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ARTICLE

Fabrication and Properties of Micro-arc Oxidation Coatings on Sintered NdFeB Permanent Magnets

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Abstract: In order to improve the corrosion resistance of the sintered NdFeB permanent magnets, Al_2O_3 ceramic coatings were prepared by a two-step micro-arc oxidation process in an aluminate solution. During the micro-arc oxidation process, the voltage-time curve could be divided into four regions consistent with the valve metals. Results show that the coating exhibits a typical micro-arc oxidation porous surface with the thickness of ~5 μm, and is only composed of Al_2O_3 crystalline phase with some Fe elements and a few Nd and P elements. The surface roughness of coated NdFeB magnets is higher than that of uncoated sample, while the corrosion resistance is enhanced by one order of magnitude. Unfortunately, the magnetic properties (remanence and maximum energy product) of coated NdFeB sample decrease in different degrees.

Key words: sintered NdFeB; permanent magnet; micro-arc oxidation; corrosion resistance; magnetic property

The powder-sintered NdFeB permanent magnets have been widely applied in various emerging and conventional industries, such as wind power generators, energy-saved industrial motors, new energy vehicles, acoustics, microwave technology, medical apparatus, and airplane industries due to their outstanding magnetic properties[1-3]. However, the low corrosion resistance of NdFeB permanent magnets in high temperature and humid environments have severely restrained them from further applications and development[4,5]. Surface treatment/coating is a viable approach to improve the corrosion resistance of NdFeB magnets. Recently, many coating techniques have been employed to protect NdFeB magnets such as electrodepositing[6], magnetron sputtering[7], plasma immersion ion implantation and deposition (PIIID)[8] and electrophoretic deposition[9]. Micro-arc oxidation (MAO), also named as plasma electrolytic oxidation (PEO), is a high voltage plasma-assisted anodic oxidation process, widely employed for preparing ceramic coatings on Al, Mg, Ti and their alloys to improve the surface properties, such as micro-hardness, corrosion resistance, wear resistance, biocompatibility or other various functional properties[10]. With the development of the MAO technique, except valve metals, it has been applied in the modification of NiTi alloys[11] and carbon steels[12] non-valve metals. In this paper, the sintered NdFeB magnets were treated by micro-arc oxidation for the first time to prepare the ceramic coatings. At the same time, the surface and cross-section morphologies, phase and element composition, corrosion resistance of the coatings were investigated as well as the magnetic properties of the coated NdFeB magnets.

1 Experiment

Commercial sintered NdFeB permanent magnets (unmagnetized N35), supplied by Jiangxi JLMAG Rare-Earth Co., LTD, were cut into 13 mm×13 mm×3 mm as the substrate materials. The cut substrates were successively polished with

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SiC paper from 100# to 1500#, and then ultrasonically cleaned in acetone and distilled water. The polished samples were dipped into 5% nitric acid solution for approximately 40 s at room temperature, and rinsed with distilled water. The acid-washed sample (named as uncoated NdFeB magnet) was as an anode while the wall of the stainless steel container was used as the cathode. A 10 kW homemade pulsed bipolar power supply was employed to prepare MAO coatings on NdFeB magnets. An aqueous electrolyte was prepared from an aqueous solution of sodium aluminate and sodium hypophosphite with concentration of 0.15 mol/L and 0.01 mol/L, respectively. During the experiment process, the electrolyte solution was stirred and cooled below 35 ºC. The coated samples were flushed with water after the treatment and dried in air at room temperature.

The surface and cross-sectional morphologies of coated and uncoated NdFeB magnets were investigated by a field emission scanning electron microscopy (SEM, FEI Quanta 200) equipped with energy dispersive X-ray (EDS, INCA 6650). The phase composition of the coated samples was identified by X-ray diffraction (XRD, Bruker D8 Advance) and Grazing incidence XRD (Shimadzu 6100) with a glancing angle of 1º. The surface roughness R_a of the samples was tested by a surface roughmeter (SJ-301, Mitutoyo, Japan). The corrosion resistance of the coated and uncoated samples in 3.5% NaCl solution at room temperature was evaluated by potentiodynamic polarization test through CHI650D electrochemical analyzer. The polarization scan rate was controlled at 1 mV/s. The magnetic properties (remanence, intrinsic coercive force and maximum energy product) of the uncoated and coated NdFeB samples (Φ2 mm× 3 mm) were tested by physical properties measurements system (PPMS, Quantum Design) equipped with a 9 T vibrating sample magnetometer (VSM). Average values of magnetic properties were calculated from three samples.

2 Results and Discussion

A two-step process was employed during the MAO treatment. In the first step, a constant current density of 80A/dm^2 was applied until the anodic potential reached a preset value of 420 V. Then, in the second step, a constant voltage of 420 V was applied for 30 min. Fig.1 shows the typical voltage-time curve and current density-time curve during the MAO treatment process on NdFeB magnets. It can be seen that the current density reaches 80 A/dm^2 at 1.5 min holding for about 3.5 min, and the voltage reaches 420 V at 5 min. The voltage-time curve can be divided into four regions as follows: (1) the voltage exhibits a rapid and nearly linear increase with treatment time (0~1.5 min). At this stage, there mainly contain the metal dissolution and the electrolysis of water. For the valve metal, this stage represents the conventional anodization process; (2) the voltage exhibits a slow and non-linear increase with treatment time (1.5~4 min). At this stage, the metal dissolution and the electrolysis of water continue, while the barrier film is formed through the electrophoretic effect and deposition. Moreover, the deposition rate of the barrier film is faster than that of the metal dissolution rate; (3) the voltage exhibits a rapid and nearly linear increase with treatment time again (4~5 min). The dielectric breakdown of the barrier film occurs at this stage and the fine spark discharges can be observed on the surface of the NdFeB samples. This stage is also named as "spark discharge" and the breakdown voltage is about 226 V. (4) the voltage keeps 420 V, while the current density rapidly decreases first, and then nearly keeps a stable value of 7.8 A/dm^2 (5~35 min). At this stage, the discharge sparks grow in size with a change in their color from white to orange, and this stage is also termed as "micro-arc discharge".

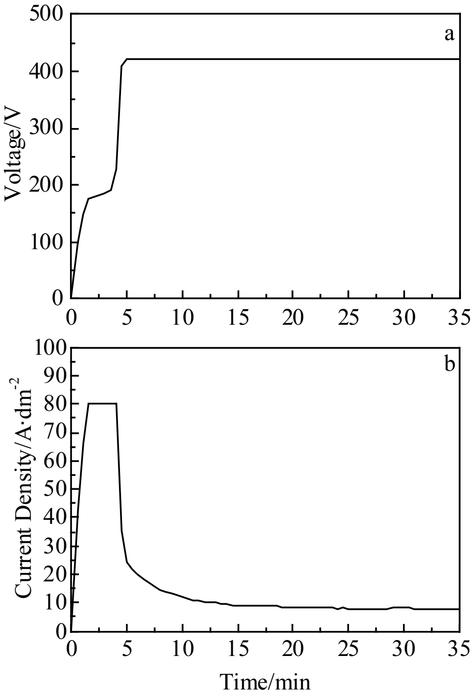

Fig.1 Typical voltage-time curve (a) and current density-time curve (b) during the MAO treatment process on NdFeB magnets

Fig.2 shows the surface morphology of the uncoated NdFeB magnet and the surface and cross-sectional morphologies of the coated NdFeB magnets as well as EDS spectrum. Many defects remained from powder sintering can be observed on the surface of the uncoated NdFeB magnet (Fig.2a). Those defects are covered completely by the MAO coating, and many crater-like pores are uniformly distributed over the surface of MAO coating, which is the typical MAO coatings porous structure formed when the molten oxide and gas bubbles (O_2) are thrown out of micro-arc discharge channels[13]. The diameter of the pores ranges from 0.5 μm to 2.5 μm with the average of 1.5 ± 0.6 μm. No micro-cracks can be observed over the whole surface, which is beneficial to

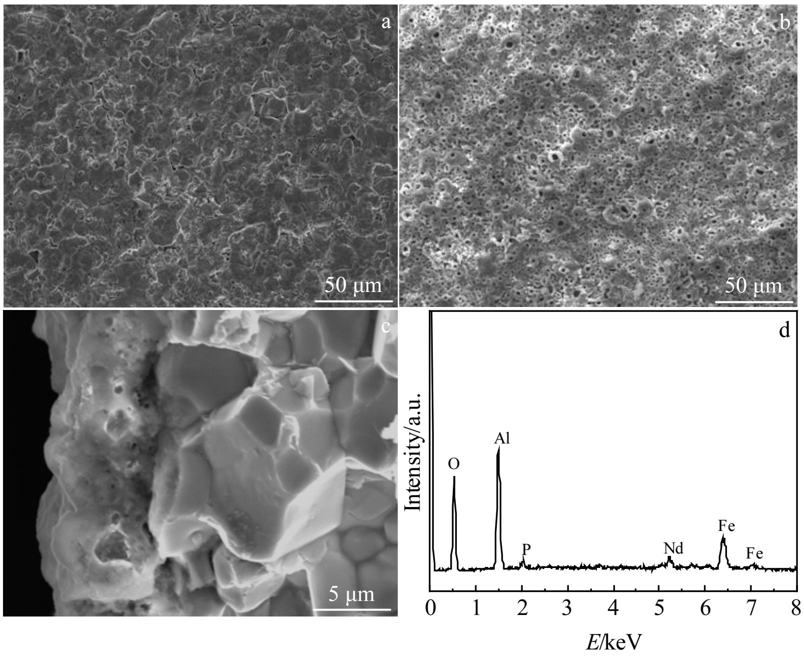

Fig.2 Surface morphologies of the uncoated (a) and coated (b) NdFeB; cross-sectional morphology (c) of the coated NdFeB, and (d) EDS spectrum of the coated NdFeB magnets

improve the corrosion resistance. The surface roughness of the coated NdFeB magnets is 1.32±0.04 μm, higher than that of the uncoated NdFeB magnets of 0.95±0.03 μm. It can be seen from Fig.1c that the coating has a thickness of ~5 μm and there are no apparent defects or cracks throughout the cross-section of the coating as well as no distinct discontinuity between the coating and the substrate, which indicates that the coating can be tightly adhered to the substrate. The EDS result reveals that the MAO coating mainly consists of O, Al, Fe, Nd and P, with the atomic concentration of 62.52%, 23.29%, 10.91%, 1.92% and 1.35%, respectively. The concentration of Fe and Nd from substrate in the coating is greatly lower than that of Al from the electrolyte, indicating that the components of NdFeB substrate do not directly participate in the formation of coating. Furthermore, the Fe concentration is high up to 10.91%, which is not beneficial to the corrosion resistance of the MAO coating.

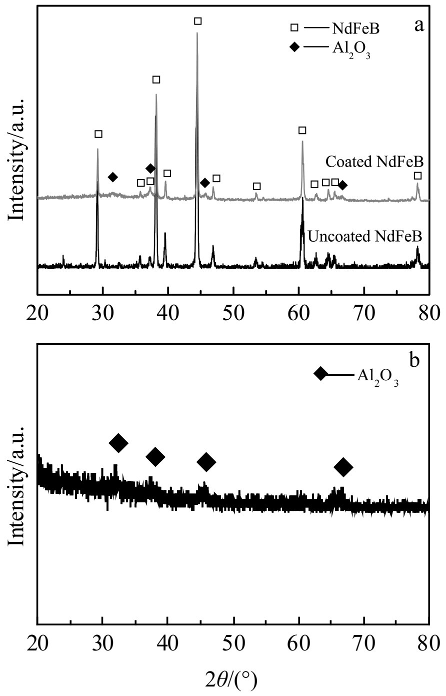

Fig.3 XRD (a) and TF-XRD (b) patterns of the coated NdFeB samples

Fig.3 shows the XRD and TF-XRD patterns of the coated and uncoated NdFeB samples. Besides the peaks of NdFeB substrate, three new peaks can be clearly observed at 31.7°, 45.7° and 66.7° corresponding to the (220), (400) and (440) plane of the Al_2O_3 crystal phase, respectively, which indicates that the MAO coating prepared on the NdFeB is mainly composed of Al_2O_3 phase. The consistent result is obtained from the TF-XRD pattern (Fig.3b). No Fe oxide or compound can be detected by XRD or TF-XRD, indicating that the Fe element may be in the form of amorphous state. This result is highly consistent with Ref. [11]. During the MAO process, a large number of aluminates ions (in the form of $Al(OH)_4^-$) present near the anodic electrode surface and then arrested into the micro-arc area due to the effect of the electric field, which leads to the formation of the Al_2O_3 in the coating according to the following reaction:

$$2\mathrm{Al(OH)}^{4-}\rightarrow \mathrm{Al_2O_3}+2\mathrm{OH}^{-}+3\mathrm{H_2O} \qquad (1)$$

The Al_2O_3 coating is calcined by micro-arc time after time, which results in the formation of the crystallized Al_2O_3. Moreover, the formation mechanism of the Al_2O_3 MAO coating on the NdFeB will be discussed detailedly in the future.

Fig.4 shows the potentiodynamic polarization curves of the uncoated and coated NdFeB samples in 3.5% NaCl, and the results of the potentiodynamic corrosion test of NdFeB samples are shown in Table 1. A shift of the whole polarization curve towards the region of lower current density and the higher potential can be obviously observed after NdFeB sample treated by MAO. The values of corrosion potential and corrosion current density are −0.833 V and 2.17×10^{-6} A/cm^2 for the coated NdFeB sample, and −1.112 V and 3.79×10^{-5} A/cm^2 for the uncoated sample, respectively. The corrosion potential of the coated sample is shifted in the noble direction by 279 mV relative to the uncoated sample, and the corrosion current density of the coated sample is one order of magnitude lower than that of the uncoated sample. The corrosion protection efficiency is calculated using the following equation[14]:

$$P=(1-i_{\mathrm{corr}}/i^{0}_{\mathrm{corr}})\times100\% \qquad (1)$$

where P is the corrosion protection efficiency of the coating, i_{corr} and i^{0}_{corr} are the corrosion current density of the coated sample and the uncoated sample, respectively. According to the calculation of Eq.(1), the P value of the coating is up to 94.3%. Therefore, it can be concluded that the corrosion resistance of sintered NdFeB sample is significantly improved due to the existence of the MAO coating.

The protective coatings could effectively improve the corrosion resistance of the NdFeB magnets, but some coatings deteriorated the magnetic properties, such as a loss of coercivity by 24% and of remanence by 16% due to the existence of the Ni-P coatings[15] and the decrease of remanence by 3.9% and the decrease of maximum energy product by 3.7% due to the existence of the Al films[16]. Therefore, it is necessary to investigate the effect of the MAO coating on the magnetic properties of NdFeB magnets. The hysteresis curves of the coated and uncoated NdFeB samples are shown in Fig.5 and the results of magnetic properties are shown in Table 2. It can be seen from Fig.5 that there is no obvious change in the intrinsic coercive force (H_{cj}), while both of the remanence (B_{r}) and maximum energy product ($(BH)_{\mathrm{max}}$) of the coated NdFeB samples decrease compared to that of uncoated NdFeB sample. After micro-arc oxidation treatment, the intrinsic coercive force of the coated NdFeB magnet increases by 0.44%, while the remanence decreases by 8.89% and the maximum energy product decreases by 19.5%. It is well known that the alumina is a non-magnetic material. Therefore, the decrease of magnetic properties of coated NdFeB sample might be related with the existence of a large number of Fe element (10.91%) on the coating, which plays a shielding effect on the magnetic properties. Moreover, the existence of Fe also exerts a negative effect on the corrosion resistance of coated NdFeB. Therefore, reducing and eliminating the Fe concentration in the MAO coating is an important research aspect in the future.

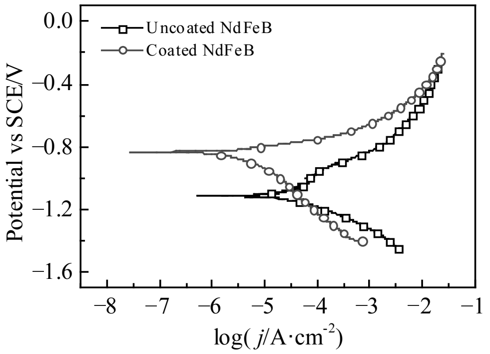

Fig.4 Potentiodynamic polarization curves of the uncoated and coated NdFeB samples in 3.5 % NaCl solution

Table 1 Sesults of the potentiodynamic corrosion test

Sample	E_{corr}/V	j_{corr}/A·cm^{-2}	P/%
Uncoated NdFeB	−1.112	3.79×10^{-5}	-
Coated NdFeB	−0.833	2.17×10^{-6}	94.3

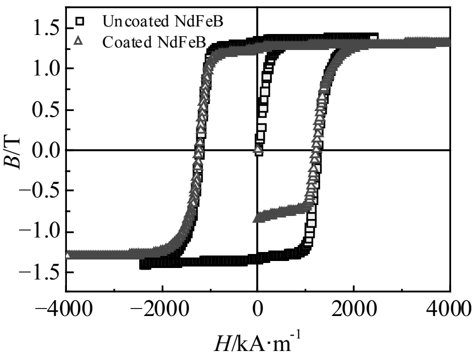

Fig.5 Hysteresis curves of the coated and uncoated NdFeB samples

Table 2 Magnetic properties of coated and uncoated NdFeB samples

Samples	B_{r}/T	H_{cj}/kA·m^{-1}	$(BH)_{\mathrm{max}}$/kJ·m^{-3}
Uncoated NdFeB	1.35 ± 0.02	1230.5 ± 0.7	342.3 ± 9.2
Coated NdFeB	1.23 ± 0.01	1236.0 ± 1.4	274.5 ± 9.9
Variation/%	−8.89	0.44	−19.5

3 Conclusions

1) Micro-arc oxidation coatings are fabricated on sintered NdFeB permanent magnets through a two-step process.

2) The coating consists of Al_2O_3 crystalline phase with 10.91% Fe element and a few Nd and P elements.

3) The coating exhibits a typical crater-like micro-arc oxidation porous surface with the thickness of ~5 μm. After treated by MAO, the surface roughness of NdFeB magnet increases, while the corrosion resistance is greatly improved and the corrosion protection efficiency of the coating is up to 94.3%. However, the remanence decreases by 8.89% and the maximum energy product decreases by 19.5% due to the existence of the MAO coating.

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烧结 NdFeB 永磁体表面微弧氧化涂层的制备及性能

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摘 要：为了提高烧结 NdFeB 永磁体的耐蚀性，在铝酸盐溶液中采用二步微弧氧化工艺在烧结 NdFeB 永磁体表面制备了氧化铝陶瓷涂层。微弧氧化过程中，电压-时间曲线可大致分为 4 个阶段，与阀金属处理的曲线基本一致。烧结 NdFeB 表面制备的涂层呈现出典型的微弧氧化多孔形貌，厚度大约为 5 μm。涂层中仅含有 Al_2O_3 结晶相，并含有少量的 Fe、Nd 和 P 元素。微弧氧化处理后，烧结 NdFeB 的表面粗糙度有所增加，耐蚀性较基体提高了 1 个数量级。然而，微弧氧化处理后烧结 NdFeB 磁体的剩磁和最大磁能积较未处理 NdFeB 有所下降。

关键词：烧结 NdFeB；永磁体；微弧氧化；耐蚀性；磁性能

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