Structure, corrosion, and hardness properties of Ti/Al multilayers coated on NdFeB by magnetron sputtering

Tingting Xie, Shoudong Mao, Chao Yu, Shaojie Wang, Zhenlun Song*

Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 519 Zhuangshi Road, Ningbo 315201, China

A R T I C L E I N F O

Article history:
Received 13 January 2012
Received in revised form 7 March 2012
Accepted 7 March 2012

Keywords:
NdFeB magnet
Ti/Al multilayer
Magnetron sputtering
Corrosion resistance

1. Introduction

Sintered NdFeB permanent magnets are widely used for their excellent magnetic properties. However, the low corrosion resistance of NdFeB magnets in common ambient environments due to their multiphase microstructure limits their applications. The galvanic corrosion between the matrix phase Nd₂Fe₁₄B and electrochemically highly active Nd-rich phase, which normally exists in the intergranular region surrounding the matrix phase grains, is responsible for the low corrosion resistance [1–3]. The preferential corrosion of the Nd-rich phase may ultimately cause pulverization of the magnet. Efforts have been exerted to improve the corrosion resistance of NdFeB magnets by alloy addition [4–7] and surface coatings [8,9–13]

In industry, coatings such as electroplated Ni, Zn, and Ni–Cu–Ni are generally applied because of their good corrosion performance and low processing cost. However, electroplating is often accompanied by environmental concerns and deterioration of magnetic properties [14]. As an environmentally friendly method, physical vapour deposition has attracted increasing attention and been utilized to improve corrosion resistance [15–19]. The current techniques used to protect NdFeB magnets include Al coatings prepared by evaporation, ion vapour deposition, or magnetron sputtering [8,20,21]. Coatings deposited by sputtering are denser and have better adhesion with a substrate due to the higher kinetic energy of sputtered atoms (typically 1–10 eV) compared with that of evaporated atoms (approximately 0.1 eV). However, magnetron sputtered Al coatings also exhibit a distinct columnar structure with inter-column defects, which can provide a fast diffusion path for aggressive medium [21]. When an aggressive medium gains access to the substrate via the permeable defects, the NdFeB substrate becomes prone to galvanic corrosion because of its negative potential [22]. By interrupting columnar structure growth with multilayered coatings, the permeable defects between the columnar crystals of Al coatings can be reduced [23–26]. Ductile Al coatings also easily break, resulting in failed protection. With multilayered coatings, the hardness of coatings can be enhanced [24,26].

Al coatings deposited on NdFeB magnets present a face-centred cubic (fcc) structure [27]. Ti thin films with hexagonal close packed (hcp), fcc, and body-centred cubic structures have been identified [28,29]. Due to its distinct space lattice, Ti with an hcp structure is expected to interrupt the columnar structure growth of Al. Ti and Al also have similar standard electrode potentials (−1.662 V for Al/Al³⁺ and −1.628 V for Ti/Ti²⁺). Thus, galvanic corrosion between them might be inconspicuous. In this report, Ti/Al multilayers were deposited on sintered NdFeB magnets. Ti layers and Al layers were deposited alternately by magnetron sputtering with ion-beam assistance. The structure, corrosion resistance, and hardness properties of the Ti/Al multilayers were investigated.

* Corresponding author. Tel.: +86 574 87911131; fax: +86 574 86685159.
E-mail addresses: songzhenlun@nimte.ac.cn, xietina1123@163.com (Z. Song).
2. Experimental details

Sintered NdFeB magnet specimens ( unmagnetized; 20 mm × 10 mm × 3 mm in size) were mechanically polished to a mirror surface and then ultrasonically cleaned in alcohol followed by acetone.

All coatings were deposited on freshly cleaned NdFeB and Si specimens (for structure identification and hardness measurement) by direct current magnetron sputtering with ion-beam assistance from pure Al (99.999%) and Ti (99.995%) targets. The sputtering chamber was evacuated to a base pressure of 9.0 × 10⁻⁴ Pa using a mechanical roughing pump followed by a turbo pump. Deposition was carried out under an Ar atmosphere. The main deposition parameters are summarized in Table 1. Before deposition, the specimens were cleaned for 45 min by Ar⁺ ion beams provided by two end-Hall ion guns, which helped to achieve the adhesion strength between coatings and substrates [21,30].

During deposition, the specimens were static in front of the Ti or Al targets alternately. Given the lower standard electrode potential of Al than Ti, the Al layer was deposited as the outermost layer. The Ti/Al multilayers, which had 5, 10, and 25 bilayers of Ti and Al, were prepared. The thickness of each Ti layer was kept constant at 50 nm. By changing the thickness of each Al layer, the total thickness was fixed at around 4.5–5.5 μm. For comparison, pure Al and Ti single layers were also prepared. The specific deposition parameters are listed in Table 2.

A surface profilometer (Alpha-Step, IQ) was employed to measure the thickness of the coatings with a step formed by a shadow mask. The surface and cross-section micrographs of the coatings were observed by a scanning electron microscope (SEM, S-4800, Hitachi) equipped with an energy dispersive spectrometry (EDS) instrument. The multilayered structure was observed in the backscatter electron images. The structure and preferred growth orientation were examined by an X-ray diffraction (XRD, D8, Bruker) with Cu Kα radiation. The corrosion properties of the coatings were investigated by potentiodynamic polarization in a 3.5 wt.% NaCl solution at about 25 °C using a potentiostat (PGSTAT302, Autolab). No buffer was used. The electrolyte had an original pH of 5.8–6.2 and was not deaerated. A conventional three-electrode cell was used. A saturated calomel electrode (SCE) and a platinum sheet (1 cm × 1 cm) were applied as reference and counter electrodes, respectively. Before measurement, the specimens were immersed in a 3.5 wt.% NaCl solution for 1 h to obtain the stationary potential. Polarization curves were measured at a potential scanning rate of 1 mV/s.

Hardness measurements were performed by a Nanolindenter using a system with a Berkovich indenter (XP, MTS) in a continuous stiffness mode. The indentor penetrated the coatings at constant speed to a depth of about 2 μm.

3. Results and discussion

3.1. Morphology of coatings

Fig. 1 shows the backscatter electron images of the cross-sections of Al and Ti single layers as well as 5-, 10-, and 25-period Ti/Al multilayers. Weak hcp Ti (100), (101), (102), and (103) peaks and a hcp Al (111) and (200) peaks superposed on the XRD patterns of the Ti/Al multilayers. For the Al and Ti single layers, the X-ray diffraction peak intensity and X-ray radiation. The corrosion properties of the coatings were investigated by potentiodynamic polarization in a 3.5 wt.% NaCl solution at about 25 °C using a potentiostat (PGSTAT302, Autolab). No buffer was used. The electrolyte had an original pH of 5.8–6.2 and was not deaerated. A conventional three-electrode cell was used. A saturated calomel electrode (SCE) and a platinum sheet (1 cm × 1 cm) were applied as reference and counter electrodes, respectively. Before measurement, the specimens were immersed in a 3.5 wt.% NaCl solution for 1 h to obtain the stationary potential. Polarization curves were measured at a potential scanning rate of 1 mV/s.

Hardness measurements were performed by a Nanolindenter using a system with a Berkovich indenter (XP, MTS) in a continuous stiffness mode. The indentor penetrated the coatings at constant speed to a depth of about 2 μm.

3. Results and discussion

3.1. Morphology of coatings

Fig. 1 shows the backscatter electron images of the cross-sections of Al and Ti single layers as well as 5-, 10-, and 25-period Ti/Al multilayers on the NdFeB specimens. Both Al and Ti single layers exhibited a columnar structure, as shown in Fig. 1(a) and (b), respectively. Fig. 1(c)–(e) show the Ti and Al layers as white and black regions, respectively. The columnar structure growth of Al layers was successfully interrupted by the intercalated Ti layers. The permeable inter-column defects were inhibited in the Ti/Al multilayers due to the interfaces between the Ti and Al layers.

The Ti and Al layers were identified with the aid of the EDS results of an element line-scan across the 5-period Ti/Al multilayer (Fig. 2). The five peaks of elemental Ti corresponded to the slightly decreased elemental Al concentration, indicating the location of the Ti layers. The discrepancies among the peak intensities of different Ti layers could be caused by the fracturing of the ductile Al layers and rough cross-section.

Fig. 3 shows SEM micrographs of the surfaces of Al and Ti single layers as well as Ti/Al multilayers on the NdFeB specimens. Micropores in the grain boundaries can be observed in the Al single layer. A number of humps were found in the Ti single layer. The 5-period Ti/Al multilayer had similar morphology to the Al single layer. With decreased bilayer period, the Ti/Al multilayers showed more compact and uniform surfaces, which may be related to the interrupted columnar structure growth.

3.2. Structure of coatings

Fig. 4 shows the XRD patterns of the Al and Ti single layers as well as Ti/Al multilayers. For the Al and Ti single layers, the X-ray peaks were indexed to fcc Al and hcp Ti, respectively. The fcc Al (111) and hcp Ti (002) peaks superposed on the XRD patterns of the Ti/Al multilayers. Weak hcp Ti (100), (101), (102), and (103) peaks were also observed, whereas three major diffraction peaks of fcc Al (200), (220), (311) and (222) were identified. These findings indicated that Ti layers with an hcp structure were attained in the Ti/Al multilayers. With decreased bilayer period, the relative intensities of the hcp Ti (100), (101), (102), and (103) peaks increased due to the increased Ti content in the Ti/Al multilayers.

3.3. Corrosion properties of coatings

The potentiodynamic polarization curves of the bare NdFeB specimen and the NdFeB specimens coated with Al and Ti single layers as well as Ti/Al multilayers were measured after 1 h of immersion in a 3.5 wt.% NaCl solution (Fig. 5). The corrosion potential 

\[ E_{corr} \]

and corrosion current density 

\[ I_{corr} \]

were calculated near zero overall current by GPES software are listed in Table 3. The corrosion potential of the Al-coated NdFeB specimen was approximately –0.97 V (vs. SCE), whereas that of the Ti-coated NdFeB specimen was around –0.96 V (vs. SCE). The corrosion current density values were compared. The corrosion current density of bare NdFeB specimen was about \( 8.4 \times 10^{-5} \) A/cm². For the NdFeB specimens coated with Al and Ti single layers, the corrosion current density was approximately
1.9 x 10^{-5} \text{ A/cm}^2. \text{ Thus, the Al and Ti single layers can slightly protect NdFeB. For the 5-period Ti/Al multilayer, the corrosion current density was approximately 1.1 x 10^{-7} \text{ A/cm}^2, about two orders of magnitude lower than that of the Al single layer. This finding revealed that the corrosion resistance of the Al single layer was improved by the intercalation of Ti layers.}

The significant enhancement in corrosion resistance was closely related to the transformation of the coating structure. First, the Al coating corrodes via pitting corrosion and its surface defects (e.g., micropores) may be prone to the initiative sites of its pitting corrosion \cite{22,31}. The pitting corrosion resistance of the Ti/Al multilayers could be better than that of the Al single layer due to their fewer surface defects. Second, given the nobler corrosion potential of Al than the Nd-rich phase in the sintered NdFeB magnet, the Al single layer cannot provide complete sacrificial protection for NdFeB \cite{22}. In the Ti/Al multilayers, the Ti/Al interfaces can act as barriers by inhibiting the permeable voids and prolonging the path for aggressive medium to access the NdFeB substrates. The higher effective surface area of the Al-coated NdFeB specimen may also contribute to its higher corrosion current density because of its rougher surface.

With decreased bilayer period, the corrosion current density and corrosion rate further decreased slightly. The 25-period Ti/Al multilayer presented the best corrosion resistance with the lowest
Fig. 3. Surface micrographs of (a) Al single layer, (b) Ti single layer, (c) 5-period Ti/Al multilayer, (d) 10-period Ti/Al multilayer, and (e) 25-period Ti/Al multilayer on the NdFeB specimens, respectively.

Fig. 4. XRD patterns of Al and Ti single layers as well as Ti/Al multilayers on the Si specimens.

Fig. 5. Potentiodynamic polarization curves of the bare NdFeB specimen and the NdFeB specimens coated with Al and Ti single layers as well as Ti/Al multilayers in a 3.5 wt.% NaCl solution.
corrosion current density of about $7.9 \times 10^{-8}$ A/cm². This result can be attributed to its most compact and uniform surface, as well as highest number of Ti/Al interfaces.

3.4. Hardness properties of coatings

The hardness of coatings depended on the coating structure, as shown in Fig. 6. All Ti/Al multilayers presented higher hardness values compared with the Al single layer. The hardness value of the Al single layer was about 0.75 GPa. A greater number of alternated Ti/Al bilayers corresponded to a higher hardness, consistent with other multilayers reported previously [23,24]. The 25-period Ti/Al multilayer presented the highest hardness value of 2.56 GPa, more than three times that of the Al single layer. The enhancement in hardness can be ascribed to the combined effects of the increasing numbers of Ti component and Ti/Al interfaces.

4. Conclusions

1. There was no epitaxial relationship between the Al and Ti layers in the Ti/Al multilayers. With the intercalation of Ti layers, the columnar structure growth of Al layers was successfully interrupted. The Ti/Al multilayers on the sintered NdFeB magnets showed more compact surfaces than the Al single layer. The surfaces of multilayers also presented gradually increased compactness and uniformity with decreased bilayer period.

2. The sintered NdFeB magnets coated with Ti/Al multilayers presented improved corrosion resistance compared with the Al single layer. With decreased bilayer period, the corrosion resistance was improved further. The compact and uniform surfaces as well as Ti/Al interfaces may contribute to the improved corrosion resistance. However, Ti content was also a variable factor. Further studies are necessary to confirm its effects.

3. The hardness of the Al coating was increased by the intercalation of Ti layers.

Acknowledgement

This work was financially supported by the National Key Technology R&D Program (2012BAE02B01) and Natural Science Foundation of Ningbo (090305VA16).

References


