemical potential, and tends to dissolve in preference to other phases by galvanic corrosion when exposed to moisture [7].

Many investigations have been conducted to use surface protection technology to improve the corrosion resistance of sintered NdFeB magnets [8,9]. Physical vapor deposition (PVD) method has received considerable interests due to its environmental friendliness and simple processing [10]. Mao et al. [11] revealed that Al coatings had an excellent protective performance on NdFeB magnet by magnetic sputtering. But Al coatings had a lower hardness and poor scratch resistance, and may fail by even a small mechanical scratch [12]. Cheng et al. [13] prepared Ti/TiN multilayers on sintered NdFeB by radio frequency magnetron sputtering, but the wear properties were not good.

The Cr_2O_3 coating has the advantages of chemical inertness, high mechanical strength, high hardness and good optical characteristics [14]. It has been widely used for optical instruments, solar energy absorption materials [15], wear resistant coating [16], anti-corrosion coating [17], etc. In general, Cr_2O_3 can be deposited by various techniques, including magnetron sputtering [18], arc ion plating [19], cathodic arc evaporation plating [20], electron beam evaporation [21]. Among these methods, magnetron sputtering Cr_2O_3 coating has been drawn considerable attention for strong applicability with targets, good substrate adhesion, high deposition rates. Liu et al. [14] reported that the corrosion resistances of Cr_2O_3 coatings were higher than that of 316 L stainless steel and the Cr_2O_3 coatings deposited at 10sccm O_2 flux had the best corrosion resistance. Barshilia et al. [18] deposited a Cr_2O_3 coating with a thickness

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of ~0.8 μm on mild steel substrate by pulsed-direct current reactive unbalanced magnetron sputtering, and found the coating showed corrosion resistance improvement in 3.5% NaCl solution by 5 times by comparison with the uncoated substrate. Bhushan et al. [16] prepared Cr_2O_3 coatings by reactive RF-sputtering with a 10-nm thick Cr interlayer. The Cr_2O_3 coating exhibited excellent durability in accelerated and functional lifetime testing.

It has been established that Cr_2O_3 coating has good mechanical properties and high durability. But nevertheless, no report can be found regarding the application of magnetron sputtering Cr_2O_3 coating on sintered NdFeB magnets so far. In our previous work, we applied an alumina coating on NdFeB by magnetron sputtering and obtained good anti-corrosion properties and little magnetic property loss. However, due to the characteristics of alumina, the mechanical performance of the coating was not satisfactory [22,23]. The present work was thus initiated to prepare Cr_2O_3 coatings on NdFeB magnets by DC pulsed reactive magnetron sputtering method. The mechanical and anti-corrosion properties of PVD Cr_2O_3 coatings were evaluated. The effect of O_2 flux and ion beam on the crystallographic structure, surface morphology, and properties of Cr_2O_3 coating was investigated.

2. Experimental

Sintered NdFeB magnet specimens (N35, Yunshen) with a size of 20 mm × 10 mm × 3 mm were ground and polished to a mirror surface and then ultrasonically cleaned in acetone followed by alcohol before PVD treatment.

Deposition was carried out in a magnetron sputtering apparatus specially designed for magnets protection. The chamber was pumped to a base pressure of 8.0×10^{-4} Pa. Before deposition, the specimens were cleaned by Ar^+ ion beam for 30 min using two end-Hall ion guns with an energy of 150 V × 1 A. The pure Cr transition layers of ~500 nm were deposited by magnetron sputtering from Cr targets (99.999%) on sintered NdFeB to increase the adhesion. Then the Cr_2O_3 coatings were prepared by reactive magnetron sputtering with $Ar{-}O_2$ gas mixture. Detailed deposition parameters are shown in Table 1.

The thickness of the coatings was measured by a surface profilometer (Alpha-Step, IQ) employing a step formed by a shadow mask. Morphology of the specimen was obtained with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS, FEI Quanta FEG 250). The structures of the samples were studied by means of X-ray diffraction (XRD, D8 Advance with Cu Kα radiation). The hardness of the coatings was measured using a nano indenter (NANO G200, MTS). The adhesive strength between the coating and the substrate was characterised by vertical tensile testing using a universal testing machine (CMT 5105). Wear experiments were carried out by means of the Multi-functional friction and wear testing machine Rtec (MFT 5000) against a 6 mm diameter Si_3N_4 ball at 20 mm/s under a normal load of 5 N at room temperature in air. The wear resistance was evaluated in terms of the wear volume within 30 min. Corrosion behaviour of the coatings was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) utilizing a Potentiostat/Galvanostat (273A, Princeton) in a 3.5 wt% NaCl solution at a temperature of 25 ± 3 °C. The potentiodynamic polarization and EIS were performed with a conventional three-electrode cell with an SCE electrode (saturated KCl) as the reference electrode, and a platinum sheet (20 mm × 10 mm) as the auxiliary electrode. For comparison, the magnetic properties of the sintered NdFeB with and without coating were investigated by a NIM-2000 hysteresgraph at 25 ± 1 °C.

3. Results and discussion

3.1. Structure and compositions of Cr_2O_3 coatings

The morphologies of Cr_2O_3 coatings obtained without IBAD (ion-beam- assisted-deposition) in different O_2 flux are shown in Fig. 1. In general, both the pure Cr transition layer and Cr_2O_3 layer exhibit typical columnar crystal structure. The samples prepared at lower O_2 flow rates (5, 10, 15 sccm) show incomplete columnar grains along the thickness direction with many holes around the grains. Whereas the samples prepared under higher O_2 flow (17, 20 sccm) show the columnar grains penetrating through the entire coating with much reduced holes around the grains. It can also be seen that the grain size of the columnar grains decreases with the increase of O_2 flow, and the grain boundary becomes flatter with the increasing O_2 flow.

The surface morphology of Cr_2O_3 coatings deposited with IBAD is shown in Fig. 2. Apparently, columnar crystals are eliminated and the coatings become more dense by comparison with the coatings shown in Fig. 1. This may be because the Ar^+ concentration is much improved in the chamber with the application of ion beam. The improved Ar^+ concentration increases the collision chance of Ar^+ and Cr atoms and enlarges the energy of the atoms, leading to easier migration of Cr atoms to the surface of substrates [24].

Fig. 3 shows XRD patterns of Cr_2O_3 coatings deposited without and with IBAD at different O_2 flow rates. When the O_2 flow is lower than 17 sccm (pattern D), the Cr_2O_3 crystal structure can be detected in the coatings prepared without IBAD. However, because some diffraction angles of Cr_2O_3 and Cr are close, Cr phase can not be excluded. This is different from some studies which reported the structure of α-Cr_2O_3 structure was the only phase observed when CO_2 was more than 10% [25]. It was also reported the O_2 partial pressure did not change the crystal type of the Cr_2O_3 coating, but affected the crystal orientation of Cr_2O_3. No Cr was observed in the high oxygen partial pressure [26]. In our investigation, Cr is likely to exist in the coatings due to the low temperature and high target power density. When the O_2 flow rate reaches 17 sccm and above, the Cr_2O_3 coating may show a structure of Cr_2O_3 with (110) as dominating direction. It is also shown in Fig. 3b, when the O_2 flow is lower than 17 sccm with the application of IBAD, the XRD pattern for the coating is similar to the pattern of the coating without IBAD. When the O_2 flow rate reaches 17 sccm and above, the Cr_2O_3 shows a structure with (214) as dominating direction.

The content of elements Cr and O in the Cr_2O_3 coating under different O_2 flow is shown in Fig. 4. Combining Figs. 3 and 4, we can determine the existence of Cr in the coatings prepared at low O_2 flows (5, 10 sccm) since the O/Cr is less than 0.57. With the increase of O_2 flow to 17 sccm, the O/Cr value increases to ~1.69, which is close to the standard Cr_2O_3. Moreover, the O/Cr value increases with the increase of the O_2 flow, indicating the decrease of Cr existing in the coating in high O_2 flow.

3.2. Deposition rate of Cr_2O_3 coatings

Deposition rate has become an important property of PVD coatings in the view of industrial applications. The deposition rate of Cr_2O_3 coating is plotted against flow rate of O_2 in Fig. 5. The deposition rate with and without IBAD both varies with the increase of the O_2 flow rate in a parabolic way and a maximum deposition rate of ~3.3 $\mu m h^{-1}$ is achieved. It is noted that the deposition rates with IBAD is lower than those without IBAD when the O_2 flow rate is lower than 17 sccm, and vice versa when the O_2 flow rate is higher than 17 sccm.

The effect of O_2 is two-folded in reactive magnetron sputtering. On the one hand, O_2 reacts with the sputtered metal Cr atoms as the