Microstructure and corrosion behaviors of AZ31 alloy with an amorphous-crystallin nano-composite film

Fumin Xu¹, Lan Luo¹,², Yong Liu¹,², Jun Wan³ and Guixing Xu²

¹ Key Laboratory of Lightweight and High Strength Structural Materials of Jiangxi Province, Nanchang University, Nanchang 330031, People’s Republic of China
² School of Materials Science and Engineering, Nanchang University, Nanchang 330001, People’s Republic of China
³ College of Metrology & Measurement Engineering, China Jiliang University, Hangzhou 310018, People’s Republic of China

Keywords: magnesium alloys, nano-composite film, corrosion resistance, ALD

Abstract
Magnesium (Mg) alloy has drawn considerable attention for lightweight structural and functional materials, whereas its corrosion resistance still requires to be enhanced. A new strategy for corrosion resistance has been proposed as making an amorphous-crystalline nano-composite film on Mg alloys. The film as the composition as Al₂O₃/GaN with a thickness of 20 nm was prepared on AZ31 Mg alloy by atomic layer deposition. Grazing incidence x-ray diffraction, scanning electron microscopy equipped with energy-dispersive spectroscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, and nano indentation tester have been used to characterize the film in details. It is verified the sample has an amorphous/crystalline/Mg interface structure, and a surface with homogeneous elemental distribution and higher hardness. Neutral salt spray test shows the film changes the corroded mode from pitting corrosion to uniform corrosion. Furthermore, electrochemical measurements indicate that the film would raise E_{corr} (ΔE_{corr} = +0.295 V), drop i_{corr} (about 1/10 times), and make electrical equivalent circuits change from R_s (CPE R_L (R_1 L)) to R_L (CR_L) (CPE R_L (R_1 L)). All evaluations show that better corrosion resistance has been by inducing the amorphous-crystallin nano film. The amorphous layer in the film would make a more homogeneous Cl⁻ distribution on the surface and act as a barrier to block the penetration of corrosion medium in the early stage. During corrosion, the interface between the layers in the film could retard the corrosion crack propagating further. The film would be favored to form a denser corrosion product layer finally. A more uniform and lower corrosion occurs for AZ31 Mg alloy with this nano-composite film.

1. Introduction
Magnesium (Mg) alloys exhibit lots features such as low density, high specific strength and biodegradability. It has been attracting attentions in various potential applications for lightweight equipment, electronics industries and biomedical fields [1, 2]. Nevertheless, the poor corrosion resistance due to the low electrode potential and non-compact natural oxidation passive film [3, 4], is still the major drawback [5, 6]. Surface modification is a main strategy to protect Mg alloys from corrosion [7–9]. Generally, the surface modifications can provide a barrier to avoid Mg alloy contacting with the corrosive medium. It has been reported that the composite film would exhibit better protective capability than just mono film because it can develop synergic effect. For instances, hydroxyapatite/bio-glass composite coating (about 1 μm) on Ti-6Al-4V alloy, has better bio-activity and higher adhesive strength than mono hydroxyapatite coating [10]. The micro-arc oxidation layer sealed with poly composite layer (about 70 μm) on Mg alloy, would has significantly improvement in corrosion resistance and less stress corrosion cracking, compared with mono micro-arc oxidation coating [7]. The Al₂O₃–CeO₂ composite coating (about 29 μm) on 7075 aluminium alloy, has the about 1/10^{3} i_{corr} as that of mono Al₂O₃ film [11]. Would the composite film in nanometer still have a significant protective effect for Mg alloy?
Herein, an amorphous–crystallin nano-composite film are fabricated by atomic layer deposition (ALD, it can deposit continuous ultra-thin films which are conformal and pinhole-free on any kind matrix owing to the sequential, self-limiting and self-saturating surface chemical reacting process) [12–15]. The amorphous layer is designed as Al₂O₃, which has been applied for Mg alloy with satisfied results [16, 17]. The composition of crystalline layer is GaN, which is a common protective film for metals and semiconductor [18]. This amorphous-crystallin nano-composite film on Mg alloy is firstly characterized carefully in morphology, composition, thickness, ion valence, interface structure, and then mechanical properties are investigated. Finally, the corrosion behaviour is studied by neutral salt spray test and electrochemical measurement. The corrosion mechanism for Mg alloy with this nano-composite film is deduced too.

2. Experiment

2.1. Material preparation
AZ31 Mg alloy sheets (3.04 wt.% Al, 0.94 wt.% Zn, 0.44 wt.% Mn and balanced Mg) in a size of 25 × 25 mm² were applied as the substrates. Before film deposition, the AZ31 Mg alloy substrates were grounded mechanically with SiC sandpapers from P200 progressively up to P1200 and polished by diamond with 0.05 μm. Then the AZ31 Mg alloy were ultrasonically cleaned with acetone and arided by N₂ atmosphere. The bare substrates were named as SB.

The substrates were loaded into the ALD reactor, heating via a resistive heater under N₂ ambient (10 mbar). The heating temperature was measured by a thermocouple near the wafer and controlled by a PID controller. The deposition was conducted in a flow reactor at a pressure about 10⁻² mbar. GaN film was deposited by 100 cycles at 400 °C (each cycle was consisted of Ga(CH₃)₃ (0.02 s) → N₂ purge (60 s) → NH₃ (0.02s) → N₂ purge (60 s), 1 Å/cycle). Directly after GaN film deposition, Al₂O₃ film was prepared by another 100 cycles at 250 °C (each cycle contains Al(CH₃)₃ (0.02 s) → N₂ purge (60 s) → H₂O (0.02 s) → N₂ purge (60 s), 1 Å/cycle). The thickness of film can be precisely regulated by controlling the ALD deposition cycles. After ALD-deposited GaN/Al₂O₃ film, the AZ31 Mg alloy substrates were named as SF.

2.2. Microstructure characterization
The phase constitution was analyzed by Grazing incidence x-ray diffraction with the Cu-Kα radiation (GIXRD, PANalytical X Pert PRO, incidence beam angle is 1° at 40 kV and 40 mA). Film thickness was figured out via x-ray reflectivity (XRR, PANalytical). The surface and cross-section morphology were observed using scanning electron microscopy (SEM, FEI Quanta 200F). The analysis of film interface microstructures and compositions was conducted via transmission electron microscopy (TEM, JEOL, JEM-2100) working at 200 kV and equipped with energy-dispersive x-ray (EDS, Oxford X-man) microanalysis hardware. The coated side of two SF samples were adhered together and placed in the center of 3 mm diameter copper ring for TEM observation. Before TEM observation, the samples were mechanically thinned to 30 μm firstly, and then electropolished in 10 wt.% perchloric acid at −5 °C with the voltage of 20 V. Finally, the TEM observational requirement was met using ion milling. The chemical bonds were confirmed using a x-ray photoelectron spectroscopy analysis (XPS, ESCALAB250XI, monochromatic Al Kα excitation source 1486.6 eV) along with in situ ion etching. The adventitious carbon (C1s) core level peak at 284.6 eV was applied to calibrate the binding energies (BEs) of samples.

2.3. Mechanical properties
The mechanical properties were determined by a nano indentation tester (Fischerscope, HM2000) at a constant loading rate of 10 mN s⁻¹ with the range of 0 ~ 100 mN.

2.4. Corrosion behavior
2.4.1. Neutral salt spray test
Neutral salt spray test was used to determine the long-term corrosion behavior of samples and the test followed ASTM B-117. After corrosion, the samples were ultrasonically cleaned with distilled water for 10 min. Then the samples were arided by cooling N₂ gas for further experiments. The corroded were then studied by SEM, EDS and GIXRD.

2.4.2. Electrochemical measurements
The corrosion behavior of the samples was studied by electrochemical workstation (CHI650D). Electrochemical measurements were carried out in 3.5 wt.% sodium chloride (NaCl) aqueous solution by applying a conventional three-electrode method, which the sample (exposing 0.5 cm²), saturated calomel and platinum plate was the working, reference and counter electrodes, respectively. The scan rate of potentiodynamic...
polarization (PDP) curves is 1 mV s\(^{-1}\) from approximately −350 mV to 450 mV. The frequency range of electrochemical impedance spectra (EIS) measurements is \(10^{-2} \sim 10^5\) Hz with 10 mV the sinusoidal voltage signal amplitude. To resolve EIS plots, the Zview software (Solartron Analytical, UK) was applied to get appropriate equivalent circuit (EC) models (\(\sigma < 10\%\) and \(\chi^2 < 0.01\) for the individual parameters).

3. Results and discussion

3.1. Surface characterization

The SEM images and EDS mapping of SB and SF are shown in figure 1. According to figure 1(a), there are still some grinding scratches on the SB surface clearly, while SF also exhibits same surface morphology with SB (figure 1(b)). From the inset of figure 1(b), the surface is flat and free of voids and porosity after coating, whereas the grinding scratches still can be found. Table 1 lists the chemical compositions of red rectangle marked in figure 1. It shows that the Al, O, Ga and N contents increases apparently while the Mg and Zn elements contents decreases after ALD-deposited GaN/Al\(_2\)O\(_3\) nano-composite film. This means that the composite film has deposited on Mg alloy successfully. Besides, the corresponding EDS mapping indicates that the Al, O, Ga and N elements distributes over the surface uniformly. So, the results show that the surface of AZ31 Mg alloy is covered evenly by the GaN/Al\(_2\)O\(_3\) nano-composite film.

Figure 2 shows the GIXRD patterns of SB and SF. As shown in figure 2(a), SB exhibits the obvious characteristic peaks of \(\alpha\)-Mg phase which are ascribed to AZ31 Mg alloy matrix. After ALD-deposited GaN/Al\(_2\)O\(_3\) film, the relative intensities of planes as (100), (002), (101) increase due to the deposition of crystallized GaN layer, and bulging near the planes as (321), (441) appear attributing to amorphous Al\(_2\)O\(_3\) layer. Film thickness (D) is evaluated by XRR (figure 2(b)) and the film thickness can be calculated out by the following
equation (1) [19, 20]:

\[ D = \frac{\lambda}{2} \sqrt{\theta_{m+1}^2 - \theta_{c}^2} - \frac{1}{\sqrt{\theta_{m}^2 - \theta_{c}^2}} \]  

(1)

In which \( \lambda \) is x-ray wavelength, \( \theta_{c} \) is the critical angle of total reflection, \( \theta_{m,m+1} \) is constructive interference diffraction peaks of incident angle. GaN/Al2O3 nano-composite film thickness can be calculated out as 20 nm.

Figure 3 shows TEM image and EDS results for the cross-section of SF. TEM image reveals that the GaN/Al2O3 composite film is well bonded on the surface without any peeling or voids. Mg, Al, O, Ga and N elements is observed distinctly by EDS mapping in figure 3(b), indicating that the composition of nano-composite film is same as the designed one.

XPS with ion etching is performed to determine the composition and structure of the nano-composite film interface (figures 4(a)–(c)). The XPS survey spectrum of SF consists of several BE (binding energy) peaks belongs to electronic states as Mg2p, O1s, N1s, Al2p, and Ga3d (49.8 eV, 532.0 eV, 397.3 eV, 73.9 eV, 18.1 eV, figure 4(a)). High resolution XPS spectra of N 1s has a typical peak located at 397.3 eV which is origin from the N-Ga bonding [21–24]. For Ga3d spectrum, there are two peaks located at 19.9 eV and 18.1 eV, the former Ga3d5/2 peak ascribed to GaN [24], the latter Ga3d3/2 peak ascribes to metal Ga [25]. O1s spectrum has 534.8 eV and 531.7 eV, which ascribe O1s to adsorbed O2 and Al2O3, respectively [26, 27]. Al 2p spectrum has a peak at 73.9 eV related to Al2p3/2 in Al2O3 [28–30]. After ion etching 12 nm (figure 4(b), Al2O3 layer had been stripped and GaN layer exposure), the peaks assigned to O1s, Al2p3/2 in Al2O3 decrease, the peaks of N1s, Ga 3d3/2 in GaN increase, and the peaks of O1s in O2 and Al2p3/2 in metal Al [27] increase, comparing with SF result (figure 4(a)). After ion etching 25 nm (figure 4(c), GaN layer had been stripped and substrate exposure), the peaks of N1s, Ga 3d3/2 in GaN disappear, and the peaks of O1s in O2 and Al2p3/2 in metal Al increase comparing with figure 4(b) result.

Figure 2. (a) Grazing incidence x-ray diffraction patterns (GIXRD) and (b) x-ray reflectivity (XRR).

Figure 3. (a) Transmission electron microscopy image (TEM) and (b) EDS for SF cross-section.
From the above characterizations, it is self-evident that a GaN/Al$_2$O$_3$ nano-composite film was deposited on the surface of AZ31 Mg alloy successfully by ALD. The film, consisting of amorphous Al$_2$O$_3$ upper-layer and crystallin GaN sub-layer, covers the surface with excellent conformity and uniformity, and attaches well to the Mg alloy substrate.

3.2. Mechanical properties
The nanohardness, Young’s modulus and stiffness of the SB and SF is studied by Nano indentation tester. Figure 5(a) shows the typical load-depth curves of samples after instrumented indentation testing. The curve of SF is fluent without any zigzag fluctuation and disconnection, which indicates that GaN/Al$_2$O$_3$ nano-composite film is smooth and no-cracking during the loading process. The results of nano indentation tester (figure 5(b)) show the GaN/Al$_2$O$_3$ nano-composite film improves the nanohardness and Young’s modulus whereas the stiffness decreases [31, 32].

3.3. Corrosion behaviour
3.3.1. Neutral salt spray test
To evaluate the long-term corrosion resistance of the GaN/Al$_2$O$_3$ film, the neutral salt spray test is carried out. Figure 6 shows the surface SEM images after corrosion. Figure 6(a) exhibits that the SB suffers from severe pitting corrosion and there are obvious pits and cracks distribute on the surface. According to previous study [1], the cracks mainly results from the volumetric expansion by the accumulation of corrosion products on the
surface of matrix. As for SF, it exhibits different surface corrosion morphology from SB, having less pits and cracks (figure 6(b)). So, the corrosion of matrix can become milder and uniform by ALD-deposited GaN/Al$_2$O$_3$ film.

Figure 7 exhibits the cross-sectional SEM images and EDS mapping of SB and SF after salt spray test. As can be seen in figure 7(a), SB exhibits irregular and thick corroded layer that made of oxides and hydroxides (as shown in the elemental mapping images) [33], and the corroded pits of SB shows deep depth with many cracks. After ALD-deposited GaN/Al$_2$O$_3$ film, the sample is subjected to a milder and more uniform corrosion. Only a thin corroded layer forms on the surface and remains unaltered in depth (figure 7(b)). Thus, the GaN/Al$_2$O$_3$ film can obviously promote the corrosion resistance of AZ31 Mg alloy.

Figure 8 is the GIXRD patterns of surface for samples after salt spray test. As it can be seen, the main characteristic peaks of samples are still the peaks of $\alpha$-Mg while the peaks of corrosion products (MgAl$_2$O$_4$ and Mg(OH)$_2$) can also be detected. However, the peak intensities of the corrosion products decrease after GaN/Al$_2$O$_3$ film covering, which indicating that GaN/Al$_2$O$_3$ film has good corrosion resistance.
These results indicate that the uniform distribution of GaN/Al₂O₃ nano-composite film leads to uniform corrosion pattern without pitting corrosion. Besides, it can furthermore conduce to promote the corrosion resistance of matrix.

### 3.3.2. Electrochemical test

PDP curves and corrosion data are shown in figure 9 and table 2. After ALD-deposited GaN/Al₂O₃ film, the corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) of SB increases from $-1.621 \text{ V}$ to $-1.326 \text{ V}$ and decreases from $6.171 \times 10^{-5} \text{ A cm}^{-2}$ to $1.457 \times 10^{-6} \text{ A cm}^{-2}$, respectively. These results imply that the tendency of corrosion initiation for AZ31 Mg alloy reduces and the corrosion rate also becomes slower apparently [34]. It can be seen initially that GaN/Al₂O₃ composite film exhibits good corrosion resistance. All these results show that the condense GaN/Al₂O₃ film can largely hinder Cl⁻ permeation and improve corrosion resistance [35, 36]. In addition, the polarization resistance ($R_p$) is calculated using simplified Stern-Geary relationship to evaluate the corrosion rate, as shown in follow (equation (2)) [37]:

\begin{equation}
R_p = \frac{1}{i_{corr}}
\end{equation}
In which $\beta_a$ is the anode Tafel slope and $\beta_c$ is the cathodic Tafel slope. $R_p$ value increases from $6.06 \times 10^5$ to $2.18 \times 10^7 \Omega \cdot \text{cm}^2$. In addition, the corrosion rate can be figured out via the Faraday's law by equation (3) as [38]:

$$R_p = \frac{\beta_a \times \beta_c}{2.303 \times i_{\text{cor}} (\beta_a + \beta_c)}$$

(2)

In which $\beta_a$ is the anode Tafel slope and $\beta_c$ is the cathodic Tafel slope. $R_p$ value increases from $6.06 \times 10^5$ to $2.18 \times 10^7 \Omega \cdot \text{cm}^2$. In addition, the corrosion rate can be figured out via the Faraday's law by equation (3) as [38]:

$$\text{corrosion rate} = \frac{A \times i_{\text{cor}}}{n \times F \times \rho} \times 87600$$

(3)

In which $A$ is the atomic weight of the metal, $\rho$ is the density, $n$ is the number of electrons exchanging in the dissolution reaction, and $F$ is the Faraday constant ($26.801 \, \text{A} \cdot \text{h/mol}$). The corrosion rates obtained from the method could be ranked in the increasing order: SF ($0.03 \, \text{mm y}^{-1}$) < SB ($1.41 \, \text{mm y}^{-1}$). $A^{-1}l^{-1}$ these results presented clearly that the corrosion resistance of SB is improved evidently after ALD-deposited GaN/Al$_2$O$_3$ composite film.

The corrosion behavior of SB and SF was further studied by EIS. As the figure 10(a) shown, it can be found that both samples consist of capacitive and inductive loops, but SB only has one capacitive loop and SF has two capacitive loops. Generally, the capacitive loop can be assigned to the charge transfer reaction and layer effects. The inductive loop can be assigned to the physical adsorption processes and pitting corrosion of Mg matrix [8, 39]. Compared with the curves between SB and SF, the diameter of the curves in medium frequency range increases remarkably after coating in figure 11(a), and Bode plots shows the impedance modulus ($|Z|$) value is higher at low frequency range in figure 10(b), which indicates a better corrosion protection for GaN/Al$_2$O$_3$ film [5, 40].

After ALD-deposited GaN/Al$_2$O$_3$ film, it can be seen in figure 10(c) that two well defined time constants arise in the frequency-phase angle diagram, which is coherent to the two capacitive loops in figure 11(a). It also indicates that the GaN/Al$_2$O$_3$ composite film induce another corroded mode to Mg alloy [35].
In addition, to more accurately interpret EIS plots, the equivalent circuits (ECs) were done to figure out the electrochemical properties and physicochemical process during corrosion. By fitting EIS plots in figure 10(a), ECs and individual parameter values have been obtained, shown in figure 11 and table 3. The solution resistance and the charge transfer resistance are described by the $R_s$ and $R_{ct}$, respectively. The dissolution of AZ31 Mg alloy and corroded production during corrosion is described by $R_L$ and inductance ($L$). $R_s/R_{ct}$ and $C$ show the resistance and capacitive reactance, respectively [8]. Besides, the nonideal resistive and capacitive behavior of the samples are described by the constant phase elements (CPE), which is described by the formula [35, 41]:

$$Y_{CPE} = \frac{1}{Y_0} (j\omega)^{-n} (0 < n \leq 1)$$  \hspace{1cm} (4)

Where $Y_{CPE}$ is CPE constant, $n$ is empirical exponent of CPE. CPE is the pure capacitive when $n = 1$, and CPE is the pure resistance while $n = 0$. The corrosion mode changes from $R_s$ (CPE $R_{ct}$ ($R_L$) for SB to $R_s$ ($C_{Rf}$) (CPE $R_{ct}$ ($R_L$) for SF, in figure 12. New parameters as ($C_{Rf}$) add to ECs after GaN/Al$_2$O$_3$ composite film coating. $R_{ct}$ value also raises as 118.20 $\Omega$·cm$^2$ for SB and 174.00 $\Omega$·cm$^2$ for SF. All these results indicate that the corrosion resistance of matrix can be improved effectively by ALD-deposited GaN/Al$_2$O$_3$ film [42]. From the results in section 3.3, it is obvious that the GaN/Al$_2$O$_3$ composite film make a more uniform and slower corrosion for Mg alloy.
4. Discussion

AZ31 Mg alloy exhibits severe corrosion, mainly caused by galvanic effect between α-Mg matrix and the noble second phase [35, 43]. During corrosion, the Cl\(^−\) non-homogeneous distribution causing by non-uniform microstructure would accelerate the non-uniformly corrosion [44]. Exposed in chloride-containing media, Cl\(^−\) would concentrate on inhomogeneity area such as scratches and protruding second phase particles for SB, while the distribution of Cl\(^−\) would be more uniform due to the covering of GaN/Al\(_2\)O\(_3\) composite film for SF (figures 12(a1) and (b1), based on figure 1). At the beginning of corrosion, the corrosion of matrix would be accelerated as serving as anode while the noble second phase hardly corrodes [43, 45]. The main corrosion products are magnesium oxide and hydroxide. Cracks in corrosion product layer may be produced by the cooperative effects of hydrogen pressure and expansion stress due to the formation of magnesium hydride during corrosion [46]. However, GaN/Al\(_2\)O\(_3\) composite film can act as a physical barrier and corrode homogeneously, and the corrosion possess in early stage would be more uniform and slower than SB (figures 12(a2) and (b2), based on figures 9~11) [47~49]. As the time goes on, the corrosion product layer of SB become thicker and the cracks propagate in layer. Furthermore, the noble second phase would fall down to form pits when the matrix is dissolved around them for SB (figure 12(a3), based on figures 6 ∼ 7) [45]. As for SF, the corrosion product layer become thicker too but the interfaces (in the composite film itself and between film and matrix) would retard the crack propagating in layer (figure 12(b3), based on figures 6~7) [44, 50]. Finally, the aggressive Cl\(^−\) would assemble in the cracks and pits more serious, which would result further severe pitting corrosion. A fragile corrosion product layer is formed on the surface of SB, which cannot prevent further corrosion. However, a relative tight corrosion product layer exhibit better protect effect for SF (figures 12(a4) and (b4)).

The amorphous-crystallin composite film can make a more homogeneous Cl\(^−\) distribution in the surface and act as a barrier to block the penetration of corrosion medium in the early stage. During corrosion, the film can retard the corrosion crack propagating further, and form a denser corrosion product layer finally. A more uniform and lower corrosion occurs for AZ31 Mg alloy with the nano-composite film.

5. Conclusions

An amorphous-crystallin nano-composite film as GaN/Al\(_2\)O\(_3\) has been deposited on the surface of AZ31 Mg alloy by atomic layer deposition (ALD). The composite film on Mg alloy are characterized firstly (such as morphology, composition, thickness, etc), then corrosion behavior is evaluated by neutral salt spray test and electrochemical measurement. The conclusions are deduced as follows:

1. a compact GaN/Al\(_2\)O\(_3\) nano-composite film could be made on Mg alloy by ALD with a thickness of 20 nm, and the film exhibits uniform coverage and makes the element distribution in surface more homogeneous. This nano-composite film consists of amorphous Al\(_2\)O\(_3\) upper layer and crystallin GaN sublayer. Moreover, it is well attached to the Mg alloy substrate.

2. This nano-composite film can increase the hardness and Young’s modulus of Mg alloy whereas the stiffness decreases.

3. The salt spray test indicates that this nano-composite film introduces a uniform corrosion mode for AZ31 Mg alloy.

4. The electrochemical test shows that GaN/Al\(_2\)O\(_3\) nano-composite film improves the corrosion resistance of AZ31 Mg alloy significantly. It makes an increase in corrosion potential from −1.621 V to −1.326 V and a decrease in corrosion current density from 6.171 × 10\(^{−3}\) A-cm\(^{−2}\) to 1.457 × 10\(^{−6}\) A-cm\(^{−2}\) by PDP test.

Acknowledgments

This work was supported by National Key Research and Development Program (Nos. 2016YFB0701201 and 2016YFB0701203), National Natural Science Foundation of China (Nos. 51671101), Domain Foundation of Equipment Advance Research of 13th Five-year Plan (No. 61409220118), Natural Science Foundation of Jiangxi Province (Nos. 20171BCD40003), Key Research and Development Program of JiangXi Province (No GJJ150010).
ORCID iDs

Lan Luo  https://orcid.org/0000-0002-4176-7676

References

[1] Zhang D, Qi Z, Wei B, Shen H and Wang Z 2018 Microstructure and corrosion behaviors of conductive Hf/HfN multilayer coatings on magnesium alloys Ceram. Int. 44 9958–66
[2] Wang Y et al 2018 Turning a native or corroded Mg alloy surface into an anti-corrosion coating in excited CO₂ Nat. Commun. 9 4058
[3] Song G and Antwes A 2010 Corrosion mechanisms of magnesium alloys Adv. Eng. Mater. 11 1–33
[4] Wang B, Xu D K, Wang S D, Sheng L Y, Zeng R C and Han E 2019 Influence of solution treatment on the corrosion fatigue behavior of an asforged Mg-Zn-Y-Zr alloy Int. J. Fatigue 120 46–55
[5] Zoubi W A and Ko Y G 2018 Enhanced corrosion protection performance by organic–inorganic materials containing thiocarbonyl compounds Sci. Rep. 8 10925
[6] Zhong F, Wu H J, Jiao Y L, Wu R, Zhang J, Legan H and Zhang M 2020 Effect of Y and Ce on the microstructure, mechanical properties and anisotropy of as-rolled Mg–8Li–1Al alloy J. Mater. Sci. Technol. 39 124–34
[7] Chen L, Sheng Y, Zhou H, Li Z, Wang X and Li W 2019 Influence of a MAO plus PLGA coating on bio corrosion and stress corrosion cracking behavior of a magnesium alloy in a physiological environment Corros. Sci. 148 134–43
[8] Wang Y, Gu Z, Liu J, Jiang J, Yuan N, Pu J and Ding J 2019 An organic/inorganic composite multi-layer coating to improve the corrosion resistance of AZ31B Mg alloy Surf. Coatings Technology 360 276–84
[9] Duan G et al 2018 Designing for the chemical conversion coating with high corrosion resistance and low electrical contact resistance on AZ91D magnesium alloy Corros. Sci. 135 197–206
[10] Yin S Q, Duan W C, Liu W H, Wu L, Yu J, Zhao Z, Liu M, Wang P, Cui J and Zhang Z 2020 Influence of specific second phases on corrosion behaviors of Mg–Zn–Gd–Zr alloys Corros. Sci. 166 108419
[11] Duan M, Luo L, and Liu Y 2020 Microstructural evolution of AZ31 Mg alloy with surface mechanical attrition treatment: Grain and texture gradient, Journal of alloys and compounds J. Alloy Compd. 823 153691
[12] Mirhashemihaghighi S, Siatowska J, Maurice V, Seyeur A, Klein L H, Salmi E, Ritala M and Marcus P 2016 Interfacial native oxide effects on the corrosion protection of copper coated with ALD alumina Electrochim. Acta. 193 7–15
[13] Liu X M, Yang Q Y, Li Z Y, Yuan W, Zheng Y F, Cui Z D, Yang X J, Yeung K W K and Wu S L 2018 A combined coating strategy based on atomic layer deposition for enhancement of corrosion resistance of AZ31 magnesium alloy Appl. Surf. Sci. 434 1101–11
[14] Mirhashemihaghighi S, Siatowska J, Maurice V, Seyeur A, Klein L H, Salmi E, Ritala M and Marcus P 2016 The role of surface preparation in corrosion protection of copper with nanometer-thick ALD alumina coatings Appl. Surf. Sci. 387 1054–61
[15] Ylivaara O M E et al 2014 Aluminium oxide from trimethylaluminum and water by atomic layer deposition: the temperature dependence of residual stress, elastic modulus, hardness and adhesion Thin Solid Films 552 123–35
[16] Fedel M and Delforion F 2016 Electrochemical characterization of atomic layer deposited AL2O3 coatings on AISI 316L stainless steel Electrochim. Acta. 203 404–15
[17] Diaz B, Harkonen E, Siatowska J, Seyeur A, Maurice V, Ritala M and Marcus P 2014 Corrosion properties of steel protected by nanometre-thick oxide coatings Corros. Sci. 82 208–17
[18] Strite S 1992 CORRECTION Journal Of Vacuum Science & Technology B 10 187–187
[19] Zhang I H, Liu S J, Wu R Z, Hou L G and Zhang M L 2018 Recent developments in high-strength Mg-RE-based alloys: Focusing on Mg-Gd and Mg-Y systems J. Magnes. Alloys. 6 277–91
[20] Hasche K, Thomsen-Schmidt P, Krumrey M, Ade G, Ulm G, Stuempel J, Schaedlich S, Frank W, Procop M and Beck U 2003 Metrological characterization of nanometer film thickness standards for XRR and ellipsometry applications Proceedings of SPIE 5190 165–172
[21] Hattori A N, Endo K, Hattori K and Daimon H 2010 Surface treatments toward obtaining clean Ga(N)(001) from commercial hydride vapor phase epitaxy and metal-organic chemical vapor deposition substrates in ultrahigh vacuum Appl. Surf. Sci. 256 4745–56
[22] Elkashty N, Sinivasav R S, Major S, Sabharwal S C and Muthe K P 1998 Sputter deposition of gallium nitride films using a GaAs target Thin Solid Films 333 9–12
[23] Ould-Metidji I, Bideux L, Baca D, Gruzza B and Matolin V 2003 Nitridation of GaAs(100) substrates and GaAs/GaAs systems studied by XPS spectroscopy Appl. Surf. Sci. 212 614–8
[24] Zhang L Q, Zhang C H, Gou J, Han L H, Yang Y T, Sun Y M and Jin Y F 2011 PL and XPS study of radiation damage created by various slow highly charged heavy ions on GaN epilayers Nuclear Instruments & Methods In Physics Research Section B-Beam Interactions with Materials And Atoms 269 2835–9
[25] Kumar M, Kumar A, Thapa S B, Christiansen S and Singh R 2014 XPS study of triangular GaN nano/micro-needles grown by MOCVD technique Materials Science And Engineering B-Advanced Functional Solid-State Materials 186 89–93
[26] Borylo P, Lukaszkowicz K, Szindler M, Kubacki J, Balin K, Basaga M and Sciewczynski J 2016 Structure and properties of Al2O3 thin films deposited by ALD process Vacuum 131 139–26
[27] Wang L, Shinohara T and Zhang B-P 2010 XPS study of the surface chemistry on AZ31 and AZ91 magnesium alloys in dilute NaCl solution Appl. Surf. Sci. 256 5807–12
[28] Jatsunskyi I, Kempinski M, Janelewicz M, Zaleski K, Jurga S and Smyntyna V 2015 Structural and XPS characterization of ALD Al2O3 coated porous silicon Vacuum 113 52–82
[29] Zheng L, Cheng X, Cao D, Wang G, Wang Z, Xu D, Xia C, Shen L, Yu Y and Shen D 2014 Improvement of Al2O3 Films on Graphene Grown by Atomic Layer Deposition with Pre-H2O Treatment Acs Applied Materials & Interfaces 6 7014–9
[30] Ferguson J D, Weimer A W and George S M 2000 Atomic layer deposition of ultrathin and conformal Al2O3 films on BN particles Thin Solid Films 371 95–104
[31] Li Q Q, Yan X H, Luo L, Xu F M, Wu G, Liu C, Jing Y H, Liu Y and Lu J 2019 Mechanical properties and corrosion behaviors of AZ31 alloy with dual-phase glass-crystal coating Mater. Charact. 154 200–11
[32] Hakimizad A, Raeski K and Ashrafizadeh F 2012 Characterization of aluminum anodized layers modified in sulfuric and phosphoric acid solutions and their effect on conventional electrolytic coloring Surface & Coatings Technology 206 2438–45
[33] Guo L, Zhang F, Song L, Zeng R C, Li S Q and Han E H 2017 Corrosion resistance of ceria/poly(methylmethacrylate) modified magnesium hydroxide coating on AZ31 magnesium alloy Surface & Coatings Technology 328 121–33
[34] Cui L Y, Gao S D, Li P P, Zeng R C, Zhang F, Li S Q and Han E H 2017 Corrosion resistance of a self-healing micro-arc oxidation/polydimethyltrimethoxysilane composite coating on magnesium alloy AZ31. *Corros. Sci.* **118**, 84–95

[35] Zhang G, Wu L, Tang A, Ma Y, Song G-L, Zheng D, Jiang B, Atrens A and Pan F 2018 Active corrosion protection by a smart coating based on a MgAl-layered double hydroxide on a cerium-modified plasma electrolytic oxidation coating on Mg alloy AZ31. *Corros. Sci.* **118**, 84–95

[36] Wang C, Jiang B, Liu M and Ge Y 2015 Corrosion characterization of micro-arc oxidation composite electrophoretic coating on AZ31B magnesium alloy. *J. Alloys Compd.* **621**, 53–61

[37] Feliu V, Gonzales J A, Andrade C and Feliu S 1998 Equivalent circuit for modelling the steel-concrete interface: II. Complications in applying the Stern–Geary equation to corrosion rate determinations. *Corros. Sci.* **40**, 995–1006

[38] Frankel G S, Papavinasam S, Berke N, Brossia S and Dean S W 2008 Electrochemical techniques in corrosion: status, limitations, and needs. *J. ASTM Int.* **5**, 101241

[39] Lim T S, Ryu H S and Hong S-H 2012 Electrochemical corrosion properties of CeO2-containing coatings on AZ31 magnesium alloys prepared by plasma electrolytic oxidation. *Corros. Sci.* **62**, 104–11

[40] Liu Y, Yin X, Zhang J, Yu S, Han Z and Ren L 2014 A electro-deposition process for fabrication of biomimetic super-hydrophobic surface and its corrosion resistance on magnesium alloy. *Electrochim. Acta*. **125**, 595–603

[41] Pan T J, Zuo X W, Wang T, Hu J, Chen Z D and Ren Y J 2016 Electrodeposited conductive polypyrrole/polyaniline composite film for the corrosion protection of copper bipolar plates in proton exchange membrane fuel cells. *J. Power Sources*. **302**, 180–8

[42] Zhang Y, Li Y, Ren Y, Wang H and Chen F 2017 LDH films on aluminum alloys for active protection. *Mater. Lett.* **192**, 33–5

[43] Song G L, Atrens A, Wu X L and Zhang B 1998 Corrosion behaviour of AZ21, AZ501 and AZ91 in sodium chloride. *Corros. Sci.* **40**, 1769–91

[44] Jin W H, Wu G S, Feng H Q, Wang W H, Zhang X M and Chu P K 2013 Improvement of corrosion resistance and biocompatibility of rare-earth WE43 magnesium alloy by neodymium self-ion implantation. *Corros. Sci.* **94**, 142–55

[45] Blawert C, Heitmann V, Scharnagl N, Stoermmer M, Lutz J, Prager-Duschke A, Manova D and Maendll S 2009 Different underlying corrosion mechanism for Mg bulk alloys and Mg thin films. *Plasma Processes Polym.* **6**, S690–4

[46] Chen J, Wang J, Han E and Ke W 2008 Effect of hydrogen on stress corrosion cracking of magnesium alloy in 0.1 M Na2SO4 solution. *Mater. Res. Express*. **7**(2020) 066405

[47] Diaz B, Harkonen E, Maurice V, Świetowska J, Seyeux A, Ritala M and Marcus P 2011 Failure mechanism of thin Al2O3 coatings grown by atomic layer deposition for corrosion protection of carbon steel. *Electrochim. Acta*. **56**, 9609–8

[48] Shan D Y, Zhang R F and Han E H 2005 Effect of Al2O3 thin film on corrosion resistance of pure Mg and its anodic coating. *Materials Science Forum*, **488-489**, 863–8

[49] Ji R, Ma M, He Y, Liu C, Fang T, Zhang Z, Wang Y, He Y and Wu J 2018 Improved corrosion resistance of Al2O3 ceramic coatings on AZ31 magnesium alloy fabricated through cathode plasma electrolytic deposition combined with surface pore-sealing treatment. *Ceram. Int.* **44**, 15152–5

[50] Zhang B, Wang J, Wu B, Guo X W, Wang Y J, Chen D, Zhang Y C, Du K, Oguzie E E and Ma X L 2018 Unmasking chloride attack on the passive film of metals. *Nat. Commun.* **9**, 2559