

Short Communication

Properties of AZ91D magnesium alloy Anodized in Oxalic and Sulfuric Acids and its corrosion resistance in 3.5% NaCl solution

Tongyin Chen¹, Qingyu Zhang², Jianghuan Shi², Qiong Wu^{1,*}

¹ Materials and chemistry college, China Jiliang University, HangZhou city, China, 310018;

² Institute of Measurement and Testing, Ningbo, China, 315000;

*E-mail: qiongw_mater@yeah.net

Received: 18 September 2022 / Accepted: 26 October 2022 / Published: 17 November 2022

In the article, the AZ91D magnesium alloy was anodized to dramatically enhance its chemical and physical properties. The thickness, hardness, roughness, surface morphology and corrosion resistance of anodized magnesium alloy was investigated. The hardness of AZ91D magnesium alloy is extremely increased after anodizing treatment. The anodized magnesium prepared in oxalic acid solution is the thinnest and has the smallest roughness while the anodized magnesium obtained in sulfuric acid solution is the thickest and possesses the largest surface roughness. The surface morphology of anodized magnesium alloy is porous structure. It was discovered that the anodized magnesium prepared in oxalic and sulfuric acid solutions had a homogeneous porous surface with the maximum hardness and charge transfer resistance, resulting in the best corrosion resistance.

Keywords: AZ91D magnesium alloy; Corrosion resistance; anodizing treatment;

1. INTRODUCTION

With the progress of science and technology, automobiles have become an indispensable transportation tool for our life. The traditional material for automobile is high strength steel, copper plate and so on. Although many surface treatments can be used to improve physical and chemical properties of materials, steel and copper materials add a lot of weight to the automobile [1-4]. Aluminum alloys possess advantages of light weight, high strength and good plasticity. Anodic oxidation technology has been reported by many researchers that can greatly improve corrosion resistance and mechanical performance of aluminum alloys to meet the requirement of automobile industry [5-8]. Compared with aluminum alloy, magnesium alloy is a kind of better light alloy. The density of magnesium alloys is only 60% of pure aluminum and 25% of steel, which is close to the engineering plastic. In addition to light weight, magnesium alloys also have the advantages of strong thermal conductivity, high strength, better ductility and so on.

Anodizing technology can be used to improve corrosion resistance and mechanical performance of magnesium alloys which has been reported in many literatures [9-11]. Magnesium alloy can be anodized in sulfuric acids, oxalic acid, chromic acid and so on. In recent years, it has been found that the magnesium alloy anodized in mixed acid solutions possesses better chemical and physical properties. Therefore, in this paper, oxalic acid mixed with sulfuric acid solutions were used to anodize the AZ91D magnesium to effectively improve the corrosion resistance and hardness. The influences of different oxidation technologies on roughness, thickness, hardness, surface morphology and corrosion resistance of magnesium alloy were investigated.

2. EXPERIMENTAL

2.1 Experimental materials and chemical agents

The composition of AZ91D magnesium alloy plate used in the experiment is 90% Mg, 1% Zn and 9% Al. The chemical agents used are 98% sulfuric acid and analytically pure oxalic acid. The concentration of sulfuric acid and oxalic acid is 200 g/L and 50 g/L respectively.

2.2 Experimental process

The AZ91D magnesium plate with 3 cm×4 cm dimension was the anode electrode while the pure lead plate was the cathode electrode. The magnesium plate was polished and immersed into different acid solutions to do the anodizing process for 1 hour at the condition of 3 A/dm² current density and 10 °C temperature. After the anodizing experiment, the samples were dried by a heat gun and analyzed.

2.3 Testing method

Metallomicroscope (AOSVI M303) was used to observe the cross section of anodized magnesium alloys to calculate the thickness. The surface profiler (MMD100A) was used to test the surface roughness of samples. Surface hardness of the anodized magnesium alloy was tested by Vickers hardness (HVC 1000JMT2) while the surface morphology of samples were observed by scanning electron microscope (Hitachi S3400N). The electrochemical station (CHI660E) was selected to test the AC impedance of anodized magnesium in 3.5 % sodium chloride at the condition of 10 mV amplitude from 100 kHz to 100 mHz. Charge transfer resistance of anodized magnesium based on equivalent circuit was calculated to evaluate the corrosion resistance. The potentiodynamic polarization curve was tested in 3.5 % sodium chloride at the condition of 1 mV/s scanning rate from -0.85 V to -0.55 V. The platinum (3 cm×3 cm) is anode, while the anodized magnesium (1 cm×1 cm) is cathode. Saturated calomel electrode is the reference electrode.

3. RESULTS AND DISCUSSION

3.1 Thickness of anodized AZ91D magnesium alloy

The oxidation process of magnesium alloy mainly includes the formation of magnesium oxide, accompanied by water electrolysis and hydrogen evolution. The oxidation process of magnesium alloy is similar to that of ordinary oxidation, but possesses different characteristics which have been reported in some published paper so far [12-14]. At the initial stage of oxidation, as the voltage increases sharply, a continuous and nonporous layer is formed on the anode with high resistance, known as the barrier layer. The current distribution on the surface of the barrier layer is not homogeneous, and local chemical dissolution occurs and pores are formed. With the increase of voltage, the pores gradually increase and form porous layer. When the voltage is increased further, the heat in the pores generates gas discharge and sparks, which leads to the destruction and breakdown of the layer resulting in anodized magnesium.

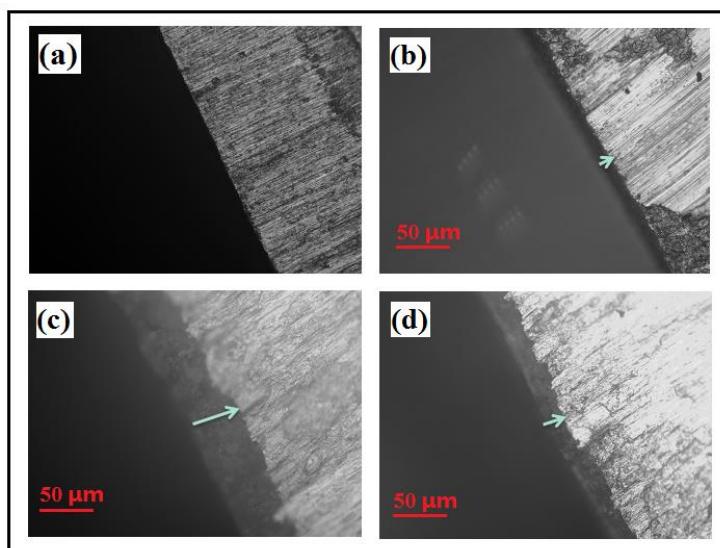


Figure 1. Thickness of anodized magnesium alloy prepared from different acid solutions; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid; Magnification 200 times;

The thickness of magnesium alloy anodizing is shown in figure 1. The thickness of magnesium alloy anodized from oxalic acid solution is minimum, which is about $15 \mu\text{m}$, because the acid of oxalic acid is weaker. However, the sample prepared from sulfuric acid possesses the maximum thickness equal to $48 \mu\text{m}$. Moreover, the thickness of anodized magnesium alloy fabricated from mixed acid solution is around $28 \mu\text{m}$. It knows that the oxalic acid in the mixed acid can reduce the corrosion ability of the solution and play a role of corrosion inhibition, so the thickness of the anodized magnesium is reduced.

3.2 Roughness of anodized AZ91D magnesium alloy

The outer layer of anodized magnesium alloy is porous. The corrosion resistance and mechanical properties of magnesium alloy are significantly improved after anodic oxidation treatment. Some researchers also study the corrosion resistance and mechanical performance of anodized magnesium alloys [15-17]. However, due to the porous structure, the pore size and porosity of the anodized magnesium alloys have a certain impact on the chemical and physical performance. For example, the effect of porosity on the corrosion resistance of materials is studied by some people [18-19]. Therefore, surface roughness of samples was tested by surface profiler to evaluate the density of anodized magnesium shown in figure 2 and table 1. The surface roughness of AZ91D magnesium alloy is only 0.1159 μm after polishing treatment. It is found out that anodizing treatment technology will increase the surface roughness of sample. Roughness of the anodized magnesium prepared from oxalic acid solution is 0.4387 μm while the anodized magnesium obtained from sulfuric acid solution has the largest roughness equal to 1.5480 μm . Oxalic acid is less acidic, so the porosity of formed porous layer is smaller, resulting in smaller roughness. The acid of sulfuric acid is relatively strong, and the dissolution of anodized magnesium is also relatively obvious, resulting in the increase of surface roughness. When oxalic acid is added into sulfuric acid oxidation solution, the corrosion rate of anodized magnesium can be slowed down during the oxidation process to reduce porosity and roughness.

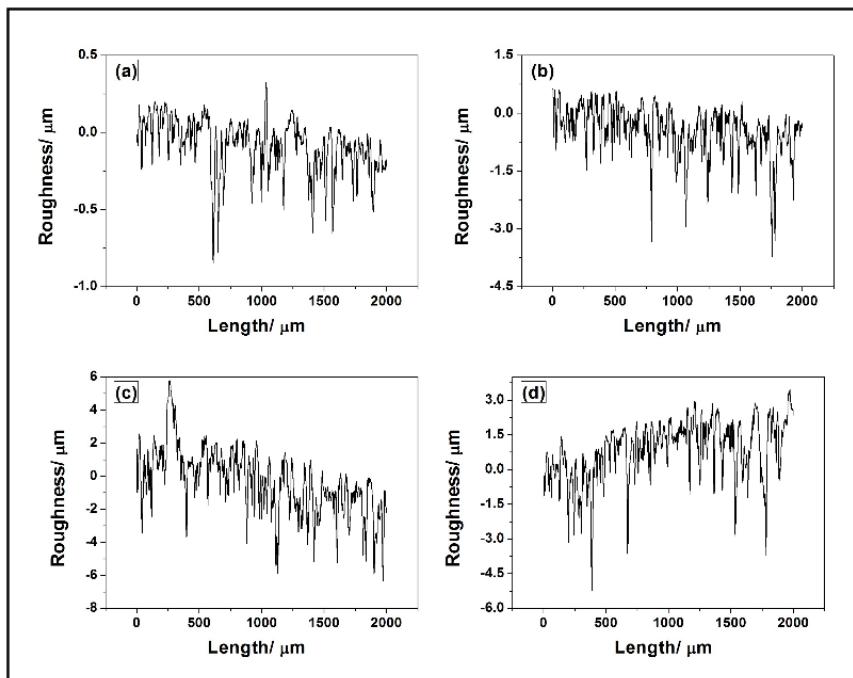


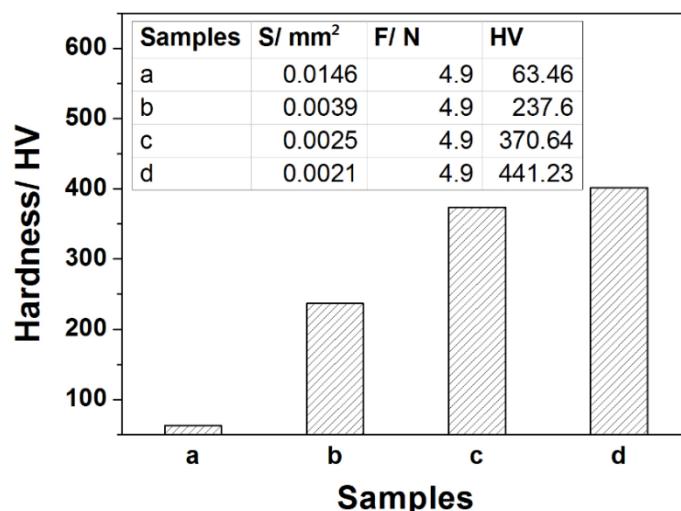
Figure 2. Roughness of anodized magnesium alloy prepared from different acid solutions; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid; Scanning length 2000 μm ; Scanning rate 50 $\mu\text{m}/\text{s}$; Sample frequency 100 Hz;

Table 1. Roughness of samples; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid;

Samples	Roughness/ μm
a	0.1159
b	0.4387
c	1.5480
d	0.8435

3.3 Hardness of anodized AZ91D magnesium alloy

Vickers hardness tester was used to test the surface hardness of magnesium alloy anodized from oxalic acid, sulfuric acid and mix acid solution respectively. Detail data is shown in figure 3. The hardness of AZ91D magnesium alloy without anodizing treatment is about 63.46 HV. Some ways to improve the hardness of AZ91D magnesium alloy are reported in some literatures [20-21]. After the anodizing treatment, the hardness of magnesium alloy increases obviously. The anodized magnesium alloy prepared from mixed solution with oxalic and sulfuric acid possesses the largest hardness 441.23 HV which is almost seven times larger than AZ91D magnesium alloy. After anodic oxidation treatment of magnesium alloy, the anodized magnesium consists of porous barrier layer and porous layer. Compared with ordinary anodic oxidation at lower voltage (lower than 20 V), anodic oxidation for magnesium alloy at higher voltage (higher than 50 V) has thicker barrier layer and porous layer with lower surface porosity, so it is more conducive to the improvement of surface hardness [22-25].

**Figure 3.** Hardness of anodized magnesium alloy prepared from different acid solutions; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid;

3.4 Surface morphology and corrosion resistance of anodized AZ91D magnesium alloy

In this section, the surface morphology and corrosion resistance of anodized magnesium alloy was investigated. Figure 4 shows the surface morphology of anodized magnesium alloy obtained from different acid solutions. According to figure 4(a), the surface of AZ91D magnesium is clear only with some scratches. After anodizing treatment, the surface of magnesium alloy becomes dark and rough. According to the magnified area of the surface morphology, many pores with different sizes could be observed on the surface of the anodized magnesium prepared from oxalic acid solution called porous layer which is also reported in some paper [26-31]. The sample obtained from sulfuric acid solution shows porous morphology with larger diameter. However, the pores on the surface of anodized magnesium alloy fabricated from mixed acid solution are more homogeneous. During the anodizing process of mixed acid solution, a small amount of oxalic acid will enter the pores of the anodized magnesium. When oxalic acid is oxidized into carbon dioxide and water, it plays a role in cooling and dilution to decrease the dissolution rate of anodized magnesium pores resulting in smaller pore size and roughness.

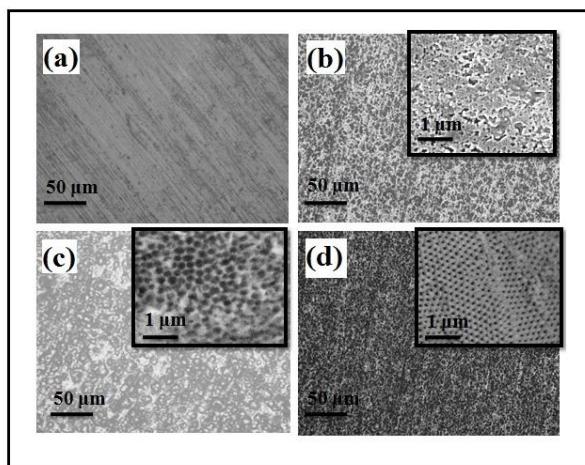


Figure 4. Surface morphology of anodized magnesium alloy prepared from different acid solutions; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid;

Figure 5 and figure 6 show the AC impedance and potentiodynamic polarization curves of magnesium alloy anodized from oxalic acid, sulfuric acid and mixed acid solution. The corrosion potential, corrosion current density and the charge transfer resistance are used to evaluate the corrosion resistance of samples. Figures 5 and figure 6 show that the charge transfer resistance and corrosion current density of magnesium alloy anodized from oxalic acid are $16975 \Omega\text{cm}^2$ and 31.622 A/cm^2 , respectively. The magnesium alloy anodized from sulfuric acid has larger charge transfer resistance and smaller corrosion current density that is around $31203 \Omega\text{cm}^2$ and $5.883 \mu\text{A/cm}^2$. It is reported that

larger charge transfer resistance is beneficial to improve corrosion resistance [32-33]. Although the sample anodized from sulfuric acid has the largest thickness, the surface porosity is large which is not conducive to improving the charge transfer resistance. However, the sample prepared from mixed acid solution has the largest charge transfer resistance and smallest corrosion current density indicating good corrosion resistance due to homogeneous surface porous structure.

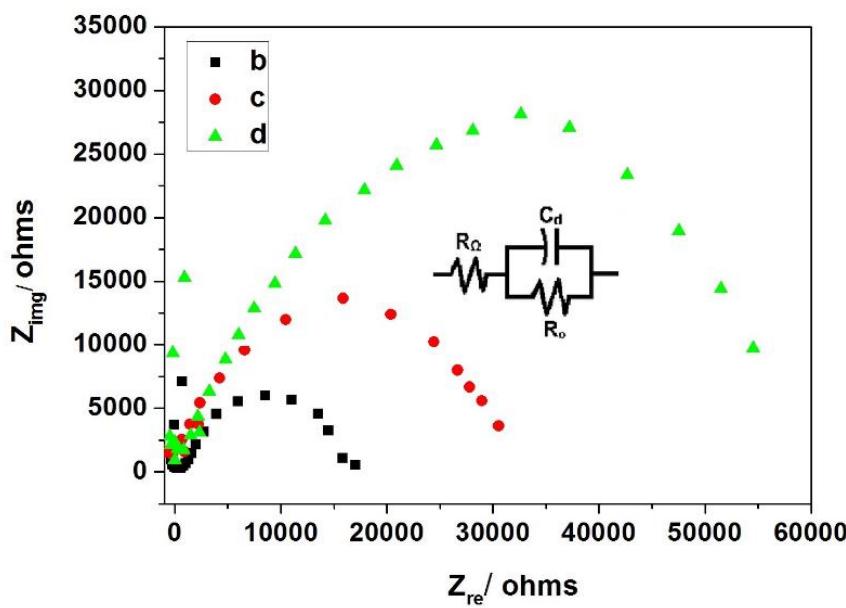


Figure 5. AC impedance of anodized magnesium alloy prepared from different acid solutions; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid; The AC impedance of anodized magnesium was tested in 3.5 % sodium chloride at the condition of 10 mV amplitude from 100 kHz to 100 mHz.

Table 2. Solution resistance and charge transfer resistance of samples; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid;

Sample	R_s/Ω	$R_c/\Omega\text{cm}^2$
b	206	16975
c	221	31203
d	263	53656

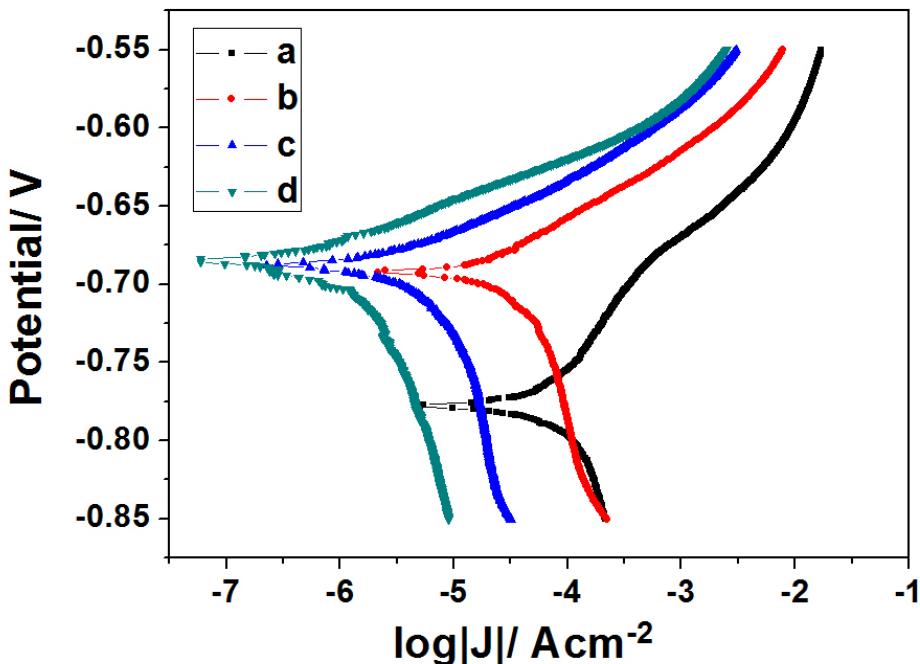


Figure 6. Potentiodynamic polarization curves of anodized magnesium alloy prepared from different acid solutions; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid; The potentiodynamic polarization curve was tested in 3.5 % sodium chloride at the condition of 1 mV/s scanning rate from -0.85 V to -0.55 V. The platinum (3 cm×3 cm) is anode, while the anodized magnesium (1 cm×1 cm) is cathode. Saturated calomel electrode is the reference electrode.

Table 3. Corrosion potential and corrosion current density of samples; a. magnesium alloy; b. magnesium alloy anodized from oxalic acid; c. magnesium alloy anodized from sulfuric acid; d. magnesium alloy anodized from mixed solution with sulfuric and oxalic acid;

Sample	E/ V	J/ μAcm^2
a	-0.908	79.433
b	-0.693	31.622
c	-0.685	5.883
d	-0.684	1.584

4. CONCLUSIONS

Anodic oxidation technology is used to anodize the AZ91D magnesium alloy to greatly improve its chemical and physical performance. It is found that anodic oxidation is more conducive to the improvement of surface hardness. The sample anodized from oxalic acid possesses the smallest thickness and roughness. However, due to the strong acid of sulfuric acid, the anodized magnesium

alloy prepared from sulfuric acid is the thickest and has largest surface roughness. It is found out that anodized magnesium prepared in oxalic and sulfuric acid shows homogeneous porous surface with largest hardness and charge transfer resistance resulting in greatest corrosion resistance.

References

1. X. S. Zhang, Q. Y. Wang, Y. R. Tang, H. C. Guo, Y. C. Xi, L. J. Dong and H. B. Zheng, *Int. J. Electrochem. Sci.*, 15 (2020) 11821.
2. S. Y. Chen, T. Liang, N. H. Wen, F. H. Liu, C. C. Tsao and C. Y. Hsu, *J. Saudi. Chem. Soc.*, 24 (2020) 704.
3. H. Tamagaki, K. Tsuji, T. Komuro, F. Kiyota and T. Fujita, *Surf. Coat. Tech.*, 54 (1992) 594.
4. L. G. Zhang, Q. M. Song, Y. Liu and Z. M. Xu, *Waste Manage.*, 108 (2020) 172.
5. J. G. Li, H. Y. Wei, K. Zhao, M. F. Wang, D. C. Chen and M. Chen, *Thin Solid Films*, 713 (2020) 138359.
6. H. S. Kim, D. H. Kim, W. Lee, S. J. Cho, J. H. Hahn and H. S. Ahn, *Surf. Coat. Tech.*, 205 (2010) 1431.
7. P. Zhang and Y. Zuo, *Mater. Chem. Phys.*, 231 (2019) 9.
8. X. W. Yu and G. Q. Li, *J. Alloy Compd.*, 364 (2004) 193.
9. P. Zhang, Y. Zuo and G. C. Nie, *J. Alloy Compd.*, 834 (2020) 155041.
10. Y. W. Song, K. H. Dong, D. Y. Shan and E. H. Han, *J. Magnesium Alloy*, 1 (2013) 82.
11. R. F. Zhang, *Corros. Sci.*, 52 (2010) 1285.
12. R. F. Zhang, S. F. Zhang, N. Yang, L. J. Yao, F. X. He, Y. P. Zhou, X. Xu, L. Chang and S. J. Bai, *J. Alloys Compd.*, 539 (2012) 249.
13. X. M. Wang, L. Q. Zhu, W. P. Li, H. C. Liu and Y. H. Li, *Appl. Surf. Sci.*, 255 (2009) 5721.
14. L. A. D. Oliveira, R. M. P. D. Silva, A. C. D. Rodas, R. M. Souto and R.A. Antunes, *J. Mater. Res. Technol.*, 9 (2020) 14754.
15. S. M. H. Mousavian and S. H. Tabaian, *Anti-Corros. Methods Mater.*, 69 (2022) 194.
16. K. Saranya, S. Bhuvaneswari, S. Chatterjee and N. Rajendran, *J. Magnesium Alloys*, 10 (2022) 1109.
17. N. A. Shirin, I. V. Roslyakov, M. V. Berekchiian, T. B. Shatalova, A. V. Lukashin and K. S. Napolskii, *Russ. J. Inorg. Chem.*, 67 (2022) 926.
18. H. L. Zhang, T. Kim, J. Swarts, Z. F. Yu, R. R. Su, L. F. Liu, W. L. Howland, G. Lucadamo and A. Couet, *Corros. Sci.*, 208 (2022) 110660.
19. M. Ghayebloo, M. T. Mostaedi and H. F. Rad, *Mater. Chem. Phys.*, 287 (2022) 126309.
20. W. X. Zhang, Z. H. Jiang, G. Y. Li, Q. Jiang and J. S. Lian, *Appl. Surf. Sci.*, 254 (2008) 4949.
21. N. S. Kumar and G. G. Sozhamannan, *Mater. Today.: Proc.*, 64 (2022) 95.
22. X. Y. Lu, X. G. Feng, Y. Zuo, P. Zhang and C. B. Zheng, *Prog. Org. Coat.*, 104 (2017) 188.
23. A. D. Forno and M. Bestetti, *Surf. Coat. Tech.*, 205 (2010) 1783.
24. R. F. Zhang, S. F. Zhang, Y. L. Shen, L. H. Zhang, T. Z. Liu, Y. Q. Zhang and S. B. Guo, *Appl. Surf. Sci.*, 258 (2012) 6602.
25. S. F. Zhang, R. F. Zhang, W. K. Li, M. S. Li and G. L. Yang, *Surf. Coat. Tech.*, 207 (2012) 170.
26. A. F. Yetim, *Surf. Coat. Tech.*, 205 (2010) 1757.
27. H. M. Mousa, K. H. Hussein, H. M. Woo, C. H. Park and C. S. Kim, *Ceram. Int.*, 41 (2015) 10861.
28. Y. H. Gao, A. Yerokhin and A. Matthews, *Surf. Coat. Tech.*, 269 (2015) 170.
29. H. Y. Wei, Q. Xu, D. C. Chen, M. Chen, M. L. Chang and X. F. Ye, *Opt. Mater.*, 122 (2021) 111722.
30. L. Zhang, M. Q. Xin, J. H. Teng and S. J. Chua, *Comput. Mater. Sci.*, 49 (2010) S153.
31. X. F. Meng, G. Y. Wei, H. L. Ge, Y. D. Yu, Y. Cao and H. Dettinger, *Int. J. Electrochem. Sci.*, 8 (2013) 10660.
32. C. Zurlini and A. Montanari, *Prog. Org. Coat.*, 105 (2017) 225.

33. F. F. Marzo, M. Alberro, A. P. Manso, X. Garikano, C. Alegre, M. Montiel, A. Lozano and F. Barreras, *Int. J. Hydrogen Energy*, 45 (2020) 20632.

© 2022 The Authors. Published by ESG (www.electrochemsci.org). 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/>).