Journal of Magnetism and Magnetic Materials 375 (2015) 124–128

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Corrosion resistance of the NdFeB coated with AlN/SiC bilayer thin films by magnetron sputtering under different environments

Lei Tao [a], Heqin Li [a,*], Jiong Shen [b], Kai Qiao [a], Wei Wang [a], Chu Zhou [a], Jing Zhang [a,c], Qiong Tang [a,c]

[a] School of Materials Science and Engineering, Hefei University of Technology, Anhui Hefei 230009, China
[b] Earth-Panda Advance Magnetic Material Co., Ltd., Anhui Lujiang 231500, China
[c] School of Electronic Science and Applied Physics, Hefei University of Technology, Anhui Hefei 230009, China

ARTICLE INFO

Article history:
Received 13 June 2014
Received in revised form
16 September 2014
Accepted 3 October 2014
Available online 11 October 2014

Keywords:
NdFeB
AlN/SiC bilayer films
RF magnetron sputtering
Corrosion resistance
Potentiodynamic polarization

ABSTRACT

The AlN/SiC bilayer and SiC monolayer thin films were deposited on sintered NdFeB by RF magnetron sputtering to improve the corrosion resistance. Their structures and morphologies were studied by XRD and AFM and SEM. The corrosion behaviors of AlN/SiC and SiC-coated NdFeB in 3.5 wt% NaCl, 20 wt% NaOH and 0.1 mol/L H_2SO_4 solutions were characterized with potentiodynamic polarization curves. The results show that AlN/SiC and SiC thin films can evidently improve the corrosion resistance of NdFeB, and the AlN/SiC films have the better resistance than the SiC film.

1. Introduction

NdFeB permanent magnets have the outstanding magnetic properties and have been widely used in voice coil motors, hard disk drives, medical instruments, automotive applications, industrial motors and generators, etc. However, the poor corrosion resistance prevents its further developments [1–4]. There are $Nd_2Fe_{14}B$ main phase, Nd-rich phase and B-rich phases in NdFeB magnets. The Nd-rich phase distributed on the grain boundaries of $Nd_2Fe_{14}B$ is the most active and the B-rich phase comes second. The Nd-rich and B-rich phases are easy to be corroded under corrosion media, which will result NdFeB magnets into powder-like, non-usable product [5,6]. Many efforts have been made to improve the corrosion resistance of the NdFeB, including adding alloy elements [7] and preparing protective coatings [8,9]. The alloying elements can improve the intrinsic corrosion resistance of NdFeB at the expense of magnetic properties, whereas the surface coating can improve the corrosion resistance of NdFeB and does not damage its magnetic properties obviously [10,11]. The electroplating is widely used for the NdFeB protective coatings in industry, however, there is the environmental pollution and the magnetic damage of the NdFeB. Magnetic sputtering coating technique is the low temperature and friendly environment, so it can replace the electroplating for preparing NdFeB protective coating. Al, Ti/Al and Ni/Al coatings have been deposited on NdFeB by thermal evaporation [12,13], however, it has not been reported that AlN/SiC bilayer films are prepared on NdFeB by magnetron sputtering. AlN has the excellent mechanical properties and thermostability, and its lattice constant and thermal expansion coefficient are between the NdFeB and SiC, so it can improve the

Table 1
NdFeB magnet composition.

NdFeB (48 M)	Pr,Nd	B	Dy	Fe	Others
wt%	29.0–30.0	1.0–1.1	1.5–2.0	65–66	0.5–3.0

Table 2
The preparing parameters of AlN/SiC bilayer thin films.

Film	Parameters			
	Working pressure (Pa)	RF power (W)	N_2/Ar (sccm)	Depositing time (min)
SiC	0.5	150	0:60	90
AlN	0.5	100	10:20	60

* Corresponding author.
E-mail address: lhqjs@hfut.edu.cn (H. Li).

http://dx.doi.org/10.1016/j.jmmm.2014.10.012
0304-8853/

adhesion strength between the SiC film and the NdFeB substrate. SiC can prevent the radiation and high temperature oxidation, at the same time, it has wear-resistance, corrosion resistance and

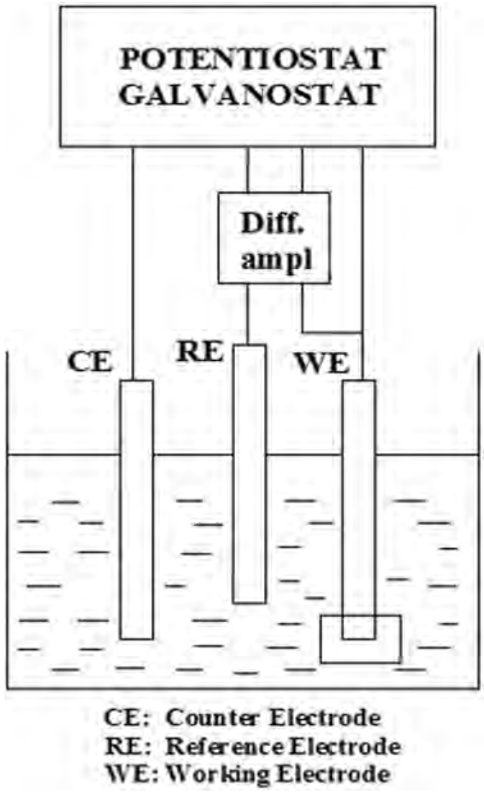

Fig. 1. The schematic diagram of three electrode cell testing system.

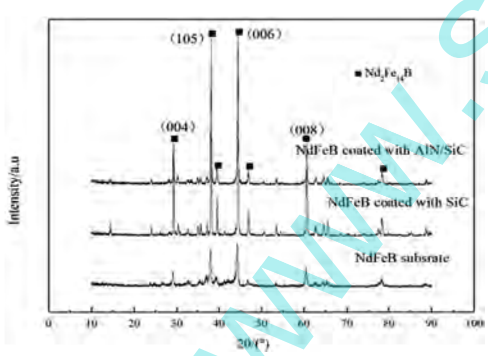

Fig. 2. XRD patterns of NdFeB substrate and SiC and AlN/SiC-coated NdFeB.

optoelectronic properties [14,15]. The AlN/SiC-coated NdFeB is a promising way to improve the corrosion resistance.

In this report, the AlN/SiC bilayer thin films were deposited on sintered NdFeB by radio frequency (RF) magnetron sputtering. The structures, morphologies and corrosion resistances of AlN/SiC and SiC-coated NdFeB are investigated.

2. Experimental details

The SiC and AlN thin films were sputtered on sintered NdFeB commercial substrates ($10.5 \times 6.5 \times 1.2$ mm^3) with a FJL560B1 Ultra-High Vacuum Magnetron and an Ion Beam Sputtering Equipment. The NdFeB compositions are in Table 1, and these substrates were successively grinded with SiC abrasive paper from 400# to 800# and polished, then cleaned in acetone and alcohol about 10 min, finally blew-dry. The sintered SiC (purity 99.5%) and metal Al (purity 99.99%) targets were used. The original vacuum was 1.0×10^{-4} Pa and high purity Ar and N_2 were entered. SiC film was sputtered under Ar gas of 0.5 Pa for 90 min and the AlN film was sputtered under Ar and N_2 mixed gases of 0.5 Pa for 60 min at room temperature. The preparing process parameters of the thin films are listed in Table 2.

The thickness, crystal structure, surface and cross-sectional morphologies of the AlN/SiC thin films were measured with a Step Apparatus (XP-1), X-ray diffraction (CuKα1, λ=0.15406 nm) (Rigaku18kW D/Max 2500 V), an atomic force microscope (AFM, CSPM5500A) and a scanning electron microscope (SEM, SU8020). The magnetic properties of NdFeB coated with AlN/SiC (remanence, coercivity and maximum energy product) were measured by a ultra-high coercivity permanent magnet pulse tester (PFM12).

The electrochemical corrosion behaviors of the specimens in 3.5 wt% NaCl, 20 wt% NaOH and 0.1 mol/L H_2SO_4 solutions were evaluated by potentiodynamic polarization test with a CHI650D electrochemical analyzer (Shanghai Chenhua, China) at 25 °C. A three-electrode cell testing system was showed in Fig. 1. Ag/AgCl was a reference electrode (RE), a platinum sheet was a counter electrode (CE) and the specimen was the working electrode (WE). The exposed surface area of the working electrode was 0.67 cm^2 and all electrodes were kept in solutions for 1 h to stabilize the stationary potential. Polarization curves were measured at a

Table 3
The AFM data of SiC and SiC/AlN thin films coated on NdFeB.

Specimen	The average grain diameter (nm)	The average roughness (nm)
NdFeB/SiC	212	6.17
NdFeB/AlN/SiC	181	3.07

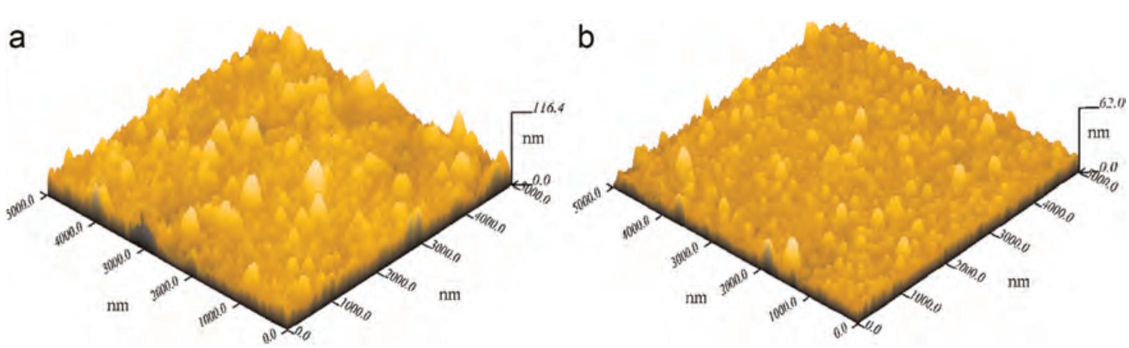

Fig. 3. The surface morphologies of SiC and AlN/SiC thin films coated on NdFeB. (a) SiC monolayer film and (b) AlN/SiC bilayer films.

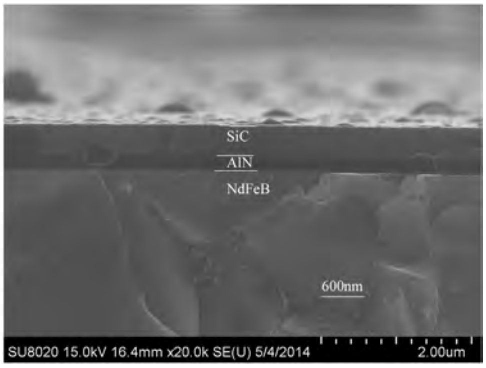

Fig. 4. The cross-sectional morphology of the AlN/SiC bilayer films coated on NdFeB.

Table 4
The magnetic properties of different specimens.

Specimens	Magnetic properties		
	Remanence, B_r /kG	Coercive force, H_{cj}/kOe	Maximum energy product, $(BH)_{max}$/MGOe
NdFeB	13.14	14.96	39.95
NdFeB/SiC	13.27	13.25	39.31
NdFeB/AlN/SiC	13.30	13.28	39.40

scanning rate of 0.01 V/s with the applied potential varied from −1.4 V to −0.2 V.

3. Results and discussion

Fig. 2 shows the XRD patterns of the NdFeB substrate, AlN/SiC and SiC-coated NdFeB. There are four $Nd_2Fe_{14}B$ main diffraction peaks at 29.2°, 38.2°, 44.2°, 60.6°, corresponding to its (004), (105), (006), (008) crystal planes respectively and no diffraction peaks of AlN and SiC exist. This means deposited AlN/SiC and SiC thin films are amorphous. In addition, there are some extra small peaks of $Nd_2Fe_{14}B$ and the intensity of main diffraction peaks strengthens after depositing. The sputtering particles bombard the NdFeB substrate during depositing thin film, which will provide the extra crystallizing energy for $Nd_2Fe_{14}B$. The AlN/SiC and SiC coated NdFeB has better crystallinity relative to the NdFeB substrate.

Fig. 3 shows the surface images of SiC and AlN/SiC thin films with AFM (scanning range is $5000 \times 5000\ nm^2$). Table 3 shows their average grain diameter and roughness. The average grain diameters of SiC and AlN/SiC thin films are 212 nm and 181 nm respectively, and corresponding average roughness are 6.17 nm and 3.07 nm. The grains of the AlN/SiC bilayer films become smaller and the surface roughness decreases, so this means the AlN buffer layer acts on the smoothing the surface of the SiC thin film.

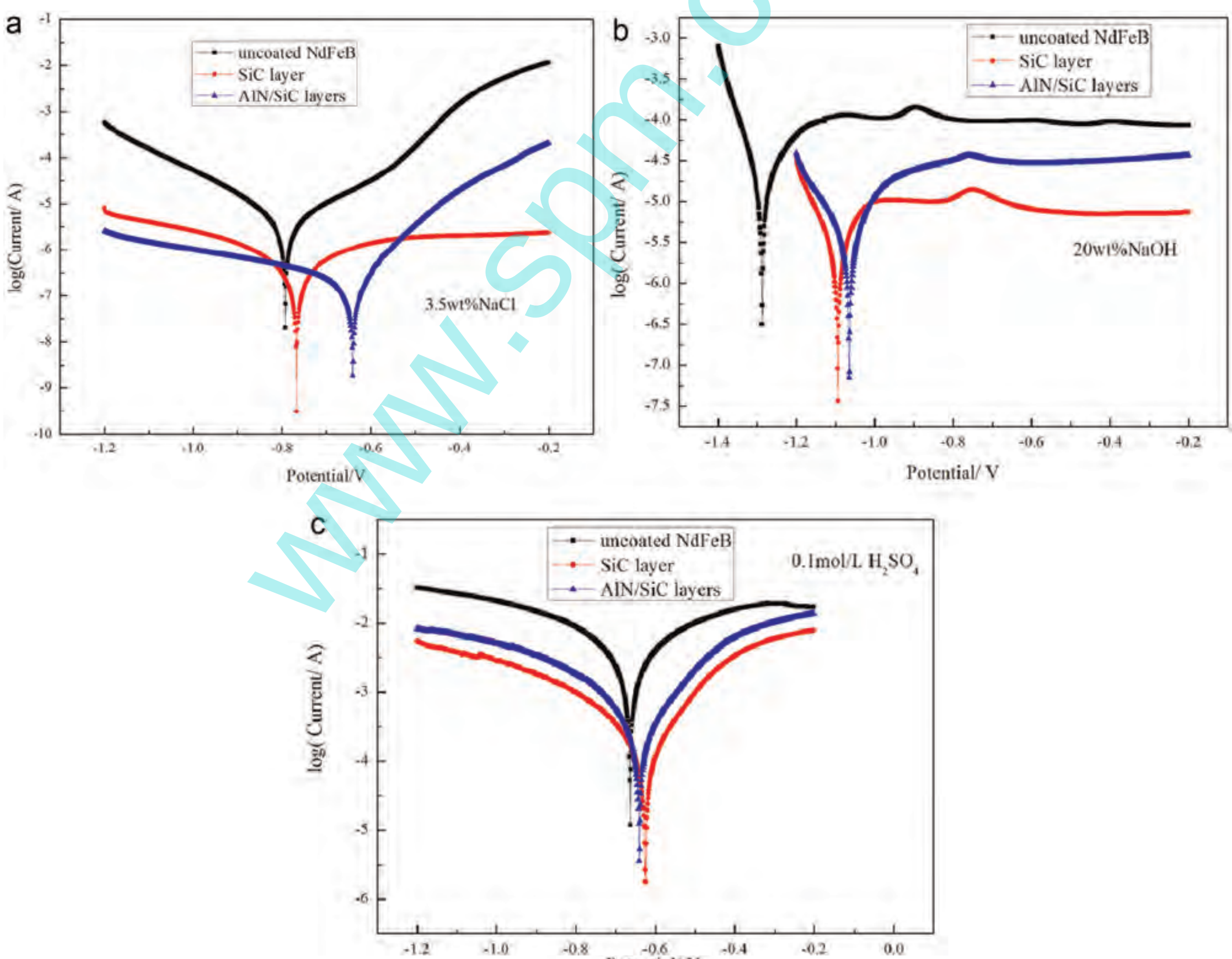

Fig. 5. Potentiodynamic polarization curves of the NdFeB substrate and SiC and AlN/SiC-coated NdFeB in (a) 3.5 wt% NaCl, (b) 20 wt% NaOH and (c) 0.1 mol/L H_2SO_4 solutions (E_{corr}/V, I_{corr} /(A cm^{-2})).

Table 5
Polarization data of SiC and AlN/SiC-coated NdFeB.

Solutions	Specimens					
	Bare NdFeB		NdFeB/SiC		NdFeB/AlN/SiC	
	E_{corr}	I_{corr}	E_{corr}	I_{corr}	E_{corr}	I_{corr}
NaCl	−0.784	2.22×10^{-6}	−0.780	1.61×10^{-7}	−0.642	8.61×10^{-8}
NaOH	−1.286	2.26×10^{-6}	−1.093	2.80×10^{-7}	−1.065	5.54×10^{-8}
H_2SO_4	−0.692	2.68×10^{-3}	−0.671	3.0×10^{-4}	−0.646	6.78×10^{-5}

Table 6
The comparison of SiC,AlN and NdFeB.

Material	Coefficient of heat expansion ($10^{-6}\,K^{-1}$)	Lattice parameter (nm)
NdFeB	3.4	0.882
AlN	4.5	0.438
SiC	4.6	0.436

Fig. 4 shows the cross-sectional morphology of the AlN/SiC bilayer films coated on NdFeB. There are NdFeB, AlN and SiC three zones from bottom to top. The thickness of AlN film is 200 nm and that of SiC film is 410 nm.

Table 4 shows the remanence (B_r), the intrinsic coercivity (H_{cj}) and the maximum energy product ($(BH)_{max}$) of SiC and AlN/SiC-coated NdFeB. They decrease slightly compare with the NdFeB substrate. The deterioration of the magnetic properties may be ascribed to two reasons. Firstly there is an internal stress in the SiC thin film, however the additional AlN thin film acted on the buffer layer can decrease the stress, so the magnetic property of AlN/SiC-coated NdFeB is better than SiC-coated one. Secondly, the NdFeB substrate has to be grinded and polished before depositing thin film, so the thickness of the magnetic materials reduces and this may bring the measurement error of magnetic property after depositing thin film.

Fig. 5 shows the potentiodynamic polarization curves for NdFeB substrate, SiC and AlN/SiC-coated NdFeB in 3.5 wt% NaCl, 20 wt% NaOH and 0.1 mol/L H_2SO_4 solutions. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) calculated from the polarization curves using Tafel extrapolation are listed in Table 5. A shift of the whole polarization curves towards the region of lower current density and the higher potential indicates the obvious improvements of the corrosion resistances of the coated NdFeB. The values of corrosion current density and corrosion potential of the NdFeB substrate are 2.22×10^{-6} A cm^{-2} and −0.784 V. After coating SiC and AlN/SiC films, the I_{corr} and E_{corr} of NdFeB are 1.61×10^{-7} A cm^{-2}, −0.780 V and 8.61×10^{-8} A cm^{-2}, −0.642 V respectively in 3.5 wt% NaCl solution. This means that coated NdFeB show better corrosion resistance. Moreover, the corrosion resistance of AlN/SiC coating is better than that of SiC one. It is similar in 20 wt% NaOH and 0.1 mol/L H_2SO_4 solutions. Finally, the corrosion resistance of NdFeB is the worst in the 0.1 mol/L H_2SO_4 solution.

As there are many micropores on NdFeB substrate, SiC thin film can effectively fill these micropores and prevent the etching solution into the substrate. The thickness of SiC and AlN films is 410 nm and 200 nm respectively. The corrosion resistance of the AlN/SiC bilayer films are superior to that of the SiC monolayer film, because the additional AlN buffer layer can improve effectively the surface toughness of the SiC thin film, and the smooth surface can decreases the electrochemistry corrosion. Moreover, there are the mismatches of the coefficient of heat expansion and lattice parameters between SiC film and the NdFeB substrate according to Table 6, and the AlN thin film can decrease the thermal stress and increase the adhesion strength of the film with the substrate.

4. Conclusions

SiC and AlN/SiC thin films coated on NdFeB are amorphous. The magnetic properties of NdFeB coated with SiC and AlN/SiC decrease slightly compare with the NdFeB substrate. The grains of the AlN/SiC bilayer films are finer and the surface roughness is lower than that of SiC monolayer film. The I_{corr} and E_{corr} of NdFeB substrate are 2.22×10^{-6} A cm^{-2} and −0.784 V, however, the I_{corr} and E_{corr} of SiC and AlN/SiC-coated NdFeB are 1.61×10^{-7} A cm^{-2}, −0.780 V and 8.61×10^{-8} A cm^{-2}, −0.642 V respectively in 3.5 wt% NaCl solution after depositing. The corrosion resistance of NdFeB coated with AlN/SiC is better than that coated with SiC and it is the worst in the 0.1 mol/L H_2SO_4 solution.

Acknowledgments

The authors would like to thank the support of Earth-Panda Advance Magnetic Material Co., Ltd. Foundation (Grant no.13-332) and Anhui University Natural Science Foundation of China (Grant no. KJ2012A228).

References

[1] Jinlong Li, Shoudong Mao, Kefei Sun, et al., AlN/Al dual protective coatings on NdFeB by DC magnetron sputtering, J. Magn. Magn. Mater. 321 (2009) 3799–3803.
[2] G.P. Wang, W.Q. Liu, Y.L. Huang, et al., Efects of sintering temperature on the mechanical properties of sintered NdFeB permanent magnets prepared by spark plasma sintering, J. Magn. Magn. Mater. 349 (2014) 1–4.
[3] I. Gurappa, Corrosion characteristics of permanent magnets in acidic environments, J. Alloys Compd. 360 (2003) 236–242.
[4] M. Yan, H.G. Ying, T.Y. Ma, Preparation of coatings with high adhesion strength and high corrosion resistance on sintered Nd–Fe–B magnets through electroless plating, Mater. Chem. Phys. 113 (2009) 764–767.
[5] Mingxiang Pan, Pengyue Zhang, et al., First-order-reversal-curve analysis of exchange-coupled Sm/Co/NdFeB nanocomposite alloys, J. Magn. Magn. Mater. 361 (2014) 219–223.
[6] Yuanyuan Cheng, Xiaolu Pang, Kewei Gao, et al., Corrosion resistance and friction of sintered NdFeB coated with Ti/TiN multilayers, Thin Solid Films 550 (2014) 428–434.
[7] J.L. Xu, Z.X. Huang, J.M. LuO, et al., Effect of titania particles on the microstructure and properties of the epoxy resin coatings on sintered NdFeB permanent magnets, J. Magn. Magn. Mater. 355 (2014) 31–36.
[8] W. He, L. Zhu, H. Chen, H. Nan, W. Li, H. Liu, Y. Wang, Electrophoretic deposition of graphene oxide as a corrosion inhibitor for sintered NdFeB, J. Appl. Surf. Sci. 279 (2013) 416–423.
[9] J. Chen, B.J. Xu, G.P. Ling, Amorphous Al–Mn coating on magnet: electrodeposition from AlCl3–EMIC–MnCl2 ionic liquid and its corrosion behavior, Mater. Chem. Phys. 134 (2012) 1067–1071.
[10] W. Wongsarat, S. Sarapiron, et al., Plasma immersion ion implantation and deposition of DLC coating for modification of orthodontic magnets, J. Nucl. Instrum. Methods Phys. Res. B 272 (2012) 346–350.

[11] Tingting Xie, Shoudong Mao, et al., Structure, corrosion, and hardness properties of Ti/Al multilayers coated on NdFeB by magnetron sputtering, Vacuum 86 (10) (2012) 1583–1588.
[12] A. Ali, A. Ahmad, K.M. Deen, Multilayer ceramic coating for impeding corrosion of sintered NdFeB magnets, J. Rare Earths 27 (6) (2009) 1003–1007.
[13] H. Yang, S. Mao, Z. Song, The effect of absorbed hydrogen on the corrosion behavior of sintered NdFeB magnet, Mater. Corros. 63 (4) (2011) 292–296.
[14] Hui Li, Heqin Li, Renjie Hu, et al., High-temperature oxidation resistance of SiC thin films deposited by magnetron sputtering, J. Trans. Mater. Heat Treatm. 34 (Suppl.) (2013) S135–S138.
[15] Shangsheng Xie, Huan He, Yuechun Fu, Development of structural characterization and properties of AlN film prepared by pulsed laser deposition, J. Mater. Rev. 24 (6) (2010) 45–49.