

Short Communication

Preparation of Duplex Film through Microarc Oxidation Coloring and Polymer Plating on Mg-Li Alloy and Its Corrosion Resistance

Wenting Hou, Zhixin Kang*

School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, PR China

*E-mail: zxkang@scut.edu.cn

Received: 18 January 2013 / Accepted: 19 March 2013 / Published: 1 April 2013

Microarc oxidation (MAO) coloring and developed polymer plating technique were applied to Mg-Li alloy to get greenish super-hydrophobic film. The formation mechanism, wettability and corrosion resistance of the film were characterized by X-ray photoelectron spectroscopy, OCA35 optical contact angle measuring instrument and potentiodynamic polarization test, respectively. The results show that after MAO coloring Mg-Li alloy with greenish ceramic coating has a water contact angle (WCA) of nearly 0° and surface free energy of 74.86 mJ/m^2 . Then the surface is covered with polymeric film by polymer plating with a WCA of 169.2° and surface free energy of 1.46 mJ/m^2 . The corrosion resistance of MAO coloring coating is enhanced obviously and has been further improved by duplex modification. Compared to the substrate, the corrosion current density of super-hydrophobic surface from potentiodynamic polarization test in 0.1 mol/L NaCl aqueous solution decreases by three orders of magnitude.

Keywords: Greenish super-hydrophobic film; Mg-Li alloy; Microarc oxidation coloring; Polymer plating; Corrosion resistance.

1. INTRODUCTION

Mg-Li alloy has attracted considerable interests due to its excellent properties, such as peculiar low density, high specific strength and stiffness, outstanding electromagnetic shielding and superior mechanical characteristics. However, its poor corrosion resistance limits its potential applications [1-4].

Recently, super-hydrophobic treatments have been used to improve corrosion resistance [5-7]. Moreover, super-hydrophobic surfaces exhibit great properties in self-cleaning, anti-fouling, anti-friction and drag-reduction [8]. In addition, the decoration performance also plays an important role in

using as the components in vehicles, instruments, etc. It is essential to develop a super-hydrophobic surface with decoration performance.

Colorful Super-hydrophobic surfaces on Mg-Li alloy have not been reported. Herein, a method for fabricating a greenish super-hydrophobic surface on Mg-Li surface was presented. First, microarc oxidation (MAO) coloring was operated on Mg-Li alloy, and then polymer plating [9] was executed to get greenish super-hydrophobic surface with a distilled water contact angle (WCA) of 169.3 °, expanding the application area of Mg-Li alloy.

2. EXPERIMENTS AND CHARACTERIZATION

The chemical composition of Mg-Li alloy is given as follows: Li 10.73%, Al 4.49%, Y 0.52%, Zr 0.18% and Mg Balance (mass fraction). The Mg-Li substrates were ground, ultrasonically cleaned in acetone and then rinsed with ethanol to remove oxide and other contamination on surface. MAO coloring process was carried out immediately in an alkaline silicate electrolyte with an AC power source to produce a greenish ceramic coating. The temperature of electrolyte solution was kept at 298 K by cooling and stirring system.

In order to produce a super-hydrophobic film on the greenish ceramic surface, MAO treated samples were polymer plating at room temperature in an IM6ex electrochemical workstation (Zahner, Germany) with a three-electrode system. The MAO coloring treated sample was used as the working electrode, while two stainless steel plates (SUS304) as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The solution of polymer plating was consisted of 1 mmol/L 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol (ATP) and 0.15 mol/L NaOH supporting electrolyte. The structure of ATP triazine dithiol monosodium can be found in reference [9].

The static WCAs and surface free energies were measured with OCA35 optical contact angle measuring instrument (Dataphysics, Germany) based on a sessile drop measuring method with a water drop volume of 1 μ L. X-ray diffraction (XRD) was used to detected the phase of the MAO colored coating. The Axis Ultra of DLD X-ray photoelectron spectroscopy (Kratos, UK) was performed to characterize chemical composition and combination of the film, the binding energies were corrected with respect to the adventitious carbon component in the C1s peak corresponded to 284.6 eV. Potentiodynamic polarization tests were carried out by IM6ex electrochemical workstation in 0.1 mol/L NaCl aqueous solution at 1 mV/s scanning rate using a three-electrode system. The test samples packaged by polyimide to leave 1 cm² exposed to the electrolyte were used as the working electrode, with platinum plate as the counter electrode and SCE as the reference electrode.

3. RESULTS AND DISCUSSION

3.1. Phase compositions of MAO coloring coating

Fig. 1 shows the XRD pattern of Mg-Li alloy treated by MAO coloring. The ceramic coating on the MAO treated Mg-Li substrate consists of MgSiO₃, MgO and MgCr₂O₄, which are the products

of a series of chemical reaction on the surface of substrate [10, 11]. MgCr_2O_4 is green, whereas MgSiO_3 and MgO are white. Thus, the coating appears greenish.

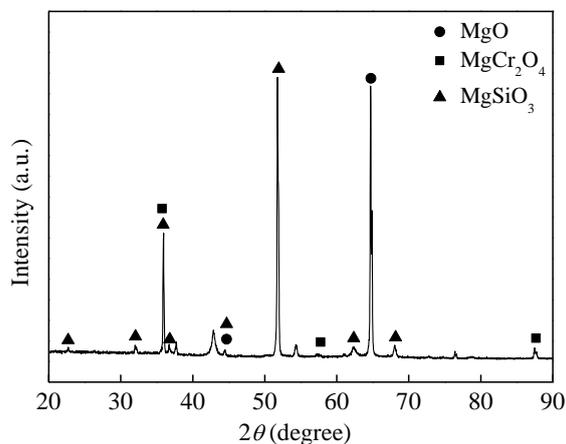
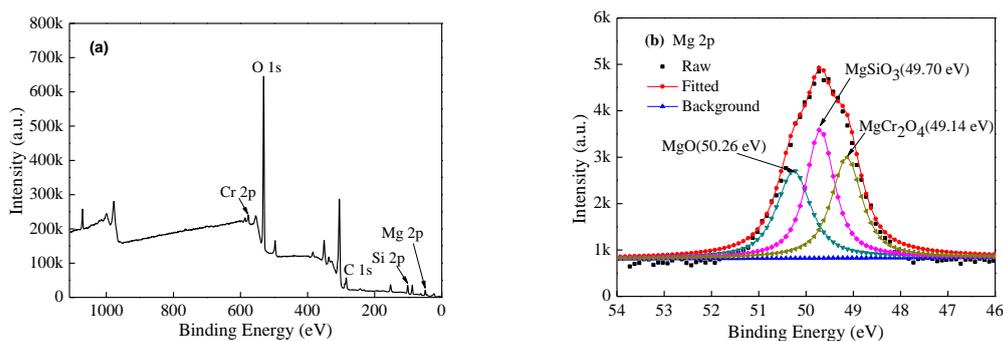


Figure 1. XRD pattern of MAO colored coating.

3.2. XPS studies of MAO colored coating

The surface of the MAO colored sample was characterized by XPS after calibrating the spectrometer, as shown in Fig. 2 (a). It turns out that the coating mainly consists of O, Cr, C, Si and Mg, not including Li, indicating that Li dissolves during the MAO coloring process due to its activity [12]. High-resolution spectra of Mg 2p, Si 2p and Cr 2p are shown in Fig. 2 (b), (c), (d), respectively. There are three main Mg 2p component peaks in Fig. 2 (b). The lowest binding energy (BE) peak at 49.14 eV with a full width at half maximum (FWHM) of 0.77 eV is assigned to MgCr_2O_4 . The intermediate BE peak is centered at 49.7 eV, indicating the co-existence of MgSiO_3 . The highest BE peak at 50.26 eV is deemed to be MgO [13]. A doublet exists in the Si 2p spectrum of the same sample corresponding to MgSiO_3 , as shown in Fig. 2 (c). The Cr 2p line was fitted as a doublet structure, where the Cr 2p_{3/2} and Cr 2p_{1/2} components' intensity ratio was 2:1. According to the literature [14], the valence state of Cr is trivalent, suggesting that the doublet is attributed to MgCr_2O_4 .



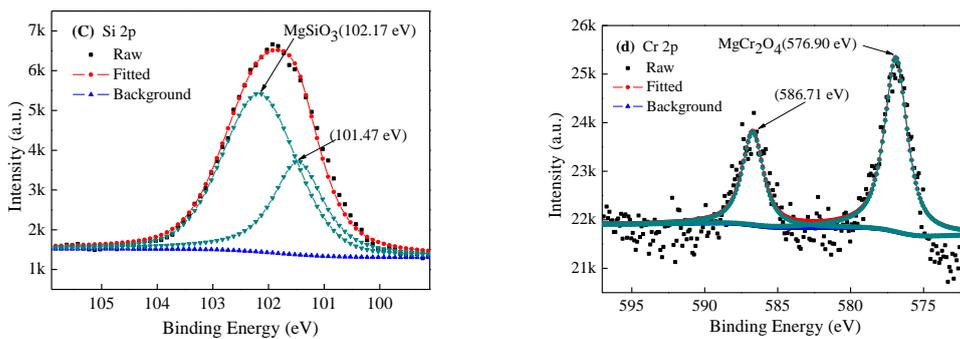


Figure 2. XPS spectra of MAO coloring coating (a) whole pattern, (b) Mg 2p, (c) Si 2p and (d) Cr 2p.

The results demonstrate that the MAO coloring coating is composed of $MgSiO_3$, MgO and $MgCr_2O_4$, which is in accordance with the result of XRD.

3.3. XPS studies of duplex film

To investigate the binding mode between ATP and greenish ceramic coating in detail, XPS measurement was operated on the duplex film as shown in Fig. 3. The doublet structures exist in S 2p peak, corresponding to the atomic orbits of S $2p_{3/2}$ and S $2p_{1/2}$ [15]. According to literatures [16, 17], S 2p curve can be divided into three doublets, each doublet has an area ratio of 2:1. S $2p_{3/2}$ component centers at 167.42 eV, corresponding to the oxide of S, namely sulfinate. S $2p_{3/2}$ at 163.82 eV represents the S-S bond, which indicates that the organic monomers have polymerized during polymer plating. S $2p_{3/2}$ at 161.33 eV is assigned to S-M bond (here M denotes metal), suggesting there has been chemical reaction between thiol group -SH and Mg-Li alloy surface.

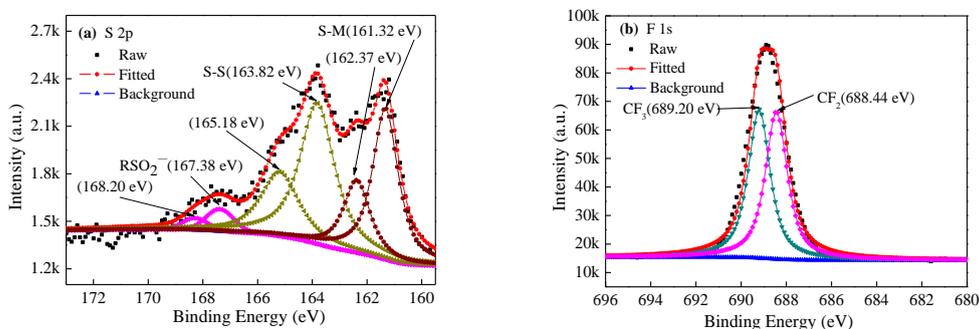


Figure 3. High-resolution spectra of duplex film (a) S 2p and (b) F 1s.

Therefore, we can deduce the combination of ATP monomers on MAO colored Mg-Li alloy surface. After MAO coloring, the Mg-Li alloy got a rough ceramic surface. Then the rough surface

was coated with ATP film through polymer plating. During polymer plating, ATP monomers were hydrolyzed, and then lost two electrons and became free radicals with the effect of voltage. Then the free radicals reacted with the MAO colored surface, generating S-M bond. The S-S bond testifies the crosslinking reaction occurred between the free radicals. Meanwhile, through the F 1s fitted spectra, it is obvious that there are two peaks at 689.2 eV and 688.4 eV, representing CF_3 and CF_2 respectively. Based on these results, we can further deduce that MAO colored surface was covered with organic thin film by polymer plating.

3.4. Wettability of different Mg-Li alloy surfaces

The changes of WCA and surface free energy are used to characterize the wettability of Mg-Li alloy with different surface treatment. The results are displayed in Fig. 4 and Table 1.



Figure 4. Contact angles of 1 μL distilled water droplet on (a) bare Mg-Li alloy, (b) MAO colored coating and (c) duplex film.

Table 1. Surface free energies and their components of different Mg-Li alloy surfaces.

Samples	Surface free energy ($\text{mJ}\cdot\text{m}^{-2}$)	Dispersion component ($\text{mJ}\cdot\text{m}^{-2}$)	Polar component ($\text{mJ}\cdot\text{m}^{-2}$)
H_2O	73.16	27.21	45.95
Bare Mg-Li alloy	51.82	24.32	27.50
MAO colored coating	74.86	39.07	35.79
Super-hydrophobic film	1.46	1.39	0.06

Fig. 4(a) shows distilled water droplet on the surface of Mg-Li alloy substrate, where the substrate possesses hydrophilic properties with a WCA of 24° and surface free energy of 51.82 mJ/m^2 . After MAO coloring, distilled water droplet spreads completely on the greenish ceramic coating with a WCA of nearly 0° , demonstrating super-hydrophilic characteristic, shown in Fig. 4(b). This phenomenon can be explained from three aspects. First, the MAO colored surface has a rough and porous structure. According to the Wenzel equation [18], the hydrophilic surface becomes more hydrophilic whereas hydrophobic surface becomes more hydrophobic as roughness increases. Due to the hydrophilicity of substrate, the MAO colored surface exhibits super-hydrophilic. Second, the MAO

colored surface has a porous structure with strong capillary adsorption force, making it even easier for the distilled water to spread on the surface [19]. Third, the MAO colored coating is mainly composed of MgO, MgSiO₃, MgCr₂O₄. As oxides generally have a high surface free energy [20], here it reaches 74.86 mJ/m² with a high polar component of 35.79 mJ/m², while the surface free energy of water is 73.16 mJ/m² with a polar component of 45.95 mJ/m². According to the principle of similar compatibility, the completely spreading of distilled water on the surface is attributed to the strong compatibility of the MAO colored surface with distilled water [21]. After polymer plating the WCA is up to 169.2 °. These results further prove that the surface has been covered by organic film that has a low surface free energy causing the change from super-hydrophilicity to super-hydrophobicity, which remarkably expands its application area.

3.5. Potentiodynamic polarization studies

The typical polarization curves pertaining to Mg-Li alloy before and after modification in 0.1 mol/L NaCl solution are presented in Fig. 5. The curve configurations are alike, indicating that electrochemical corrosion behaviors are similar.

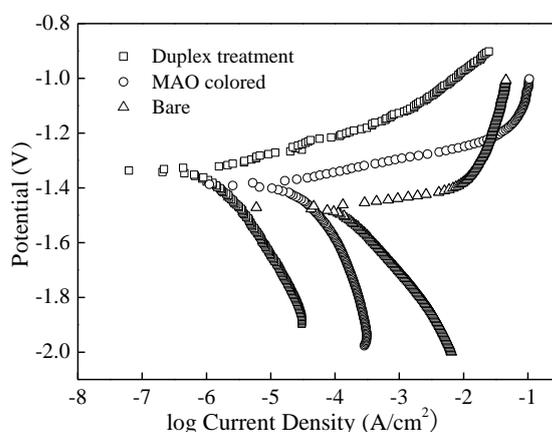


Figure 5. Potentiodynamic polarization curves of bare and treated Mg-Li alloy in 0.1 mol/L NaCl solution.

The corrosion current density (I_{corr}), corrosion potential (E_{corr}) values and anodic/cathodic tafel slopes (β_a and β_c) listed in Table 2 are calculated from the polarization curves using tafel extension method. Based on the approximate linear polarization at the corrosion potential (E_{corr}), polarization resistance (R_p) values and protection efficiency (PE) were determined by the relationships [22, 23].

$$R_p = \frac{\beta_a \beta_c}{2.3 I_{corr} (\beta_a + \beta_c)} \quad (1)$$

$$PE = \left(\frac{I_0 - I_{corr}}{I_0} \right) \times 100\% \quad (2)$$

Table 2. Parameters of potentiodynamic polarization curves and protection efficiency obtained in 0.1 mol/L NaCl solution.

Parameters	E_{corr} (V)	I_{corr} (A/cm ²)	B_a	β_c	R_p (Ω/cm ²)	PE
Bare	-1.468	1.37×10^{-4}	0.035	0.276	9.86×10^1	—
MAO colored coating	-1.395	4.39×10^{-6}	0.035	0.122	2.71×10^3	96.8%
Super-hydrophobic film	-1.343	5.60×10^{-7}	0.042	0.150	2.55×10^4	99.6%

The corrosion current density I_0 of Mg-Li alloy substrate is 1.37×10^{-4} A•cm⁻², while corrosion potential E_{corr} is -1.468 V. After MAO coloring, I_{corr} decreases by two orders of magnitude to 4.39×10^{-6} A•cm⁻² and E_{corr} increases to -1.395 V, calculated PE reaching 96.8%. The potentiodynamic polarization test reveals a far lower I_{corr} of duplex film than that of substrate, as I_{corr} decreases by three orders of magnitude and E_{corr} increases to -1.343 V with PE further improved to 99.6%. The results show that the MAO colored coating prevents the penetration of corrosive medium into the interface between the film and the substrate, making an improvement in corrosion resistance. The MAO colored coating followed by polymer plating shows super-hydrophobicity, which can hinder the dispersion and migration of the Cl⁻ from solution to the Mg-Li alloy. The duplex film plays a role in protection and leads to a further improvement in corrosion resistance.

4. CONCLUSIONS

Mg-Li alloy is coated with greenish ceramic coating by MAO coloring. After polymer plating, the surface is covered by organic film to get greenish duplex film with a WCA of 169.2 °.

Mg-Li alloy after MAO coloring has better corrosion resistance than substrate through potentiodynamic polarization test in 0.1 mol/L NaCl solution, evidenced by the fact that the the corrosion current density decreases by two orders of magnitude, after polymer plating it decreases by three orders of magnitude, The duplex film plays a role in protection and leads a further improvement in corrosion resistance.

ACKNOWLEDGMENTS

We appreciate the supports of the National Natural Science Foundation of China (No. 51075151) and Key Program of Guangdong Natural Science Foundation (No. 10251064101000001).

References

1. B.L. Mordike and T. Ebert, *Mater. Sci. Eng.*, A302 (2001) 37-45
2. P. Crawford, R. Barrosa, J. Mendez, J. Foyos and O.S. Es-Said, *J. Mater. Process. Technol.*, 56

- (1996) 108-118
3. L.L. Shi, Y.J. Xu, K. Li, Z.P. Yao and S.Q. Wu, *Curr. Appl. Phys.*, 10 (2010) 719-723
 4. N. Ma, Q.M. Peng, X.J. Li, H. Li, J.H. Zhang and Y.J. Tian, *Int. J. Electrochem. Sci.*, 7 (2012) 8020-8034
 5. Z.X. Kang, Q. Ye, J. Sang and Y.Y. Li, *J. Mater. Process. Technol.*, 209 (2009) 4543-4547
 6. T. He, Y.C. Wang, Y.J. Zhang, Q. Lv, T.G. Xu and T. Liu, *Corros. Sci.*, 51 (2009) 1757-1761
 7. B. Yin, L. Fang, A.Q. Tang, Q.L. Huang, J. Hu, J.H. Mao, G. Bai and H. Bai, *Appl. Surf. Sci.*, 258 (2011) 580-585
 8. Y.C. Hong, S.C. Cho, D.H. Shin, S.H. Lee and H.S. Uhm, *Scripta Mater.*, 59 (2008) 776-779
 9. Z.X. Kang, X.M. Lai, J. Sang and Y.Y. Li, *Thin Solid Films*, 520 (2011) 800-806
 10. A.L. Yerokhin, X. Nie, A. Leyland, A. Matthews and S.J. Dowey, *Surf. Coat. Technol.*, 122 (1999) 73-93
 11. M.Q. Tang, H.C. Liu, W.P. Li and L.Q. Zhu, *Mater. Lett.*, 65 (2011) 413-415
 12. X. Jing, Y. Yuan, F. Yu, L. Song, M. Zhang, T. Wang and G. Zhu, *Rare Metal Mater. Eng.*, 38 (2009) 1154-1157
 13. R. Jerome, Ph. Teyssie, J.J. Pireaux and J.J. Verbist, *Appl. Surf. Sci.*, 27 (1986) 93-105
 14. X. Zhang, C. van den bos, W.G. Sloof, A. Hovestad, H. Terryn and J.H.W. de Wit, *Surf. Coat. Technol.*, 199 (2005) 92-104
 15. D.G. Castner, K. Hinds and D.W. Grainger, *Langmuir*, 12 (1996) 5083-5086
 16. C. Amato, S. Devillers, P. Calas, J. Delhalle and Z. Mekhalif, *Langmuir*, 24 (2008) 10879-10886
 17. J.J. Senkevich, G.R. Yang and T.M. Lu, *Colloids Surf.*, A207 (2002) 139-145
 18. T.Y. Han, J.F. Shr, C.F. Wu and C.T. Hsieh, *Thin Solid Films*, 515 (2007) 4666-4669
 19. J.W. van Honschoten, N. Brunets and N.R. Tas, *Chem. Soc. Rev.*, 39 (2010) 1096-1114
 20. G.T. Gu, Z.J. Zhang and H.X. Dang, *Prog. Chem.*, 14 (2002) 159-166
 21. F. Tian, B. Li, B.P. Ji, J.H. Yang, G.Z. Zhang, Y. Chen and Y.C. Luo, *Food Chem.*, 113 (2009) 173-179
 22. K.V. Subramaniam and M.D. Bi, *Corros. Sci.*, 52 (2010) 2725-2735
 23. A.Y. El-etre, *Corros. Sci.*, 40 (1998) 1845-1850