Corrosion behaviour of sintered NdFeB coated with Al/Al2O3 multilayers by magnetron sputtering

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ABSTRACT

Al/Al2O3 multilayers were deposited on sintered NdFeB magnets to improve the corrosion resistance. The amorphous Al2O3 films were used to periodically interrupt the columnar growth of the Al layers. The structure of the multilayers was investigated by Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM). It was found that the columnar structure was effectively inhibited in the multilayers. Subsequent corrosion testing by potentiodynamic polarization in 3.5 wt.% NaCl and neutral salt spray test (NSS) revealed that the Al/Al2O3 multilayers had much better corrosion resistance than the Al single layer. Furthermore, for multilayers with similar thickness, the corrosion resistance was improved as the period decreased.

1. Introduction

Sintered NdFeB magnets have been widely used for their excellent magnetic properties since 1984 [1]. However, their poor corrosion resistance in various environments hinders their further applications [2–6]. Microstructurally the sintered NdFeB magnet is comprised of three basic phases: the matrix phase, which is ferromagnetic tetragonal compound Nd2Fe14B, the Nd-rich phase Nd4Fe, and the B-rich phase Nd1+εFe4B4. Galvanic corrosion is easy to happen between the matrix phase and the electrochemically highly active Nd4Fe, which normally locates at the intergranular region of the matrix phase grains [5,7].

To improve the corrosion resistance of the NdFeB magnets, two kinds of method have been employed, including alloy additions [8–10] and surface coatings [11–16]. Current industrial practice is to apply electroplated coatings, such as Zn, Ni or Ni/Cu/Ni, for their good performance and low processing costs [11,12]. However, the electroplated coatings often involve in environmental concerns and inferior adhesion [17,18], plus the undesirable deterioration of the magnetic properties [12]. As an environmentally kind method, physical vapour deposition (PVD) method, such as evaporation [13] or ion vapour deposition (IVD) [14] has been applied for Al coating in industry. Al is well suited to corrosion protection [19,20] and would not affect the magnetic properties of the magnets [21]. However, due to the low kinetic energy of evaporant atoms (∼0.1 eV) [22], the coating prepared by evaporation always presents a columnar structure with a high concentration of inter-column defects (such as voids and micropores). The columnar structure and the porosity could result in premature failure of coatings by providing fast diffusion paths for aggressive media [23]. Although kinetic energy of the atoms in IVD progress can be higher than that in evaporation, the coating prepared by IVD still presents columnar structure and low density. Consequently, a post-deposition shot peen is always used to densify the coating. This has led to very poor control over the thickness and uniformity of the coating, and preexposure cannot be carried out by such techniques [24].

Since the kinetic energy of sputtered atoms (typically 1–10 eV) is higher than that of evaporation, the coatings prepared by sputtering are dense and well adhesive with the substrate [22,25]. In our previous work [26], magnetron sputtered Al single layer and AlN/Al bilayer have improved the corrosion resistance of the sintered NdFeB magnets effectively with good adhesion. The AlN/Al bilayer exhibited better corrosion resistance. However, both coatings still presented evident columnar structure. In order to further increase the corrosion resistance, it is therefore of great interest to inhibit the columnar growth of the sputtered Al based coatings.

Microstructurally, two methods have been reported to inhibit the columnar growth of the single-layer coatings. One typical way is to utilize the multilayered structure in which two different layers are deposited alternatively. Examples of this kind include Ti/ZrN and Al/AlN multilayers which have improved corrosion resistance due to the interruption of the columnar structure [27,28]. The other way is doping impurity to change the structure of metal coatings. For instance, by increasing the oxygen concentration during depo-
sition, Barna et al. [29–31] can tune the structure of Al films from columnar polycrystalline, through nanocrystalline, and finally to amorphous structure of Al$_2$O$_3$. Therefore, replacement of the pure Al single layers by Al/Al$_2$O$_3$ multilayers should inhibit the columnar grown and improve the corrosion resistance of the sintered NdFeB magnets. In addition, since Al$_2$O$_3$ is an excellent insulator, there should not be galvanic couple effect between the Al layers and the Al$_2$O$_3$ films. The Al/Al$_2$O$_3$ multilayers prepared by evaporation with ion beam assisted deposition (IBAD) have been successfully applied on CK45 steel by Xue et al., and good corrosion protection has been obtained [32,33].

In this work, Al/Al$_2$O$_3$ multilayers were deposited by DC magnetron sputtering. The Al layers and the amorphous Al$_2$O$_3$ films were deposited alternately on sintered NdFeB magnets. The structure of the Al/Al$_2$O$_3$ multilayers and the corresponding corrosion resistance were studied. The correlation between them was also discussed. It was found that as the columnar structure was inhibited in the multilayers, the corrosion resistance was improved accordingly.

### 2. Experimental details

Sintered NdFeB magnet specimens (35H, Yunshen Co. Ltd, in demagnetisation state) with a size of 20 mm $\times$ 10 mm $\times$ 3 mm were ground and polished to a mirror surface and then ultrasonically cleaned in acetone followed by alcohol.

Deposition was carried out in a magnetron sputtering apparatus designed for magnets protection. The chamber was evacuated to a base pressure of $5 \times 10^{-4}$ Pa. Before deposition, the specimens were cleaned by Ar$^+$ ion beams which were provided by two end-Hall ion guns with an energy of 150 V $\times$ 1 A for 30 min. For depositing Al/Al$_2$O$_3$ multilayers, the Al layers and the Al$_2$O$_3$ film were deposited alternately on the sintered NdFeB which ran with revolution and rotation to get homogeneous coatings. The Al layers were prepared by DC magnetron sputtering from Al targets (99.999%). The Al$_2$O$_3$ films were prepared by reactive DC magnetron sputtering with Ar–O$_2$ mixed gas in which the concentration of O$_2$ was 40 at.%. Multilayers with different periods (Al + Al$_2$O$_3$) were prepared in the similar overall thickness. Al single layer was also prepared as a reference. The deposition conditions are listed 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. The deposition rate of Al layers was approximately 0.7 nm/s, and the deposition rate of Al$_2$O$_3$ films was approximately 0.04 nm/s. The cross-section micrographs of the coatings were observed by SEM equipped with energy dispersive spectrometer (EDS, S-4800, Hitachi). For detecting the structure, the Al$_2$O$_3$ film (thickness $\sim$ 40 nm) was deposited on NaCl substrate and then removed by dissolving in distilled water. The Al$_2$O$_3$ film was investigated by HRTEM (Tecnai F20, FEI). The corrosion behaviour of the specimens was investigated by potentiodynamic polarization in 3.5 wt.% NaCl solutions at 25 $\pm$ 3 $^\circ$C. A conventional three-electrode cell was used with an Ag/AgCl (saturated KCl) as the reference electrode and a platinum sheet (1 cm $\times$ 2 cm) as the auxiliary electrode. The exposed surface area of the working electrodes was 1 cm$^2$. To allow the stabilisation of the stationary potential, all systems were kept in solutions for 1 h before measurement. Single round tests were obtained at a scanning rate of 1 mV/s with the applied potential varied from $-1.1$ V (Ag/AgCl) to $-0.2$ V (Ag/AgCl). The potentiodynamic polarization experiments were performed using an Autolab potentiostat (PGSTAT302, Ecochimie). Neutral salt spray test (NSS) was also performed to investigate the corrosion resistance of specimens. The test was performed in a standard salt spray cabinet spraying NaCl solution (50 g/dm$^3$) at 35 $\pm$ 2 $^\circ$C. The evo-

![Fig. 1. XPS (a) Al 2p and (b) O 1s high-resolution spectra of the top Al$_2$O$_3$ film in the sintered NdFeB coated with three periods Al/Al$_2$O$_3$ multilayers.](image)

### Table 1

<table>
<thead>
<tr>
<th>Coatings</th>
<th>Layer</th>
<th>Thickness of each layer</th>
<th>Overall thickness of coatings (μm)</th>
<th>Gas flow rates Ar (sccm)</th>
<th>O$_2$ (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al single layer</td>
<td>Al</td>
<td>5.2 μm</td>
<td>5.2</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td>3 periods Al/Al$_2$O$_3$ multilayers</td>
<td>Al</td>
<td>1.7 μm</td>
<td>5.5</td>
<td>40</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>Top layer: 150 nm; other layer: 40 nm</td>
<td>/</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td>5 periods Al/Al$_2$O$_3$ multilayers</td>
<td>Al</td>
<td>1.0 μm</td>
<td>5.6</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>Top layer: 150 nm; other layer: 40 nm</td>
<td>/</td>
<td>40</td>
<td>26</td>
</tr>
<tr>
<td>10 periods Al/Al$_2$O$_3$ multilayers</td>
<td>Al</td>
<td>0.5 μm</td>
<td>5.6</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>Top layer: 150 nm; other layer: 40 nm</td>
<td>/</td>
<td>40</td>
<td>26</td>
</tr>
</tbody>
</table>
solution of the corrosion phenomena was visually observed up to 10 days.

3. Results and discussion

3.1. Characters of Al₂O₃ film

Fig. 1 shows the XPS Al 2p and O 1s high-resolution spectra of the top Al₂O₃ film in the sintered NdFeB coated with three periods Al/Al₂O₃ multilayers. Both the Al 2p peak (75.5 eV) and the O 1s peak (532.1 eV) are completely in the state of Al₂O₃, indicating full oxidation. The atomic concentration of Al and O was 39.9% and 60.1%, respectively. Therefore, the film should be stoichiometric Al₂O₃.

The micrographs of the Al₂O₃ film observed by HRTEM are shown in Fig. 2. It is shown that the film is dense, free of cracks or pores. The selected area electron diffraction pattern (inset) confirms the amorphous nature of the film.

3.2. Structure of coatings

Fig. 3 shows the cross-section micrographs of the sintered NdFeB coated with Al single layer and three, five, ten periods Al/Al₂O₃ multilayers, respectively. The Al single layer presents evident columnar structure (Fig. 3a), while the Al/Al₂O₃ multilayers present laminated structures (Fig. 3b–d). Fig. 4 shows the EDS results of the element line-scan across the sintered NdFeB coated with three periods Al/Al₂O₃ multilayers. The white line on the top of the image indicates the location of the line-scan. The three peaks in the element line of O indicate the location of the Al₂O₃ films. In the three, five and ten periods multilayers, the Al layers still feature columnar structure. However, due to the amorphous nature of the Al₂O₃ films, there are no epitaxial relationships between the Al layers and the Al₂O₃ films in the multilayers (Fig. 3b–d). As a result, the columnar growth structure in the different Al layers was...
single layer and Al/Al$_2$O$_3$ multilayers in 3.5 wt.% NaCl, respectively. The corrosion resistance of bare sintered NdFeB and the sintered NdFeB coated with Al single layer and Al/Al$_2$O$_3$ multilayers in 3.5 wt.% NaCl solutions.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$i_{\text{corr}}$ (nA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare sintered NdFeB</td>
<td>0.79</td>
<td>4586</td>
</tr>
<tr>
<td>Sintered NdFeB coated with Al</td>
<td>0.97</td>
<td>91</td>
</tr>
<tr>
<td>Sintered NdFeB coated with 3 periods Al/Al$_2$O$_3$ multilayers</td>
<td>0.95</td>
<td>1.8</td>
</tr>
<tr>
<td>Sintered NdFeB coated with 5 periods Al/Al$_2$O$_3$ multilayers</td>
<td>0.87</td>
<td>0.73</td>
</tr>
<tr>
<td>Sintered NdFeB coated with 10 periods Al/Al$_2$O$_3$ multilayers</td>
<td>0.83</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Fig. 5 shows the potentiodynamic polarization curves obtained from the bare sintered NdFeB and the sintered NdFeB coated with Al single layer and Al/Al$_2$O$_3$ multilayers in 3.5 wt.% NaCl, respectively. In the anodic region, the current density of bare sintered NdFeB increased sharply with the potential increasing. However, the sintered NdFeB coated with Al single layer and Al/Al$_2$O$_3$ multilayers firstly exhibited a passive-like anodic behaviour and then turned to an actively dissolving behaviour. The broad passive regions of the Al/Al$_2$O$_3$ multilayers should be ascribed to the excellent corrosion resistance of the top Al$_2$O$_3$ films, while the passive behaviour of the Al single layer should be due to the passivation of pure Al. The corrosion potential $E_{\text{corr}}$ and the corrosion current density $i_{\text{corr}}$ calculated near zero overall current by GPES software are listed in Table 2. The corrosion current density is a critical parameter to evaluate the anti-corrosion property. The corrosion current densities of the sintered NdFeB coated with Al single layer and Al/Al$_2$O$_3$ multilayers are much lower than that of the sintered NdFeB. It indicates the corrosion resistance of the sintered NdFeB was effectively improved by these coatings. Especially, the very low corrosion current densities of the sintered NdFeB coated with Al/Al$_2$O$_3$ multilayers (nA cm$^{-2}$) are about 2 orders of magnitude lower than that of the sintered NdFeB coated with Al single layer, indicating much better corrosion resistance. Furthermore, as the Al/Al$_2$O$_3$ period decreases, the corrosion current density as well as the corrosion rate in anodic region decreases.

The corrosion resistance of bare sintered NdFeB and the sintered NdFeB coated with Al single layer and Al/Al$_2$O$_3$ multilayers were also investigated by the NSS test up to 10 days. The optical photographs after 10 days test are shown in Fig. 6. The bare sintered NdFeB was full of red rusty corrosion products after 2 h in test. After 4 days, the red rusty corrosion products were detected on the sintered NdFeB coated with Al single layer. After 10 days, the specimen was completely covered by the rusty corrosion products (Fig. 6a). The time of red rusty corrosion products appearing on the sintered NdFeB coated with three, five and ten periods Al/Al$_2$O$_3$ multilayers was 5 days, 6 days and 6 days, respectively. After 10 days, the red rusty products decreased with the period (Fig. 6b–d). The evolution of the corrosion spots was same for all the sintered NdFeB coated with Al/Al$_2$O$_3$ multilayers, but the presence of lower period contributed to the lower corrosion rate. The results of the NSS test are consistent with that of the potentiodynamic polarization.

The different corrosion behaviour of these coatings is ascribed to their different structure. The column boundaries in the Al single layer are prone to the sites for defects initiation (Fig. 3a), which may result in premature pitting corrosion of the Al single layer. The improved corrosion resistance of the Al/Al$_2$O$_3$ multilayers may be ascribed to the following two reasons. Firstly, when the columnar structure in different Al layers was interrupted by the Al$_2$O$_3$ films, the defects in the Al layers may be “masked” by the Al$_2$O$_3$ films at the same time. The penetrating micropores could be inhibited. Secondly, the amorphous Al$_2$O$_3$ films, especially the top films, may act as barriers to block the diffusion of the aggressive media. Furthermore, as the period decreased, the penetrating micropores may be further inhibited and the overall thickness of the Al$_2$O$_3$ films increased in the multilayers (Fig. 3b–d). Therefore, the sin-

Fig. 6. Optical photographs of the sintered NdFeB coated with (a) Al single layer and (b) three, (c) five, (d) ten periods Al/Al$_2$O$_3$ multilayers after 10 days NSS test, respectively.
tered NdFeB coated with ten periods Al/Al2O3 multilayers have the best corrosion resistance.

4. Conclusions

1. The Al single layer prepared by magnetron sputtering presented evident columnar structure which could result in premature failure of coatings. The columnar structure was effectively inhibited in the laminated Al/Al2O3 multilayers as the period decreased.

2. The sintered NdFeB coated with Al/Al2O3 multilayers presented better corrosion resistance than the sintered NdFeB coated with Al single layer. As the period of Al/Al2O3 multilayers decreased, the corrosion resistance of the sintered NdFeB was further improved.

References