International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Effects of Rare Earth Metal Oxide Doping on Micromorphology and Corrosion Behavior of Hydroxyapatite-Graphene Oxide Composite Coating Fabriacted on AZ91 magnesium alloy

Qimin Liang, Wei Wang^{*}, Zishan Chen, Weiming Lin

School of Materials Engineering, Shanghai University of Engineering Science, Shanghai, 201620, China ^{*}E-mail: <u>wangwei200173@sina.com</u>

Received: 25 January 2021 / Accepted: 25 March 2021 / Published: 30 April 2021

Hydroxyapatite (HA)-graphene oxide (GO) composite coatings reinforced with various rare earth (RE) metal oxide (La₂O₃ and Y₂O₃) of composite coatings are electrophoretic deposited on AZ91 magnesium alloy substrate. The effects of RE metal oxide on the composition, surface morphology and corrosion behavior of HA-GO composite coatings in the solution of 0.9 wt. % have been systemically investigated. According to the experimental results, HA-GO-Y₂O₃ composite coating had displayed superior performance of corrosion prevention in 0.9 wt. % NaCl solution. Considering the results of EIS, microstructures, the surface porosity and the RE metal oxide in the HA-GO composite coatings. Taking the roles of the formation of HA-GO-RE complexes in pores/cracks of HA-GO composite coatings at the composite coatings/ the Mg (OH) $_2$ film interface in the corrosion mediums into account , the precipitation of precipitated HA-GO-RE protective film is a reasonable explanation for the corrosion resistance of AZ91 Mg alloy. The experimental results manifested that the effects of the microstructures and porosity, the formation of HA-GO-RE complexes in pores/cracks and Cl⁻ concentration in NaCl solutions on improving corrosion resistance of AZ91 Mg alloy exhibited obviously synergistic effects.

Keywords: Magnesium alloy; HA-GO; Rare earth (RE) metal oxide; Corrosion resistance

1. INTRODUCTION

As advanced lightweight and potential biodegradable materials, magnesium (Mg) alloys have attracted great attentions and been widely used in bone implant and regeneration [1-3] in recent years. However, Mg alloys are prone to corrosion in the corrosion mediums due to low potentials, thus restraining their widespread applications. In order to increase the anti-corrosion ability of Mg alloys, several methods have been developed to prevent Mg alloys, including homogenization [4], alloying [5,6] and doping rare metals [7]. However, these methods cannot effectively control galvanic corrosion. On the other hand, many surface treatments are applied to prepare protective coatings on the Mg alloy

substrates, so as to inhibit the contact of the corrosion solution and Mg alloys. Previous studies have revealed that HA/GO composite coatings can effectively increase the corrosion resistance of Mg alloys [8,9].

Recently, rare earth (RE) elements were considered to promote the corrosion resistance and mechanical properties of magnesium alloys [10,11], thus introducing graphene oxide (GO)-metal oxide nanocomposite coatings, because when metal oxide particles were added to the GO matrix, the porosity could decrease and the performance obtained by GO-metal oxide is different from the performance exhibited by each individual component [12]. According to its intrinsic properties, rare earth metal oxides have the advantages of higher chemical absorption capacity, higher thermal stability, lower toxicity, and lower cost, compared with most other metal oxides. The addition of yttrium (Y) element to the metal can improve its strength and ductility [13-15]. Due to the addition of Y, the WE43 alloy containing 4wt.% Y provides excellent corrosion resistance. In vitro experiments [16] proved that the Y element in magnesium alloy has no obvious toxicity to osteoblasts. Adding a small amount of active elements, such as Y, Ce, La, etc. to the coating can refine the grain size of the coating, improve the brittleness of the coating, and accordingly reduce the oxidation rate and improve the adhesion of the oxide layer [17,18]. Guo et al. [19] research illustrated that SiY co-deposition coating has good oxidation resistance at high temperatures. Furthermore, the addition of yttrium oxide improves the sintering characteristics and plasticity of the oxide, and reduces the stress in the scale [20]. On the other hand, yttrium oxide nanoparticles have good chemical stability and are not easily corroded by corrosive liquids, thereby achieving good corrosion resistance.

 Y_2O_3 was used as an additive for bone repair materials because its mechanical properties are similar to those of natural bone. Hydroxyapatite (HAP) powder mixed with Y_2O_3 can enhance the density and mechanical properties of HAP, and can be used as a promising material for bone regeneration and reconstruction in bone tissue engineering. The production and utilization of Y_2O_3 have developed rapidly, which has also caused serious concerns about the hazards and effects on human health. Therefore, it is important to understand the biological interaction and biocompatibility based on Y_2O_3 -NPs [21]. Moreover, in the GO/yttrium oxide nanocomposite, graphene oxide is used as a high-performance carrier, and metal oxides are dispersed on the graphene oxide. The charge transfer at the interface of these hybrid materials can exhibit synergistic effects to induce characteristics that are different from the individual components and improve the corrosion resistance of the composite coating.

Mg alloys are used as medical implants or structural components in the different corrosion mediums, such as medical implants immersed in body fluid environments and structural components affected in the seashore atmosphere. To investigate the influences of the different corrosion mediums on the corrosion protection of AZ91 Mg alloy and coated Mg alloys are in favor of the further understanding of the corrosion mechanism of the HA-GO-RE composite coatings.

In this paper, doping rate earth metal oxides in HA/GO composite coatings electrophoretic deposited on Mg alloys were studied with regard to their electro-chemical corrosion behavior in 0.9wt. % NaCl. The corrosion of Mg alloys is a major threat to biodegradable materials. The morphology and electro-chemical corrosion tests of HA-GO-RE composite coatings after 600 s of exposure in the solution of 0.9 wt. % were carried out. Additionally, the effect RE elements to GO on the morphology and corrosion characteristics of HA-GO composite coatings were investigated.

2. EXPERIMENTAL

2.1. Sample preparations

In this work, AZ91 Mg alloy (with a size of $20 \times 20 \times 3$ mm) was used as the substrate. The substrates were mechanically ground with SiC sandpapers from 180 to 2000 grits before the coatings electrophoretic deposited on Mg alloy substrate. Subsequently, they were then degreased with alkaline solution, and ultrasonically cleaned in ethanol and deionized water, and then dried in ambient air.

2.2. Preparation of composite coatings

GO was manufactured using the modified Hummers method [22]. Rare earth (RE) oxide and HA-GO suspensions were prepared by magnetically stirring in 50 mL of isopropanol solution. Before EPD, the suspensions were vigorously stirred for 10 min and followed by sonicated for 1 h. The as-prepared HA-GO composite coatings were denoted as HA-GO, HA-GO-La₂O₃, and HA-GO-Y₂O₃, respectively.

EPD was carried out by applying electric field between a stainless-steel electrode (as anode) and a Mg alloy (AZ91) substrate (as cathode). The distance between the electrodes was 2 cm. During EPD, the suspension was conducted under continuous stirring using a magnetic stirrer and a constant voltage of 150 V (deposition time was 120s) was applied between the two electrodes at room temperature. Sonicating was used to help disperse powder and reduce the agglomeration of HA and GO suspensions. After EPD, the composite coatings were removed from the cell and dried 70°C for 3 hours.

2.3. Characterization

The phase composition and surface morphological characterizations of AZ91 Mg alloy and coated specimens were determined with X-ray diffraction (XRD) and scanning electron microscope (SEM). The structural and chemical composition of AZ91 Mg alloy and coated specimens were analyzed with Fourier transform infrared (FT-IR) spectroscopy in the region of 4000–400 cm⁻¹.

The corrosion resistant properties of AZ91 Mg alloy and coated specimens were evaluated by using CHI650C electrochemical workstation in 0.9 wt.% NaCl. A classical three-electrode system consisting of a platinum plate served as counter electrode, a saturated calomel electrode (SCE) reference electrode was reference electrode, and AZ91 Mg alloy and coated specimens were used as working electrode with the exposed area of 1 cm². Prior to start electrochemical tests, the working electrode was immersed in 0.9 wt% NaCl to assure the open circuit potential (OCP) was stable. EIS measurements were scanned from 0.01 Hz to 100 kHz using a signal with an amplitude of 1 mV. The experimental impedance plots were fitted by equivalent circuits using the Zview software. Each electrochemical measurement was repeated three times to assure the reproducibility.

3. RESULTS AND DISCUSSION

3.1. Phase composition analysis

Figure 1 shows the XRD patterns of HA-GO composite nanopowders doped with different rare metal oxides. In the XRD pattern of HA-GO-La₂O₃ composite nanopowders, new phases La (PO₃)₃ and La₂O₂CO₃ appeared. The transformation of light lanthanide nanoparticles (La₂O₃) was led to the formation of "sea urchin"-like structures, manifested as needle-like protrusions [23], and attached to the surface of GO/HA to fill the holes among the coatings. Theoretically, the formation of new substances can improve the corrosion resistance of HA-GO composite coatings, as displayed in figure 1(b). In the XRD pattern of the HA-GO-Y₂O₃ composite nanopowder, a new phase Y(PO₃)₃ appears. Y₂O₃ and HA form a disordered network structure, which can be seen from the three-dimensional structure of Y(PO₃)₃. In the coating, Y(PO₃)₃ particles can act as physical barriers [24], which can improve the density of the composite coating and reduce the penetration of corrosion ions. Theoretically, the formation of new substances 1(c).



Figure 1. XRD patterns of the HA-GO composite nanopowders with different RE elements: (a) HA-GO, (b) HA-GO-La₂O₃, and (c) HA-GO-Y₂O₃.

3.2. FT-IR spectroscopy analysis of composite nanopowders

Fig. 2 illustrates FT-IR spectra of HA-GO, HA-GO-La₂O₃ and HA-GO-Y₂O₃ composite nanopowders. The absorption peak at 1620cm⁻¹ belongs to the absorption of water by the C=C group or HA powder, which indicates the presence of GO in the composite nanopowder. The absorption peak at 1040 cm⁻¹ was related to the PO_4^{3-} group. The characteristic peaks at 560cm⁻¹ and 600cm⁻¹ were correlated with the O-P-O asymmetric bending vibration of the PO_4^{3-} group. It can be found that in the crystal structure of HA, the absorption peak near 3553 cm⁻¹ was assigned to the -OH group [25-27]. Compared with the FT-IR spectrum of HA-GO composite nanopowders, sharp peaks were observed at 860cm⁻¹, 1460cm⁻¹, 1520cm⁻¹ and 1620cm⁻¹, which belong to the tensile vibration of La-O bond [28,29], thus confirming the formation of the La₂O₃ phase.



Figure 2. FT-IR spectra of the HA-GO composite nanopowders with different RE elements: (a) HA-GO, (b) HA-GO-La₂O₃, and (c) HA-GO-Y₂O₃.

3.3. Morphological features of the composite coatings

Fig.3 demonstrated surface morphological characterizations of HA-GO, HA-GO-La₂O₃ and HA-GO-Y₂O₃ composite coatings with different RE oxide contents. The surface morphology of the HA-GO composite coating doped with different RE oxides (a) (b) HA-GO composite coating (a: ×1000, b: ×10000), (c) (d) HA-GO-La₂O₃ composite coating (c: ×1000, d: ×10000), (e) (f) HA-GO-Y₂O₃ composite coating (e: ×1000, f: ×10000). The overlapping flakes, and wrinkles of the GO flakes were observed, which is related to the van der Waals force and π - π interaction among the GO flakes, and there

are Smaller HA particles. HA-GO composite coating has larger surface layers and more gaps between two layers, as shown in Fig.3 (a) and (b). Compared with HA-GO composite coating, it can be seen that there are more particles in HA-GO-La₂O₃ composite coating, as displayed in Fig.3 (c) and (d). The transition between lanthanide nanoparticles (La₂O₃) led to the formation of "sea urchin"-like structures. The surface of the HA-GO-Y₂O₃ composite coating with Y₂O₃ being added is more uniform, and the gap between the two layers is reduced, thus making the coating more dense, as shown in Fig3.(e) and (f). Y₂O₃ forms a disordered network structure with HA and covers the surface of the composite coating, thereby reducing the gaps and forming a more uniform and less porous composite coating. Theoretically, the network structure improves the corrosion resistance of the HA-GO composite coating.



Figure 3. SEM images of the surface morphology of HA-GO composite coatings with different rare metal oxide: (a) (b) HA-GO (a: ×1000, b: ×10000), (c) (d) HA-GO-La₂O₃ (c: ×1000, d: ×10000), (e)(f) HA-GO-Y₂O₃ (e: ×1000, f: ×10000)

Some HA crystals agglomerated were observed. However, as an increase in RE oxide, the presence of RE oxide caused the reduction in the size of HA-GO particles, thus resulting in the surface of

the composite coating that trended to become more compact and intact. Obviously, Figs. 3(e) and (f) illustrate a much smaller particle size and more compact composite coating. The particle size of HA is further decreased to less than 500 nm with the increase of RE oxide, as shown in Fig. 3(e,f). Obviously, the decrease of particle size of HA would also decrease the pores/cracks of the composite coating. As it is evident from Fig. 3, the sizes of the micro-pores in the HA-GO composite coatings are significantly reduced with the increase of RE oxide. Meanwhile, the pores gradually become smaller, as shown in Figs. 3(c-f). Furthermore, the addition of RE oxide to the HA-GO composite coating could functionalize as reinforcement network, thus making the HA-GO-RE composite coatings more compact than HA-GO composite coating. This uneven surface, compared with the clean and smooth surface of the HA-GO composite coating, indicates that the adsorption of HA RE oxide remarkably affected the surface morphology and corrosion resistant of the HA-GO composite coatings.

3.4. Electrochemical corrosion behaviors of composite coatings

The short-time corrosion behaviors of AZ91 Mg alloy and coated specimens in corrosive electrolytes were further investigated adopting electrochemical impedance spectroscopy (EIS) methods. The EIS Nyquist plots and Bode plots of AZ91 Mg alloy and coated specimens in 0.9 wt.% NaCl solutions are displayed in Figs. 4. The equivalent circuit is applied to fit the plots, as shown in Fig. 5 and Fig. 6.

Fig.4 (a) exhibited the Nyquist plots of AZ91 Mg alloy and coated specimens in 0.9 wt.% NaCl solution. It can be observed that AZ91 Mg alloy is characterized by two capacitive loops: One is attributed to the defect capacitance such as pores/cracks of the layer of corrosive products, and another one is associated with the capacitance of the layer of corrosive products/Mg alloy substrate interface. The low frequency inductive loop is attributed to occurring pitting corrosion on the surface of AZ91 Mg alloy substrate.

In general, the larger radii of high frequency capacitance loops suggested a noticeable enhancement of corrosion resistance of the coated specimens. Compared with the radii of high frequency capacitance loops in Figs. 4(a), it can be seen that, with the increase of RE elements additive, the radius of the semicircle in Nyquist plot increased, and reached a maximum when the Y_2O_3 was added. The HA-GO- Y_2O_3 composite coating showed the largest radius of capacitance loops, indicating the best corrosion resistance among all the specimens in the solution of 0.9 wt.% NaCl.

Similarly, the same tendency was observed in the Bode impedance plot as well, as showed in Fig. 4. The values of the impedance modulus at 0.1 Hz are often used to estimate the overall anti-corrosion resistance of the coatings. All coatings show a higher value of $|Z|_{0.1}$ than AZ91 Mg alloy (1007 Ω .cm²). The $|Z|_{0.1}$ Hz value of HA-GO, HA-GO-La₂O₃ and HA-GO-Y₂O₃ composite coatings are 1920 Ω .cm², 4098 Ω .cm² and 5121 Ω .cm², respectively. All coatings display a higher value of –Phase (°) than AZ91 Mg alloy (50 °). The –Phase (°) value of HA-GO-Y₂O₃ composite coatings is the highest (72°). According to the results of EIS measurements, the impedance moduli of AZ91 Mg alloy and coated specimens decrease as HA-GO-Y₂O₃> HA-GO-La₂O₃> HA-GO composite coating > AZ91 Mg alloy.



Figure 4. (a) Nyquist plots, (b) Bode plots (|Z|) and (c)Bode plots (Phase) of different specimens in 0.9 wt.% NaCl solutions.

To further understand the electrochemical corrosion behavior of AZ91 Mg alloy and coated specimens, the obtained Nyquist plots were analyzed using the equivalent circuits' model. Taking into account the micro structural features and chemical heterogeneities of AZ91 Mg alloy and coated specimens (shown in Fig. 3), and the typical EIS plots (shown in Figs. 4), EIS equivalent circuits were provided as shown in Fig. 5. The fitting curves and corresponding circuits are presented in Figs.6, and fitting parameters are listed in Tables 1. In the proposed equivalent circuits, R_s represents the solution resistance, and R_{coat} and R_{cp} correspond to the coating resistance and the defects resistance (such as pores/cracks of coated specimens or the layer of corrosive products), respectively. The time constant (CPE_{cf}-R_{cf}) is associated with the layer of corrosive products at the electrolyte solution/Mg alloy substrate surface or the coating/ the layer of corrosive products interface. The inductive behavior is characterized by resistance R_L and inductance L, suggesting the onset of pitting corrosion. Inductance L is related to relaxation processes due to the dissolution of Mg that causes to form loose corrosive products on Mg alloy substrate surface or the relaxation reaction of the precipitated protective film in pores/cracks of HA-GO composite coatings at the coating/ the layer of corrosive products interface. In this present paper, CPE, replacing the capacitor (C), is due to the defects in the coating, such as pores/cracks [30].

As for the coated specimens in the low Cl^{-} concentration of 0.9 wt.% NaCl solution, it can be observed from Table 1 that the R_{cf} values of all coated specimens were found to increase with the increase of RE elements, due to the decrease in the porosity of the loose $Mg(OH)_2$ corrosive products,

and consequently a decrease in penetration through the corrosive products by the addition of RE elements to the HA coating. Furthermore, with the addition of RE elements, both the values of R_{coat} and R_{cp} were significantly increased. The increase of R_{cp} revealed that corrosion paths were reduced. It was obvious that the value of R_{cp} was higher than that of R_{cf} , suggesting that precipitated protective film in pores/cracks of HA-GO composite coatings at the coating/ the layer of corrosive products interface was more corrosion resistant than adsorbed loose corrosive products at the electrolyte solution/Mg alloy substrate surface. Thereby, the precipitated protective film in pores/cracks of HA-GO composite coatings resistance.

Yu et al. [31] observed that graphene layers accelerated the rate of the corrosion rate because of the formation of a galvanic coupling between the graphene layer and the aluminum alloy substrate. The influence of the Cl⁻ concentration was more apparent for the aluminum alloy compared with AZ91 Mg alloy. Adding RE elements to the HA-GO coating can further improve corrosion protection of AZ91 Mg alloy, which was possibly associated with the functionalities of the RE elements as reinforcement network, thus leading to the formation of a compact and tightly adhered HA-GO-RE composite coatings. What's more, it can be explained by the possibility that it could also be due to the deprotonation of carboxyl groups (-COOH) and enolic and phenolic groups (-OH) on the GO sheets, which enhanced the interaction between the GO and Mg ions in NaCl solution and formed HA-GO-RE complexes. The HA-GO-RE complexes acted as a filler provide locking effects between the micro-pores/cracks presented in the HA-GO composite coatings and loose Mg (OH)₂ film. In the present study, the obtained results on corrosion can be further discussed based on the formation of HA-GO-RE complexes combined with the microstructure of SEM observation and XRD, FTIR and EIS analyses of AZ91 Mg alloy and coated specimens. More details on the protection mechanism of HA-GO composite coatings have been presented in the following sections. The value of R_{cp} is one of the most relevant to evaluate the corrosion protection of the HA-GO composite coatings, because the precipitated protective film gave a prominent corrosion protection besides the sizes of the pores/cracks in the composite coatings. These observations manifested that the effects of microstructures and porosity in NaCl solutions on improving corrosion resistance of AZ91 Mg alloy exhibited obviously synergistic effects. The above results implied that the excellent corrosion resistance is supplied by a higher density and compaction of the HA-GO-RE composite coatings as a result of filling up the micro-pores.



Figure 5. The equivalent electrical circuit by simulation of EIS for analysis of different specimens.



Figure 6. EIS fitting plots of different specimens in 0.9 wt.% NaCl solution. (a) AZ91 Mg alloy; (b) HA-GO composite coating; (c) HA-GO-La₂O₃ composite coating; (d) HA-GO-Y₂O₃ composite coating

Table 1. Electrochemical data obtained via equivalent circuit fitting of the EIS curves of different specimens in 0.9 wt.% NaCl solution.

Samples	Mg alloy	HA-GO	HA-GO-La ₂ O ₃	HA-GO-Y ₂ O ₃
$R_s(\Omega cm^2)$	52.7	169.2	69.84	31.69
$R_{coat}(\Omega \cdot cm^2)$	/	4591	5121	5951
$C_{coat}(\Omega^{-1} \cdot s^{n} \cdot cm^{-2})$	9.79×10 ⁻⁶	3.30×10 ⁻⁶	8.63×10 ⁻⁶	6.04×10 ⁻⁶
$R_{cp}(\Omega cm^2)$	948	4706	6919	8286
$C_{cp}(\Omega^{-1} \cdot s^{n} \cdot cm^{-2})$	/	3.60×10 ⁻⁷	3.34×10 ⁻⁷	6.77×10 ⁻⁷
$R_{cf}(\Omega cm^2)$	195	673.8	1824	2949
$C_{cf}(\Omega^{-1} \cdot s^{n} \cdot cm^{-2})$	5.78×10 ⁻⁵	2.01×10 ⁻⁶	5.42×10 ⁻⁶	1.75×10 ⁻⁶
$R_L(\Omega cm^2)$	151	933.5	2804	6196
L	28.56	156.1	268.0	512.1
$R_T (\Omega cm^2)$	1346	11073.5	16737.84	23413.69
η/%	/	89.5	92.0	94.3
$ Z (\Omega cm^2)$	1007	1920	4098	5121

In order to further in vitro and in vivo studies are required for a better understanding of the corrosion resistance of Mg alloys with and without surface composite coatings for applications, we compared it with that composite coatings reported in the relative references [32-40]. As shown in Table

2, the reported works of different coatings on AZ31 Mg alloy and AZ91 Mg alloy, including coating techniques and the electrolytes.

Table 2. Reported works of different coatings on	AZ31 Mg alloy and AZ91 Mg alloy, including coating
techniques and the electrolytes.	

Ref.	Alloys	Coating technique	Electrolyte	Coating type
[32]	AZ31 Mg alloy	micro-arc oxidation (MAO)	Na ₃ PO ₄ , NaOH ,CaCO ₃ , GO	HA/GO and MAO
[33]	AZ91 Mg alloy	biomimetic method	NaOH , PO4 ³⁻ , Ca ²⁺ ,GO	HA/GO-1d、 HA/GO-2d
[34]	AZ31 Mg alloy	spin coat	Ca-EDTA, KH ₂ (PO ₄) ₃	HA-GO
[35]	AZ31B Mg alloy	hydrothermal treatment	Ca(NO ₃) ₂ ·4H ₂ O , KH ₂ PO ₄ ·3H ₂ O,GO	rGO x/Apatite
[36]	Mg alloys	Electrophoretic deposition	HapNP , graphene oxide,KOH	GO/HapNP
[37]	AZ91 Mg alloy	Electrophoretic deposition	$(Ca(NO_3)_2 .4H_2O, P_2O_5, C_2H_5OH, HPF_6)$	FHAp-MAO
[38]	AZ31 Mg alloy	plasma electrolytic oxidation	Na ₃ PO ₄ .12H ₂ O, KOH, hydroxyapatite powder, triethanolamine and ethylene glycol	MgO/HA
[39]	AZ91 Mg alloy	electrophoretic deposition	Sodium alginate, nano-titania(n-TiO ₂), ethanol and water	TiO ₂ /alginate
[40]	AZ91 Mg alloy	Electrophoretic deposition	Ca(NO ₃) ₂ .4H ₂ O, P ₂ O ₅ , C ₂ H ₅ OH	MgF2/n-HAp , MAO/n-HAp

4. CONCLUSIONS

It must be noted that the mechanism discussed above is a reasonable explanation for short exposure times. In summary, the electrochemical corrosion results discussed demonstrated that the corrosion protection of HA-GO coated AZ91 Mg alloy in NaCl solutions was also strongly controlled by Cl⁻ concentration and was also obviously dependent on microstructures, the surface porosity, the GO content in the HA-GO composite coatings and the formation of HA-GO-RE complexes in pores/cracks. The main conclusions are as follows:

(1) The microstructure of HA-GO composite coating with RE elements being added was uniform, and, as an increase in Y_2O_3 , the presence of Y_2O_3 caused reduction in the sizes of HA-GO particles, thus resulting in that the surface of the composite coating trended to become more compact and intact.

(2) Compared with HA-GO composite coating, it can be seen that there are more particles in HA-GO-La₂O₃ composite coating. The transition between lanthanide nanoparticles (La₂O₃) led to the formation of "sea urchin"-like structures. The surface of the HA-GO-Y₂O₃ composite coating with Y₂O₃ being added was more uniform, and the gap between two layers was reduced, thus making the coating

more dense because Y_2O_3 formed a disordered network structure with HA and covered the surface of the composite coating, thereby reducing the gaps and forming a more uniform and less porous composite coating. The network structure improves the corrosion resistance of the HA-GO composite coating.

(3) With the increase of RE elements, the radius of the semicircle in Nyquist plot increased, and reached a maximum when Y_2O_3 was added. According to the results of EIS measurements, the impedance moduli of AZ91 Mg alloy and coated specimens decreased as HA-GO- Y_2O_3 > HA-GO-La₂O₃> HA-GO composite coating > AZ91 Mg alloy, indicating the best corrosion resistance among all the specimens in the solution of 0.9 wt.% NaCl.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (51271111).

References

- 1. B. Manne, H. Thiruvayapati, S. Bontha, R. M. Rangarasaiah, M. Das and V. K. Balla, *Surf. Coat. Technol.*, 347 (2018) 337-349.
- J. Li, Y. Song, S. Zhang, C. Zhao, F. Zhang, X. Zhang, L. Cao, Q. Fan and T. Tang, *Biomater.*, 31 (2010) 5782-5788.
- 3. N. Hort, Y. Huang, D. Fechner, M. Stormer, C. Blawert, F. Witte, C. Vogt, H. Drücker, R. Willumeit, K. U. Kainer and F. Feyerabend, *Acta Biomater.*, 6 (2010) 1714-1725.
- 4. R. Shi, J. Miao and A. A. Luo, Scr. Mater., 171 (2019) 92-97.
- 5. J. Zhao, B. Jiang, Y. Yuan, A. Tang, Q. Wang, T. Yang, G. Huang, D. Zhang and F. Pan, *Mater. Sci. Eng.*, *A.*, 785 (2020) 139344.
- Y. Wu, Y. Wang, S. Tian, Y. Jing, J. Zhuang, L. Guo, D. Jia and Y. Zhou, *Appl. Surf. Sci.*, 470 (2019) 430-438.
- 7. H. Kwak and S. Chaudhuri, J. Alloys Compd., 509 (2011) 8189-8198.
- 8. Z. Zhou, B. Zheng, Y. Gu, C. Shen, J. Wen, Z. Meng, S. Chen, J. Ou and A. Qin, *Surf. Interfaces*, 19 (2020) 100501.
- 9. M. Zhang, S. Cai, S. Shen, G. Xu, Y. Li, R. Ling and X. Wu, J. Alloys Compd., 658 (2016) 649-656.
- 10. A. S. Hamdy and D. P. Butt, *Electrochim. Acta*, 108 (2013) 852-859.
- 11. D. Liu, D. Yang, X. Li and S. Hu, J. Mater. Res. Technol., 8 (2019) 1538-1549.
- 12. B. G. Ghule, N. M. Shinde, S. D. Raut, S. F. Shaikh, A. M. Al-Enizi, K. Ho. Kim and R. S. Mane, J. Colloid Interface Sci., 589 (2021) 401-410.
- 13. S.Y. Qian, Z. H. Xu, H.N. Xie, C. S. Shi, N. Q. Zhao, C .N. He and E. Z. Li, *Appl. Surf. Sci.*, 533 (2020) 147489.
- 14. K. Kakehi, S. Banoth, Y. Kuo and S. Hayashi, Scr. Mater., 183 (2020) 71-74.
- 15. CH. S. Vidyasagar and D. B. Karunakar, Trans. Nonferrous Met. Soc. China, 30 (2020) 288-302.
- 16. X. N. Gu, Y. F. Zheng, Y. Cheng, S. P. Zhong and T. F. Xi, Biomater., 30 (2009) 484-498.
- 17. W. H. Yu, J. Tian, W. Tian, J. Zhao, Y. Q. Li and Y. Z. Liu, J. Rare Earths, 33 (2015) 221-226.
- 18. P. Zhang and X. P. Guo, Surf. Coat. Technol., 206 (2011) 446 454.
- 19. Y. Q. Li, F. Q. Xie, X. Q. Wu and X. Li, Appl. Surf. Sci., 287 (2013) 30-36.
- 20. R. J. Chrstensen, V. K. Tolpygo and D. R. Clarke, Acta Mater., 45 (1997) 1761-1766.
- 21. S. Yang, G. Li and Y. Wang, Microchim. Acta, 183 (2016) 1351–1357.
- 22. M. V. Jaime, J. A. A. Orozco, C. E. D. Ascencio, A. L. S. Robles, M. M. Rosales, A. S. Robles and S. C. Andrade, *J. Environ. Chem. Eng.*, 8 (2020) 104416.

- 23. S. Bernal, F. J. Botana, R. García and J. M. Rodríguez-Izquierdo, React. Solids, 4 (1987) 23-40.
- 24. R. Li, Z. Ji and C. H. Chang, ACS NANO, 8 (2014) 1771-1783.
- 25. C. Wen, X. Zhan, X. Huang, F. Xu, L. Luo and C. Xia, Surf. Coat. Technol., 317 (2017) 125-133.
- 26. B. Ramachandran, S. Chakraborty, R. Kannan, M. Dixit and V. Muthuvijayan, *Carbohydr. Polym.*, 206 (2019) 132-140.
- 27. M. Li, Q. Liu, Z. Jia, X. Xu, Y. Shi, Y. Cheng, Y. Zheng, T. Xi and S. Wei, *Appl. Surf. Sci.*, 284 (2013) 804-810.
- 28. S. Shanavas, A. Priyadharsan, K. Dharmaboopathi, I. Ragavan, C. Vidya and P. M. Anbarasan, *ChemistrySelect*, 3 (2018) 12841–12853.
- 29. S. Jayapandi, P. Packiyaraj, S. Premkumar, J. Mayandi, and K. Anitha, *Ionics*, 23 (2017) 2909–2917.
- 30. S. R. Fardi, H. Khorsand, R. Askarnia, and R. Pardehkhorram, *Ceram. Int.*, 46 (2020) 18297-18307.
- 31. F. Yu, L. Camilli, T. Wang, D. M. A. Mackenzie, M. Curioni and R. Akid, *Carbon*, 132 (2018) 78-84.
- 32. C. Wen, X. Zhan, X. Huang, F. Xu, L. Luo and C. Xia, Surf. Coat. Technol., 317 (2017) 125 133.
- 33. F. Gao, C. Xu, H. Hu, Q.Wang, Y. Gao, H. Chen, Q. Guo, D. Chen and D. Eder, *Mater. Lett.*, 138 (2015) 25 28.
- 34. F. Peng, D. Zhang, D. Wang, L. Liu, Y. Zhang and X. Liu, Mater. Lett., 264 (2020) 127322
- 35. Y. Wu, Y. Wang, S. Tian, Y. Jing, J. Zhuang, L. Guo, D. Jia and Y. Zhou, *Appl. Surf. Sci.*, 470 (2019) 430 438.
- 36. C. Santos, C. Piedadea, P. J. Uggowitzer, M. F. Montemor and M. J. Carmezim, *Appl. Surf. Sci.*, 345 (2015) 387 393.
- 37. R. Rojaeea, M. Fathi, K. Raeissic and A. Sharifnabi, Ceram. Int., 40 (2014) 15149 15158.
- 38. D. Sreekanth and N. Rameshbabu, Mater. Lett., 68 (2012) 439 442.
- 39. L. Cordero-Arias, A. R. Boccaccini and S. Virtanen, Surf. Coat. Technol., 265 (2015) 212 217.
- 40. R. Rojaee, M. Fathi and K. Raeissi, Appl. Surf. Sci., 285P (2013) 664 673.

© 2021 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).