18th IFHTSE CONGRESS
International Federation for Heat Treatment and Surface Engineering
ANAIS
PROCEEDINGS
ISSN 1516-392X

EFFECT OF ALUMINUM COATING BY MAGNETRON SPUTTERING ON CORROSION RESISTANCE OF MAGNESIUM ALLOYS[1]

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Abstract

In this study, aluminum coatings were prepared by DC magnetron sputtering on AZ31B magnesium alloys. The influence of sputtering parameters (include sputtering current, argon pressure and deposition time) on corrosion behavior was investigated by potentiodynamic polarization tests in 3.5% NaCl solutions. The corrosion morphology was examined in detail by scanning electron microscopy (SEM) and macroscopic, respectively. It was found that the corrosion current density of magnesium alloys with aluminum coating on it was 2~3 orders of magnitude less than that of bare alloys. The corrosion potential with aluminum coating had been positive shift. The corrosion resistant properties of coatings were strongly affected by its structure and residual stress, which depended on the process condition. The severe corrosion will occur after aluminum coating damaged due to the interaction of galvanic corrosion and other corrosion form.

Key words: Magnesium alloys; Magnetron sputtering; Aluminum coating; Corrosion resistance.

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[1] *18th IFHTSE Congress - International Federation for Heat Treatment and Surface Engineering, 2010 July 26-30th, Rio de Janeiro, RJ, Brazil.*

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1 INTRODUCTION

As the lightest of structural metals, magnesium alloy has an excellent processing performance, good biocompatibility, high thermal conductivity, high dimensional stability, high damping and good electromagnetic shielding characteristics. These properties make it valuable applied in many fields such as aerospace, automotive, electronics, telecommunications and even used as an implant metal. However, poor corrosion resistance limited its widespread use in many applications.[1] In addition, magnesium cannot form a self-healing passive surface contrast to aluminum and titanium because there is a misfit between the hydroxide lattice in the surface region and the lattice of the bulk material. Therefore, the magnesium hydroxide film is loose and the layer is undermined by corrosion process.[2] In order to improve the corrosion resistance of magnesium alloys, proper surface treatments to produce anti-corrosion protection coatings on the substrate become essential. New technology such as plasma electrolytic oxidation (PEO), metal coating (e.g. aluminum), physical vapor deposition (PVD) and ion implantation, become the focal point of worldwide attention in recent years.

Because of aluminum and its alloy has the ability of self-repair to corrosion and, Al element is one of the main compositions of Mg alloys, aluminum coating is designed to protect magnesium alloy from corrosion resistance. Aluminum coating has been given more concerns and studied in the past years. There are many ways to prepare Al coating such as thermal spray,[3-5] physical vapor deposition (PVD),[6-8] chemical vapor deposition (CVD),[9] electrodeposition[10,11] and laser cladding.[12] Wuet al. [6] prepared pure Al and Ni thin films successfully by r.f.-sputtered on AZ91D substrate. After 350 °C×24 h heat treatment in high vacuum, the 2 μm thickness of the Al film reacted completely with the substrate to form $Mg_{17}Al_{12}$ phase. Although Al film is dense, the intrinsic brittleness of $Al_{12}Mg_{17}$ phase has a low cohesive strength with the substrate and thus will influence the corrosion resistance. Wu[7,13] developed Al coating, aluminum/titanium multilayer coating and Ti-Al-N/Ti-Al duplex coating on AZ31 alloy by Multi-magnetron sputtering, most of these coatings could improve the corrosion resistance of magnesium alloy to some extent.

In the present work, aluminum coatings were prepared by magnetron sputtering on AZ31B magnesium alloys. The influence of sputtering parameters (include sputtering current, argon pressure and deposition time) on corrosion behavior were investigated by potentiodynamic polarization tests.

2 MATERIALS AND METHODS

2.1 Substrate Material

The rolled AZ31B magnesium alloys substrates (25 mm×25 mm × 1 mm) were used in this study. Composition of AZ31B substrates was 2.5~3.5 Al, 0.20~1.0 Mn, 0.6~1.4 Zn, ≤0.04 Cu, ≤0.10 Si, ≤0.005 Ni, ≤0.005 Fe and balance Mg. The substrates firstly rinsed in 192g/l CH_3COOH+50g/l $NaNO_3$ solution for eliminating the surface oxides and secondly polished up to 1000# SiC paper. Then, they were cleaned in acetone for 10 min and in ethanol 10 min by ultrasonic cleaning.

2.2 Deposition Process

Aluminum coatings were deposited by D.C. (direct current) magnetron sputtering. The deposition chamber was equipped with a magnetron source (FJL560A ultra-high vacuum system) with an Al (99.99%) target placed at a distance of 60 mm from the substrate. Argon ion cleaning before deposition was carried out to avoid contamination and improve adhesion. The deposition process was performed at room temperature without any heating to substrate additionally. The base pressure in the system prior to sputtering was 4.0×10^{-4} Pa.

The sputtering current, argon pressure and deposition time of the sputtering system were chosen as the main process parameters and the Al coatings were deposited by varying these parameters. The deposition experiments include three parts. The first four runs were performed at different sputtering current of: 0.82 A (D1), 0.92 A (D2), 1.22 A (D3) and 1.62 A (D4). The other process parameters were kept constant for these four experiments: 0.5 Pa of argon pressure and 150 min of deposition time; The second five runs were performed at different argon pressures of: 0.3 Pa (Q1), 0.4 Pa (Q2), 0.5 Pa (Q3), 0.7 Pa (Q4) and 0.9 Pa (Q5). The other process parameters were kept constant for these five experiments: 1.02 A of sputtering current and 150 min of deposition time; The third three runs were performed at different deposition time of: 120 min (S1), 300 min (S2) and 330 min (S3). The other process parameters were kept constant for these five experiments: 1.02 A of sputtering current and 150 min of deposition time.

2.3 Corrosion Measurements and Coating Characterization

Corrosion studies were made in 3.5% NaCl solution using a potentiodynamic polarization unit (M273, EG&G) consisting of three electrodes. One of the electrodes (areas 2.84 cm^2) served as the working electrode and a platinum electrode served as the counter electrode, which was kept parallel to the working electrode. A saturated calomel electrode (SCE) with a capillary acted as the reference electrode. This electrode was kept near the surface of the working electrode and measured the potential of the working electrode.

The samples were masked leaving only 2.84 cm^2 area exposed. The samples were immersed in the solution for approximately half hour so that a steady state equilibrium potential, known as the open circuit potential (OCP), was attained. The polarization of the samples was carried out, first cathodically and then anodically at 1 mV/s at room temperature. Current and potential were recorded simultaneously. Tafel plots were made from the data. The corrosion current density (I_{corr}) and corrosion potential relative to SCE (E_{corr}) were determined by extrapolating the straight-line section of the anodic and cathodic Tafel lines. The specimen was taken out and ultrasonically washed in pure alcohol after corrosion test. Then, its surface morphology was observed in scanning electron microscopy (SEM, JSM-6460LV) operating at 20kV and macroscopic, respectively.

3 RESULTS AND DISCUSSION

3.1 Corrosion Behavior in 3.5% NaCl Solution

The potentiodynamic polarization curves obtained for Al coating samples under different deposition parameters in 3.5% NaCl solution are shown in Figure 1. The polarisation behavior of the bare AZ31B magnesium alloy is also depicted in Figure 1, and it had registered a corrosion potential of -1.527 mV vs. SCE, and corrosion current density of 89.1 μA /cm^{-2}. Moreover, the passive-like behavior was observed after coated aluminum during the anodic polarization. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) derived from these curves and resulting data are summarized in Table 1. According to the results of Table 2, the effect of different processes (i.e., sputtering current, argon pressure and deposition time) on the I_{corr} and E_{corr} of samples is shown in Figure 2.

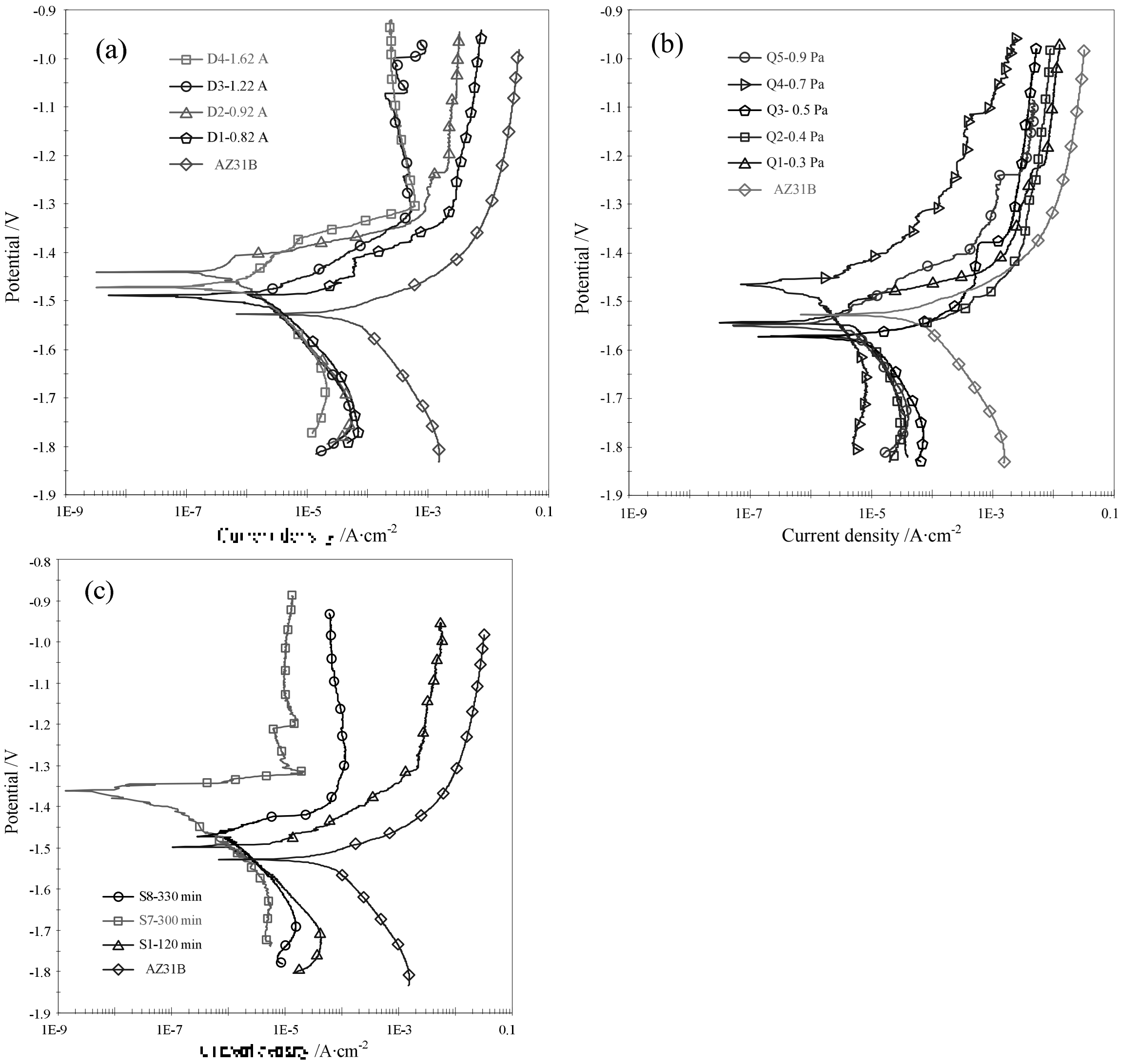

Figure 1. Polarization curves of samples (a) different sputtering current, (b) different argon pressure and (c) different deposition time on AZ31B Mg alloys in 3.5 wt.% NaCl solution.

Table 1. Polarization data of Al coating on AZ31B Mg alloys

Sample	E_{corr} [V]	I_{corr} [μA·cm^{-2}]
AZ31B	-1.527	8.91E+01
D1	-1.487	5.44E+00
D2	-1.442	2.48E+00
D3	-1.486	4.10E+00
D4	-1.469	4.75E+00
Q1	-1.545	8.64E+00
Q2	-1.568	1.25E+01
Q3	-1.571	1.18E+01
Q4	-1.463	2.97E+00
Q5	-1.547	5.96E+00
S1	-1.497	2.48E+00
S2	-1.361	3.39E-02
S3	-1.470	1.78E+00

The crystallographic and geometric structure as well as internal stress depended on the process condition. Figure 2 shows that the corrosion potential of sample deposited with different sputtering current (a), argon pressure (b) and deposition time (c) respectively. As shown in the figure, the corrosion potential of samples was positive shifted to -1.442 (D2), -1.463 (Q6) and -1.361 V (S2) respectively after being deposited with different aluminum films. In addition, both anodic and cathodic current densities of the magnesium alloys after deposited Al coating moved to a lower value. It also showed that I_{corr} decreased from 89.1 to 0.034 μA/cm^2 (S2), was 2~3 orders of magnitude less than that of bare alloys. The test results indicate that the corrosion resistance of Al coated AZ31B alloys improved, but the degree of improvement was quite different due to the properties of coating were strongly affected by the sputtering parameters.

As shown in the photograph by macroscopic, the corroded surfaces after polarization tests also revealed the differences in the corrosion damage of the Al coatings. It can be seen that the surface of the bare AZ31B magnesium alloy appeared corrosion pitting. Moreover, The higher magnification micrograph shown in Figure 3(a) also demonstrated that its surface was completely covered by a thick and uneven film of corrosion products $Mg(OH)_2$.

Compare to the bare substrate, the surface of the coated samples did not appear severe corrosion and the corrosion rates slow down. Figure 2 (a) showed that there were many micro cracks and pinhole (shown in Figure 3(b)) appeared in the surface, owing to the interaction between Cl^- and electrochemical effect. It was indicated that there were numerous defects in coatings when sputtering current was 0.8A. With increase of sputtering current, the amount of micro crack decrease. However, large single crack occurs after tests because the residual stress and properties of samples did not match (shown in Figure 3(c)). When the sputtering current increased to 1.6A, there is no significant corrosion damage in the D4 sample except a few corrosion spots. With increasing sputtering current, argon ions from the plasma become more energetic. They can hence release higher energies to target atoms during sputtering process. The sputtered atoms have consequently left the target with higher kinetic energy. Therefore, sufficiently high sputtering current is essential for improve the corrosion resistance of Al coated AZ31B.

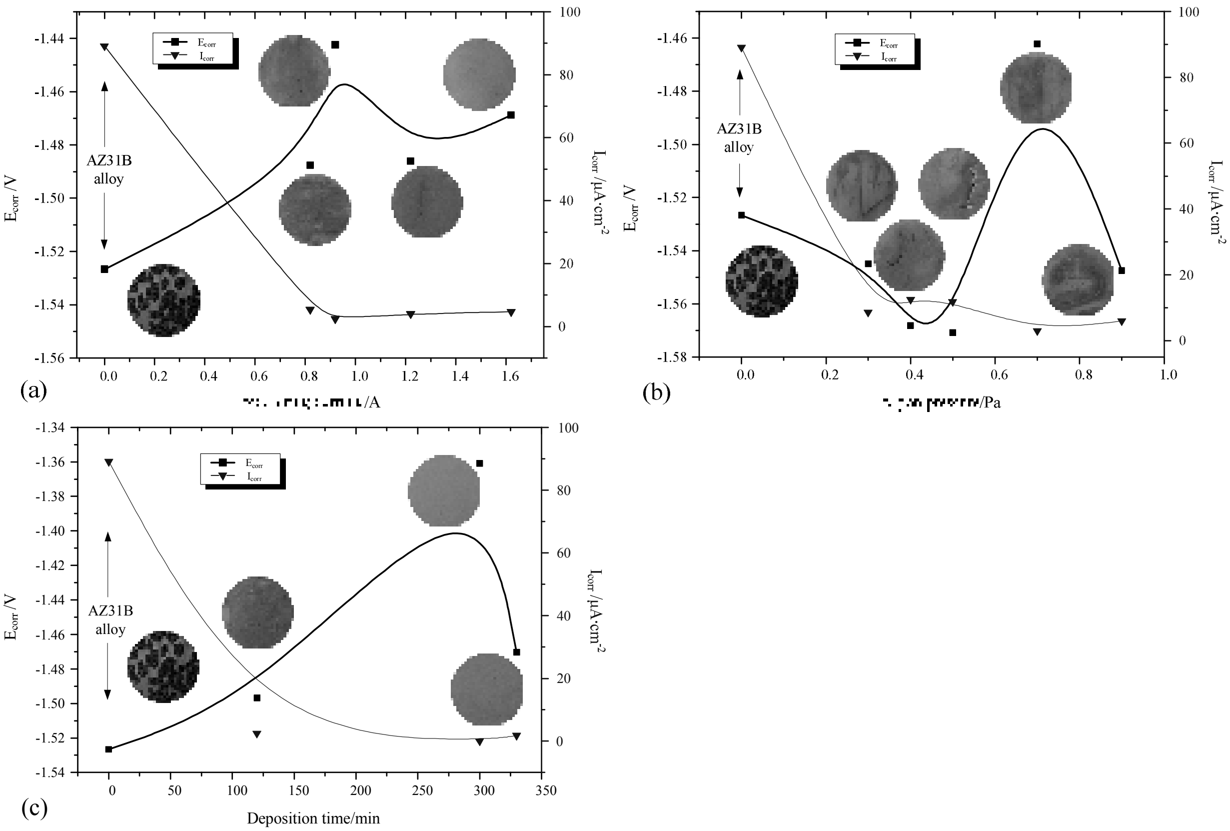

Figure 2. Variations of I$_{corr}$ and E$_{corr}$ of aluminum coating with (a) sputtering current, (b) argon pressure and (c) deposition time in 3.5% NaCl solution. Inset is surface morphology of samples after corrosion test.

Proper argon pressure also important to Al coating. At lower pressure, there are not enough atoms to bombard the target. Whereas, sputtered Al atoms experience more collisions, reach substrate at relatively lower energy and hence decreasing probability of depositing. Figure 2 (b) showed that the Al coating did not reveal a significant protective effect at lower and higher argon pressure, which can be ascribed to the loose and numerous defects in coatings. Only when the depositions were performed under the argon pressure of 0.7 Pa, the E$_{crro}$ increase compare with bare AZ31B. Additionally, there is no large crack except a few corrosion spots on the eroded surface.

With the deposition time increase, the corrosion resistance improved significantly, especially for deposited 300 min aluminum coating (S2), the corrosion potential increased of 166 mV than the bare magnesium alloy. Meantime, corrosion current density also decreased by three orders of magnitude. It was also found no corrosion damage on the surface, as same as that of before corrosion tests. In our previous work[14], it was found that the thickness and critical load of Al coatings varied greatly with deposition time, and leading to effected on the corrosion resistance of samples. Generally, longer deposition time can lead to increase thicker coating thickness, but the growth of coatings by magnetron sputtering slow down with the increase of time more than one point. Furthermore, more deposition time can changde the residual stress and structure, or even make grain grow up. Ultimately, the corrosion resistance become worse.

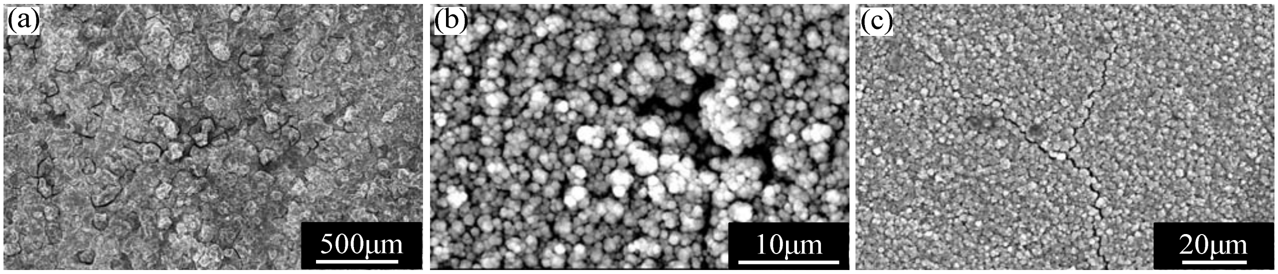

Figure 3. SEM micrographs of AZ31B substrate and Al coated sample after corrosion testing. (a) corrosion pit of substrate, (b) a pinhole and (c) a crack.

3.2 Corrosion Machanism of Al Coating on AZ31B Alloys

NaCl solution are corrosive because chlorides, even in small amounts, usually break down the protective film on magnesium. Pitting corrosion occurs around cathode-phase such as $Mg_{17}Al_{12}$ phase when AZ31B magnesium alloy in 3.5% NaCl solution. According to the results, Figure 4 schematically represent the corrosion mechanism of Al coated AZ31B magnesium alloy in 3.5% NaCl solution. First, after coated aluminum, a thick film of corrosion products $Al(OH)_3$ is formed on the samples during the corrosion attack. However, the thick film may be as a stable passive film on the substrate, which is reflected by the passive-like behavior. The defects such as pinhole and crack on surfaces of samples where the corrosive media(Cl^-) can penetrate through to the substrate, followed by galvanic corrosion occured when the Cl^- got to the Al coating/AZ31B interface thus leading to formation of new corrosion products $Mg(OH)_2$. Moreover, dissolution of the α-Mg grains and $Mg_{17}Al_{12}$ phase within the lamellar aggregate happened on substrates according to the following reactions:

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \text{ (anodic reaction)} \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-(aq) \text{ (cathodic reaction)} \quad (2)$$

Subsequently, from the α-Mg dissolution, more corrosion products $Mg(OH)_2$ formed at the interface according to reaction (3). The $Mg(OH)_2$ products grows to such a level that it exerted a compressive intrinsic stress exists in Al coatings prepared by sputtering and then lifted/damaged the coating(Figure 3(c)). In addition, where hydrogen evolution happened, would rupture to form cracks at the force of the increasing H_2 bubbles.

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s) \quad (3)$$

If the corrosion processes continue, the alkalization may be happened in thin Al films.[15] The severe corrosion will be occurred due to the interaction of galvanic corrosion and other corrosion form. Therefore, obtain thicker, dense and free-defect Al coating by optimize deposition parameters is essencial to improved corrosion resistance of AZ31B magnesium alloy.

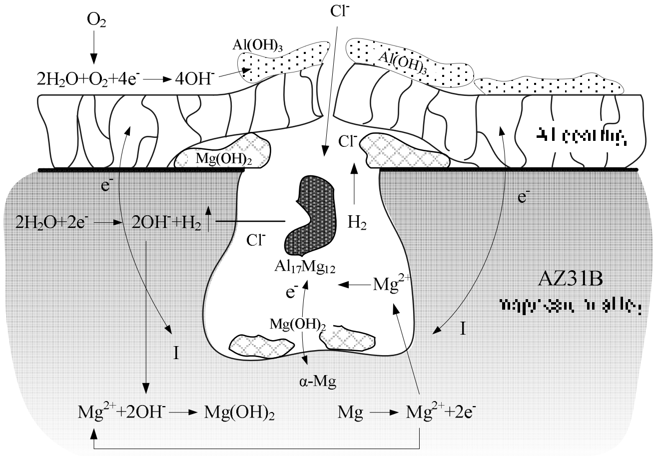

Figure 4. Schematic representation of the corrosion process of Al coated AZ31B upon immersion for 3.5% NaCl solution.

4 CONCLUSIONS

Aluminum coatings were deposited on AZ31B magnesium alloy using D.C. magnetron sputtering. The influence of sputtering parameters on corrosion behavior was investigated. The coated sample demonstrated good corrosion resistance in 3.5% NaCl solutions than that of the bare substrate. It was found that the corrosion current density (I_{corr}) of aluminum coated magnesium alloys was 2~3 orders of magnitude less than that of bare alloys. The corrosion potential (E_{corr}) of aluminum coated samples had been positive shift. Sufficiently high sputtering current (1.6 A) and proper argon pressure (0.7 Pa) is essential for improve corrosion resistance of Al coated AZ31B. With the deposition time increase, the corrosion resistance improved significantly. The severe corrosion will occur after aluminum coating damaged due to the interaction of galvanic corrosion and other corrosion form.

Acknowledgements

The authors gratefully acknowledges the Research Projects (Grant No. 9140A18060409 QT 0202) and Beijing Key Lab. for Corrosion, Erosion and Surface Technology for financial support.

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