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Effects of Al coating on corrosion resistance of sintered NdFeB magnet

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Abstract: Pure Al coating was deposited on sintered NdFeB magnet by direct current (DC) magnetron sputtering to improve the corrosion resistance of magnet. The influences of coating thickness and sputtering power on microstructure and corrosion resistance of Al coating were investigated. The surface morphology of Al coating was characterized by scanning electron microscopy (SEM). The corrosion properties were investigated by potentiodynamic polarization curves and neutral salt spray (NSS) test. The formation of the uniform and compact Al coating is a necessary condition to achieve excellent corrosion resistance. And the optimal corrosion resistance can be obtained in the sample with 6.69 μm thick Al coating deposited at 51−82 W.

Key words: NdFeB; aluminum coatings; magnetron sputtering; corrosion resistance; coating thickness

1 Introduction

Sintered NdFeB magnets have been widely used for their high remanence, high coercivity, and large maximum energy product since the discovery in 1984 [1,2]. However, their poor corrosion resistance in various environments greatly limits their further use in commercial applications [3−5]. Therefore, the improvement of corrosion resistance in NdFeB magnets has attracted much attention, up to now, two kinds of methods have been applied to improving the corrosion resistance of NdFeB magnets, including alloy additions [6,7] and surface coating by either polymeric resins or metals [6−8]. However, alloy additions method is often accompanied by deterioration in the magnetic properties [7,8], and coatings of polymer resins possess relatively low level of corrosion protection which cannot meet the urgent needs of premium products [9,10]. So, the research effort to improve the corrosion resistance of NdFeB magnets has focused on metallic coatings prepared through different techniques [9]. In industry, electroplated coatings like Ni, Zn or Ni/Cu/Ni are widely applied to protecting NdFeB for their good performance and low processing costs [11,12]. But electroplated coatings are often involved in environmental pollution problem, poor adhesion between coatings and substrates, and deterioration of the magnetic properties [12,13]. Compared with electroplating technology, magnetron sputtering method has its own advantages to prepare protective coatings for sintered NdFeB magnets. Firstly, it is an environmentally friendly method. Secondly, sputtered atoms with high kinetic energy (typically 1−10 eV) lead to the high adhesion and low porosity of sputtered coatings [14]. In addition, the plating solution would infiltrate into micro-pores of sintered NdFeB magnets in the plating process, which is harmful to the corrosion resistance of magnets, but magnetron sputtering method can effectively avoid the problem. Some coatings like Ti/Al, Al/AlN, Al and Al/Al_2O_3 deposited on sintered NdFeB magnets by magnetron sputtering have been investigated, and it was found that these coatings can improve the anti-corrosion properties of NdFeB magnets [12−16]. However, the optimal parameters of structure and preparation condition to obtain the excellent corrosion resistance of Al coating deposited on sintered NdFeB have not been investigated and these parameters are key factors for the engineering application.

In this work, pure Al coating was deposited on

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sintered NdFeB magnets by direct current (DC) magnetron sputtering. The relationships among sputtering power, coating thickness, microstructure and corrosion resistance of coatings were investigated systematically.

2 Experimental

Sintered NdFeB magnet specimens with the dimensions of 15 mm×10 mm×3 mm were used in the experiment. They were first degreased in 2.0% NaOH solution (mass fraction) at room temperature for 120 s and then immersed in 0.5% HNO_3 solution for 90 s for oxide removal, and followed by ultrasonic cleaning in alcohol for 15 min. Prior to deposition, samples were cleaned by Ar^+ ion beams for 15 min. Finally, a layer of Al coating was deposited on magnets. The base pressure was 1.6×10^{-4} Pa and the working pressure was 0.5 Pa. Al coatings with 2.23, 4.46, 6.69, 8.92 and 11.15 μm in thickness were deposited by 51 W sputtering power, respectively, corresponding to the deposition rate of 74.33 nm/min. Then the effects of sputtering power on corrosion resistance of Al coating were also investigated. In the experiment, the DC voltage was about 380 V. The detailed deposition parameters are listed in Table 1.

Table 1 Detailed deposition parameters of Al coatings

Sputtering power/W	Deposition rate/ ($nm\cdot min^{-1}$)	Controlled thickness/μm
51	74.33	6.69
82	85.62	6.85
102	150.58	6.62
154	201.58	6.65

The morphology of Al coating was observed by scanning electron microscopy (SEM, QUANTA−200). The structure of Al/NdFeB was characterized by X-ray diffraction (XRD, SIEMENS D5000) using Cu K_α radiation. The corrosion properties of Al/NdFeB were examined by potentiodynamic polarization curves in 3.5% NaCl solution using the CHI660C electrochemical workstation. A universal three-electrode cell was used with the platinum sheet as counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode. The curves were measured with potential sweep rate of 2 mV/s after the samples were immersed in NaCl solution for 600 s when the samples reach the steady state. Then the neutral salt spray (NSS) test was also performed to investigate the corrosion behavior of samples using the standard salt spray cabinet spraying (50±5) g/L NaCl solution at (35±2) °C. The variation of the corrosion process was visually observed up to 4 d.

3 Results and discussion

3.1 Effects of coating thickness on structure and properties

Figure 1 shows the XRD patterns of Al coatings with different thicknesses of 2.23, 4.46, 6.69, 8.92 and 11.15 μm, respectively. Al coatings have the face-centered cubic structure. The strongest XRD peak at approximately 2θ of 38.70° which corresponds to the Al (111) diffraction peak can be observed from all of the samples. And two weak peaks of Al, which are referred to as (200) and (220), are also found. The diffraction intensity of 2.23 μm thick Al coating is relatively weak. As the coating thickness increases, the intensity of every Al peak becomes stronger due to the increasing Al content.

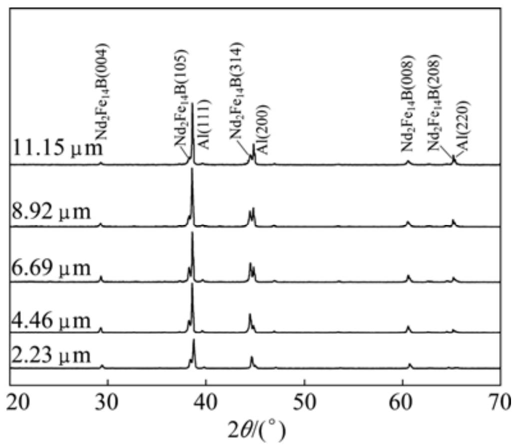

Fig. 1 XRD patterns of Al coatings with different thicknesses

Figure 2 shows the surface morphology of bare NdFeB and Al coatings with different thicknesses. Big pores brought by power metallurgical sintering process can be found from bare NdFeB. With increasing the coating thickness, the surface roughness of Al coating has a gradually decreased trend up to 6.69 μm. Some voids can be observed on the surface of 2.23 and 4.46 μm thick Al coatings. However, Al particles in the films with 8.92 and 11.15 μm in thickness have a tendency to grow up.

Figure 3 shows the potentiodynamic polarization curves of NdFeB coated with different thicknesses Al coatings in 3.5% NaCl solution. The critical parameters acquired from polarization curves, including the corrosion potential (φ_{corr}) and corrosion current density (J_{corr}), are listed in Table 2. The anode part of uncoated NdFeB presents actively dissolving and the J_{corr} increases sharply as the φ_{corr} increases, indicating that the corrosion rate is accelerated. It could be related to the existence of many pores in the magnets. On the contrary, the anode region of Al/NdFeB firstly exhibits a passive-like

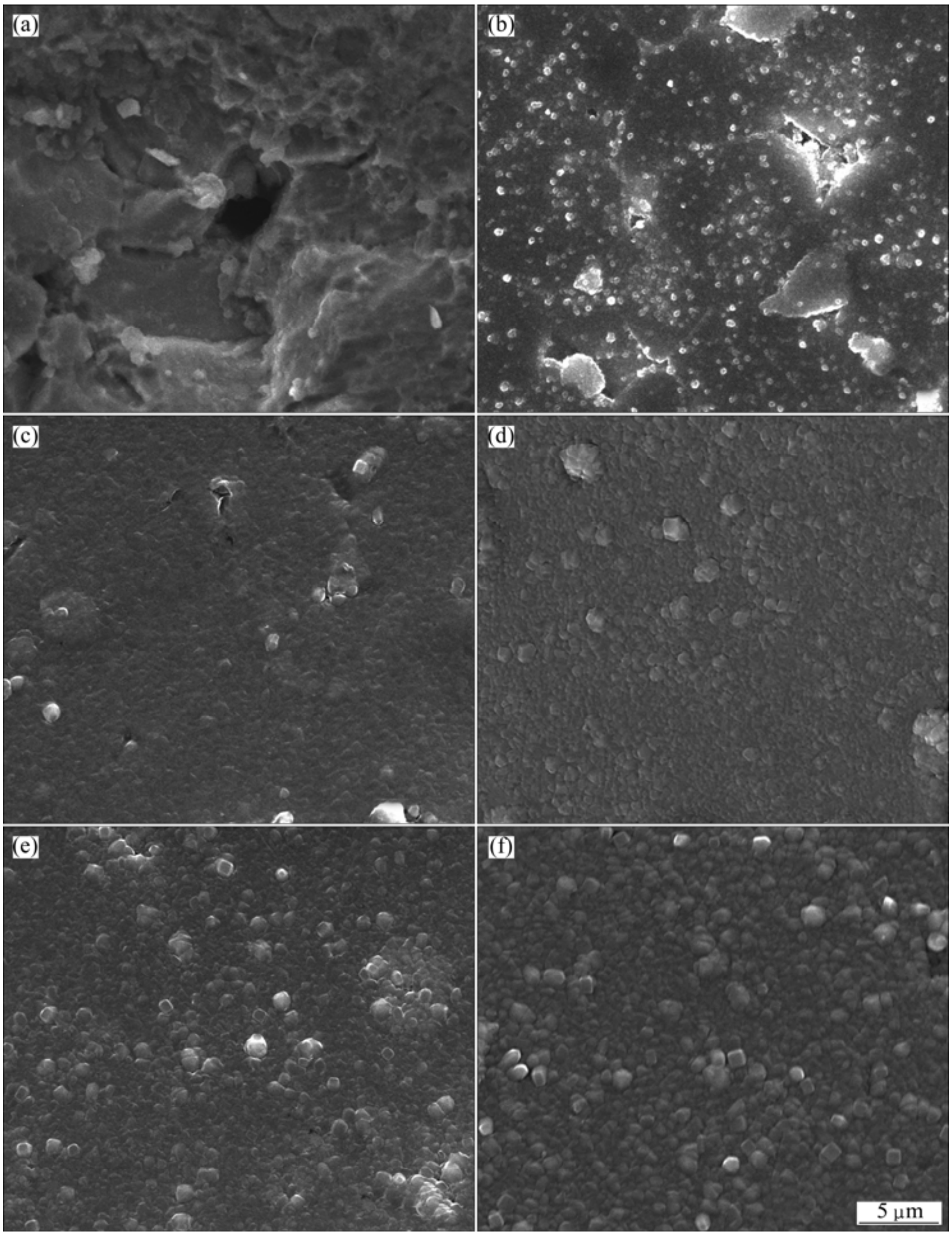

Fig. 2 SEM images of surface morphologies of NdFeB coated with Al coatings in different thicknesses: (a) 0; (b) 2.23 μm; (c) 4.46 μm; (d) 6.69 μm; (e) 8.91 μm; (f) 11.15 μm

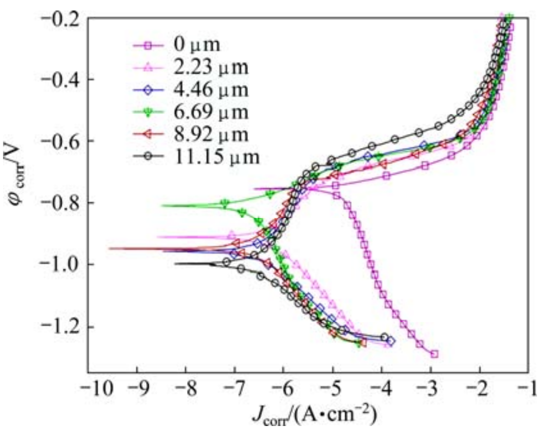

Fig. 3 Potentiodynamic polarization curves of NdFeB coated with different thicknesses Al coatings in 3.5% NaCl solution

Table 2 Polarization data obtained from different thicknesses Al coatings in 3.5% NaCl solution

Thickness/μm	φ_{corr}/V	J_{corr}/(nA·cm^{-2})
0	−0.753	24370
2.23	−0.910	622
4.46	−0.956	439
6.69	−0.808	147
8.92	−0.948	317
11.15	−0.997	347

anodic behavior and then transforms to an actively dissolving region with the increase of the potential. The passive-like anodic behavior would result from the formation of oxide films on Al coatings in the NaCl solution [15], and the J_{corr} is about two orders of magnitude smaller than that of uncoated NdFeB samples. This indicates that Al coatings have a good protective ability for NdFeB magnets, and the value of J_{corr} firstly decreases significantly and then increases with increasing the coating thickness. The minimum of J_{corr} is obtained in the sample with Al coating of 6.69 μm in thickness and its value is 147 nA/cm^2. As a result, the 6.69 μm thick Al coating exhibits the best corrosion resistance compared with others.

The corrosion resistances of bare NdFeB and Al/NdFeB were also investigated by the NSS test. The optical images after NSS test for 4 d are shown in Fig. 4. The bare NdFeB is full of red rusty corrosion products after NSS test for 1 h. The time of rusty corrosion products appearing on sintered NdFeB with 2.23, 4.46, 6.69, 8.92 and 11.15 μm thick Al coatings is 7, 24, 72, 48 and 48 h, respectively. After 4 d, 2.23 and 4.46 μm thick Al coatings are completely corroded. There is the least rust on the surface of 6.69 μm thick coating, indicating that it has the best corrosion resistance.

The evolution of corrosion resistance of Al coatings with different thicknesses can be ascribed to the variation of Al coating microstructure. The surface of sintered NdFeB magnets is rough with many pores caused by power metallurgical sintering process, and these micro-pores cannot be completely filled in the samples with the thin coating, which results in the formation of discontinuous coating with some voids. These voids can provide channel for Cl^- to penetrate into the substrates. Therefore, 2.23 and 4.46 μm thick Al coatings have the poor corrosion resistance. As the coating thickness runs up to about 7 μm, continuous and dense coatings are obtained and consequently they possess good corrosion resistance. However, Al coatings with 8.91 and 11.15 μm in thickness have not better corrosion resistance than the 6.69 μm thick Al coating. It is relevant to the growing up of Al particles, which can be attributed to the rising temperature of the samples for the long time glow irradiation. And larger particles result in the formation of some voids on coatings, which lead to the decreasing of corrosion resistance. Therefore, the formation of a continuous and dense Al coating is the basic requirement for excellent corrosion resistance.

3.2 Effects of sputtering power on microstructure and properties

In order to obtain dense Al coating, the influences of sputtering power on the microstructure of coatings were investigated. Figure 5 shows the surface morphology of Al coatings deposited at different sputtering powers. As can be seen in the Fig. 5, the average size of Al particles has little change when the sputtering power ranges from 51 to 82 W and the grains are densely packed producing smooth surface. When sputtering power exceeds 82 W, the size of Al particles increases markedly with the increasing sputtering power, and the coating surface changes to be scattered, loose and rough. The evolution of surface morphology can be ascribed to the change in energy of sputtered atoms or clusters as a function of sputtering power.

Figure 6 shows the potentiodynamic polarization curves of Al/NdFeB prepared at different sputtering powers in 3.5%NaCl solution. The corrosion potential (φ_{corr}) and corrosion current density (J_{corr}) are listed in Table 4. The J_{corr} of Al coating deposited at 51, 82, 102 and 154 W are 147, 166, 445 and 883 nA/cm^2, respectively. The corrosion resistance of Al/NdFeB increases slightly up to 82 W and then rises significantly with the increase of sputtering power. It can be noticed that Al coatings deposited at 51−82 W have the best corrosion resistance.

Figure 7 shows the optical photographs of Al/NdFeB after 4 d NSS test. The time of rusty products detected on samples prepared at 51, 82, 102 and 154 W is 72, 72, 48 and 48 h, respectively. And the rusty products increase with the increase of the sputtering power after NSS test for 4 d, demonstrating a decreasing in the corrosion resistance.

The significant decrease in corrosion resistance is closely relevant to the transformation of sputtering power. As the sputtering power increases, the DC current increases and the DC voltage is kept unchanged, and the average kinetic energy of Ar ion upon striking the target is proportional to DC applied voltage [17]. Thus, the initial kinetic energy of sputtered atoms is kept constant because the DC voltage is unchanged. But the flux of the

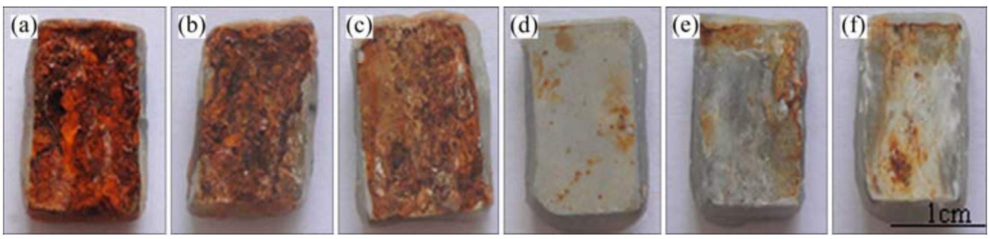

Fig. 4 Optical images of Al coatings with different thicknesses after NSS test for 4 d: (a) 0; (b) 2.23 μm; (c) 4.46 μm; (d) 6.69 μm; (e) 8.91 μm; (f) 11.15 μm

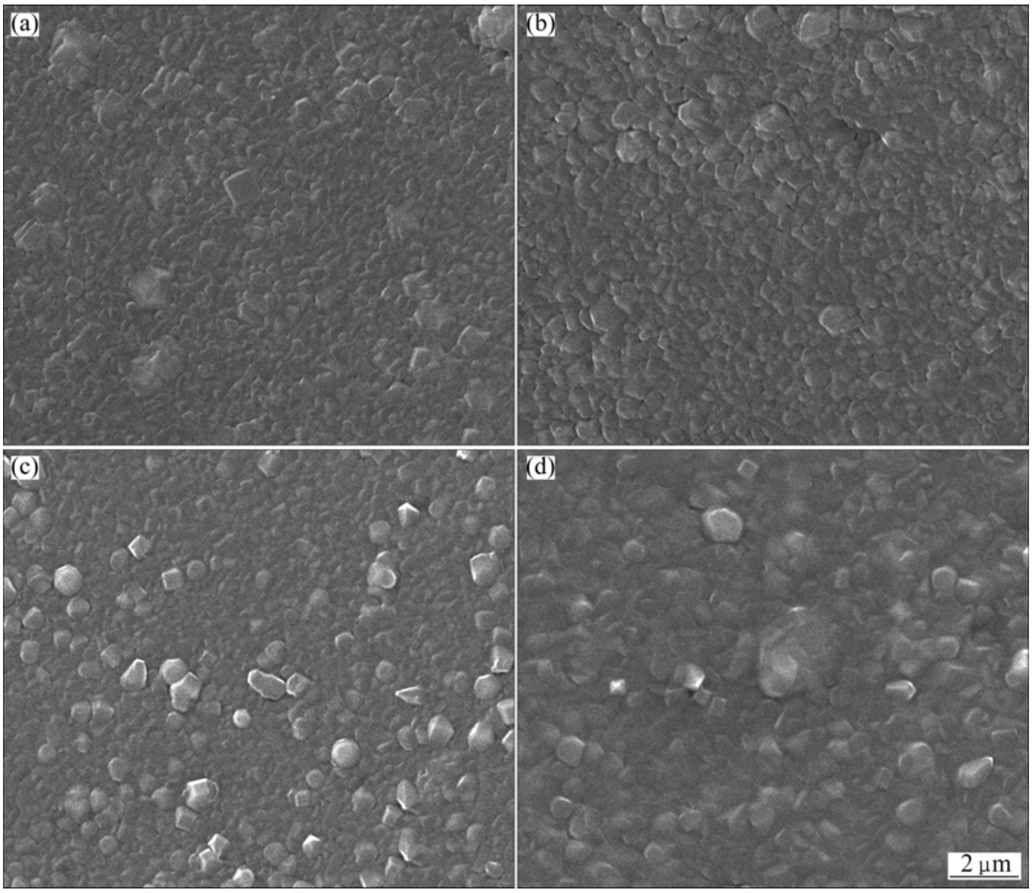

Fig. 5 SEM images of surface morphology of Al coatings deposited at different sputtering powers: (a) 51 W; (b) 82 W; (c) 102 W; (d) 154 W

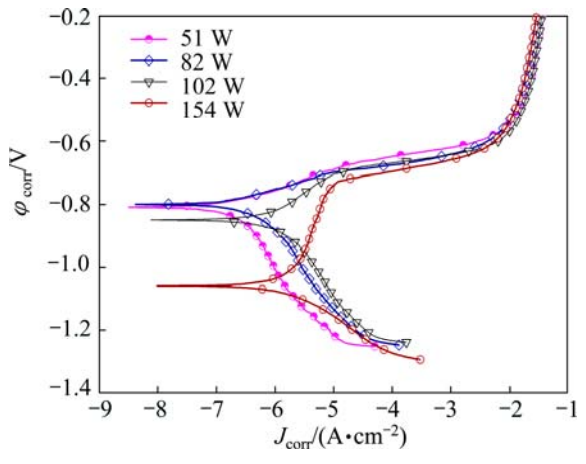

Fig. 6 Potentiodynamic polarization curves of Al/NdFeB prepared at different sputtering powers in 3.5%NaCl solution

Table 3 Polarization data obtained from Al/NdFeB prepared at different sputtering powers in 3.5%NaCl solution

Sputtering power/W	φ_{corr}/V	J_{corr}/(nA·cm^{-2})
51	−0.808	147
82	−0.800	166
102	−0.789	445
154	−0.847	883

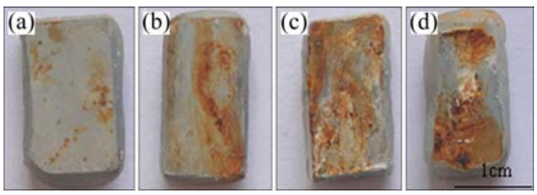

Fig. 7 Optical images of Al/NdFeB prepared at different sputtering powers after NSS test for 4 d: (a) 51 W; (b) 82 W; (c) 102 W; (d) 154 W

sputtered atoms is increased with the increasing DC current. A low flux of sputtered atoms can be obtained at low sputtering power, consequently the probability of atomic collisions is small. Therefore, sputtered atoms possess high energy when they reach the substrate, hence the probability for lattice rearrangements and surface remodeling are enhanced. When the potential energy barrier of nucleation is higher than that of growth, sputtered atoms possessing high energy are conducive to the nucleation [17]. So, many small size particles can be found on Al coatings deposited at 51−82 W and the coating surface is smooth and compact. As the sputtering power increases, the probability of sputtered atomic collisions is enhanced for the increasing sputtered atom flux. Hence, the energy of atoms is reduced when they get to substrates. The ability of surface remodeling is also decreased and the growth of particle plays the main role. As a result, Al particles having a tendency to grow up on the surface are loose and scattered. And the loose surface is easy for NaCl solution to infiltrate to substrates. So, the corrosion resistances exhibit a decreased trend with the increase of sputtering power. Therefore, the optimized sputtering powers are 51−82 W in the experiment.

4 Conclusions

1) Al coatings deposited by DC magnetron sputtering can improve the corrosion resistance of sintered NdFeB magnets. The coating thickness and DC power play an important role in the optimization of the corrosion resistance of Al coating.

2) When the coating thickness increases from 2.23 to 6.69 μm, Al coating becomes dense and there is a significant increase in the corrosion resistance of Al coating. However, the further increase of coating thickness yields further improvement in the corrosion resistance due to the growth up of Al particles.

3) As the sputtering power increases, the surface of Al coating becomes loose and scattered, consequently the corrosion resistance decreases. The optimal sputtering powers are 51−82 W.

References

[1] SAGAWA M, FUJIMURA S, TOGAWA N, YAMAMOTO H, MATAUURA Y. New material for permanent magnets on a base of Nd and Fe [J]. Applied Physics, 1984, 55: 2083−2087.

[2] YUE Ming, ZHANG Dong-tao, LIU Wei-qiang, WANG Gong-ping, ZHANG Jiu-xing. High corrosion resistance NdFeB magnet sintered by spark plasma technique [J]. The Chinese Journal of Nonferrous Metals, 2005, 15(2): 218−222. (in Chinese)

[3] ALI A, AHMAD A, DEEN K M. Multilayer ceramic coating for impeding corrosion of sintered NdFeB magnets [J]. Journal of Rare Earths, 2009, 27(6): 1003−1007.

[4] WANG Yao, DENG Yu-zhou, MA Yuan-tai, GAO Fei. Improving adhesion of electroless Ni−P coating on sintered NdFeB magnet [J]. Surface and Coatings Technology, 2011, 206(6): 1203−1210.

[5] CYGAND F, MCNLLAN M J. Corrosion of NdFeB permanent magnets in humid environments at temperature up to 150 °C [J]. Journal of Magnetism and Magnetic Materials, 1995, 139: 131−138.

[6] HE Qi-jun, LI Wei. Progress in research on anticorrosion of NdFeB permanent magnet [J]. Metallic Function Materials, 2001, 8(5): 8−13. (in Chinese)

[7] YUAN Qing-long, CAO Jing-jing, SU Zhi-jun. Progress in research on anticorrosion of sintered tybe neodymium iron boron [J]. Surface Technology, 2008, 38(1): 76−78. (in Chinese)

[8] LIU Wei-qiang, YUE Ming, ZHANG Jiu-xing, WANG Gong-ping. Intrinsic corrosion characteristic of NdFeB permanent magnets [J]. Power Metallurgy Technology, 2006, 24(3): 195−198. (in Chinese)

[9] CHEN Zhong, ALICE N, YI Jian-zhang, CHEN Xing-fu. Multi-layered electroless Ni−P coatings on power-sintered Nd−Fe−B permanent magnet [J]. Journal of Magnetism and Magnetic Materials, 2006, 302(1): 216−222.

[10] YINOWA T, YOSHIKAWA Y, HONSHIMA M. Improvement of the corrosion resistance on Nd−Fe−B magnet with nickel plating [J]. IEEE Higher Electrochemical Activity Transactions on Magnetics, 1989, 25(5): 3776−3778.

[11] LIU Wei, HOU Jin. Production status and prospect of NdFeB magnet electroplating [J]. Plating and Finishing, 2012, 34(4): 20−25. (in Chinese)

[12] XIE Ting-ting, MAO Shou-dong, YU Chao, WANG Shao-jie, SONG Zhen-lun. Structure, corrosion and hardness properties of Ti/Al multilayers coated on NdFeB by magnetron sputtering [J]. Vacuum, 2012, 86: 1583−1588.

[13] LI Jin-long, MAO Shou-dong, SUN Ke-fei, LI Xiao-min, SONG Zhen-lun. AlN/Al dual protective coatings on NdFeB by DC magnetron sputtering [J]. Journal of Magnetism and Magnetic Materials, 2009, 321: 3799−3803.

[14] MAO Shou-dong, YANG Heng-xiu, LI Jin-long, HUANG Feng, SONG Zhen-lun. Corrosion properties of aluminium coatings deposited on sintered NdFeB by ion-beam-assisted deposition [J]. Applied Surface Science, 2011, 257: 5581−5585.

[15] MAO Shou-dong, YANG Heng-xiu, SONG Zhen-lun, LI Jin-long, YING Hua-gen, SUN Ke-fei. Corrosion behaviour of sintered NdFeB deposited with an aluminium coating [J]. Corrosion Science, 2011, 53: 1887−1894.

[16] MAO Shou-dong,YANG Heng-xiu, HUANG Feng, XIE Ting-ting, SONG Zhen-lun. Corrosion behaviour of sintered NdFeB coated with Al/Al_2O_3 multilayers by magnetron sputtering [J]. Applied Surface Science, 2011, 257: 3980−3984.

[17] LIAO Guo, HE Zhi-bing, CHEN Tai-hong, XU Hua, LI Jun, CHEN Jia-jun. Effect of sputtering power on structure and properties of Bi film deposited by DC magnetron sputtering [J]. Atomic Energy Science and Technology, 2012, 46(6): 750−753. (in Chinese)

铝薄膜对烧结 NdFeB 磁体耐蚀性能的影响

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摘 要：采用直流磁控溅射的方法在烧结 NdFeB 磁体表面沉积 Al 薄膜提高磁体的耐蚀性能。研究膜厚及溅射功率对薄膜结构和耐蚀性能的影响。利用 SEM 对 Al 薄膜的微观结构进行分析，并采用动态极化曲线和中性盐雾实验分析 Al 薄膜耐蚀性能。均匀致密的 Al 薄膜的形成是获得良好耐蚀性能的必要条件。在 51~82 W 溅射功率下制备的 6.69 μm 的 Al 薄膜具有良好的耐蚀性能。

关键词：NdFeB；铝薄膜；磁控溅射；耐蚀性能；膜厚

(Edited by Chao WANG)