

Short Communication

Preparation of Iron Tetradecanoate Coating on the Surface of Mg-Li Alloy and Its Corrosion Resistance

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Received: 5 September 2020 / Accepted: 28 October 2020 / Published: 30 November 2020

Magnesium alloys were commonly used in the industry, but their lower corrosion resistance limited to their application. In this work, an iron tetradecanoate ($\text{Fe}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3$) coating was on the surface of Mg-7Li-3Al-1Si alloy prepared using an environment friendly method by one-step in order to improve the corrosion resistance of Mg alloy. Results showed that the prepared coating has an ideal corrosion resistance and a good protection performance.

Keywords: Mg-Li-Al-Si alloy, One-step method, coating, Microstructure, corrosion protection

1. INTRODUCTION

Magnesium alloys are actively being developed because of the potential usefulness for improving energy efficiency across the automobile, aircraft, and aerospace industries, in which the weight savings translate to lower energy consumption [1-3]. Although Mg alloys also possess good strength-to-weight ratio (specific strength) and castability, there are two critical factors (limited cold workability (near room temperature) and a high susceptibility to corrosion) hindering their use as potential structural materials [4-6]. The addition of lithium not only improves the plasticity of magnesium alloys, but also makes lighter. However, the disadvantage is that the strength of magnesium alloy is reduced, and the corrosion resistance is further reduced due to the activity of lithium.

Therefore, many researchers have done much work related to field of strengthening, toughening and corrosion resistance of Mg-Li alloys. Xing et al. [7] reported an ultralight magnesium alloy using precipitation strengthening, and found that physical explanation of these phenomena allowed the creation of an exceptionally low-density alloy. And this is also structurally stable by controlling the

lattice mismatch and volume fraction of the Mg₃Al nanoparticles. Liang et al. [8] reported the microstructure and mechanical properties of four hot-rolled alloys, e.g. Mg-4Li, Mg-4Li-3Al, Mg-4Li-3Al-0.38Si, and Mg-4Li-6Al-0.76Si (weight percent), and the ultimate tensile strength (UTS) of the Mg-4Li-6Al-0.76Si alloy was up to 295 MPa, compared with 143 MPa of the Mg-4Li alloy. This improvement is attributed to precipitation strengthening imparted by the Al₃Li(Mg) and Mg₂Si phases, as well as solid-solution strengthening due to Al atoms dissolved in the α -Mg matrix of the alloys. Zhao et al. [9] reported the corrosion resistance of as-rolled Mg-Li-AlSi Alloys, single α -phase alloys (Mg-4Li, Mg-4Li-3AlSi), and single β -phase alloys (Mg-12Li, Mg12Li-3AlSi), and found that the surface phase of the Mg-Li-AlSi was mainly consist of α -Mg, β -Li, Mg(OH)₂, Al₂O₃, and Mg₂Si. Peng et al. [10] reported a novel strategy for simultaneously achieving a high specific yield strength ($182 \pm 8 \text{ kNmKg}^{-1}$) and a good elongation ($21 \pm 2\%$) in the Mg13 wt% Li at room temperature, basing on the formation of a hierarchical contraction nanotwins-stacking faults (CTWSFs) structure by cryorolling followed by ultrahigh pressure.

The strength of magnesium-lithium alloys can be greatly improved by controlling the structure and phase composition, but the corrosion resistance of magnesium-lithium alloys is the critical factor limiting the service performance of the alloys during engineering application. Although many studies have reported that the corrosion resistance of Mg-Li alloys can be improved by controlling the structure of Mg-Li alloys. However, the high activation of Mg and Li indicates that the coating preparation technology is the a critical step for the industrialization of Mg-Li alloy. Zhao et al. [11] reported a one-step preparation method for the uper hydrophobic surface on magnesium alloy, and improved its corrosion protection and antifouling performance. Zhang et al. [12] reported a novel approach to fabricate a protective layered double hydroxide films on the surface of anodized Mg-Al alloy, and the corrosion resistance was also improved.

In this study, a one-step method with an environment friendly process was reported to prepare an iron tetradecanoate ($\text{Fe}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3$) on the surface of Mg-7Li-3Al-1Si alloy. The coating with micron rough structure and high contact angle can make Mg-7Li-3Al-1Si alloy have ideal corrosion resistance.

2. EXPERIMENTAL

The magnetic-levitation, high-frequency induction melting technique was used to prepare the Mg-7Li-3Al-1Si alloys (all in wt.%, unless otherwise stated). The pure magnesium, pure lithium, aluminum and Al-40 wt.%Si were melted under an argon atmosphere initially, and then were cast into a water-cooled copper mould with a dimension of $\Phi 30 \times 60 \text{ mm}$ [13]. The cast ingots were machined into $\Phi 30 \times 25 \text{ mm}$ samples. The hot extrusion was performed at 410 °C with ratio of 14:1 using a 50 T hydraulic press.

The mixture of the solution is a key step for the formation of the super hydrophobic surface. First, 2 g tetradecanoic acid was dissolved in 100 ml ethanol, and Iron (III) chloride hexahydrate (5.406 g) was added in 100 ml deionized water. Secondly, the Iron (III) chloride solution was dropwise added into the tetradecanoic acid ethanol solution while stirring magnetically at room temperature. Stirring the mixed solution until the solution was uniform and transparent. Then, the solution was placed in a 60 °C

water bath. Subsequently, the cleaned magnesium alloy substrates were immersed in it. After 2 h, the substrates were taken out and thoroughly washed several times with ethanol and deionized water, respectively. Finally, the washed substrates were dried at 60 °C for 2 h to evaporate the surface ethanol gradually.

The microstructures were examined by using an optical microscope (OM , LEICA DVM6). The FTA200 drop shape analysis system was used to measure the static water contact angle of the coating surface with a water drop of 0.5 mL. The average contact angle value was determined by measuring the same substrate at five different locations. The electrochemical properties of the obtained substrate surface were determined in 3.5 wt% NaCl aqueous solution. An electrochemical workstation (GAMRY, 25207) was used, which was equipped with a standard three-electrode system with an Ag/AgCl reference electrode. The working electrode was arranged in a homemade holder of Teflon, which had a circular window with an area 1 cm² exposed to the electrolytic. The potentiodynamic polarization curves were measured from -400 to +800 mV vs OCP at a rate of 1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 0.1 Hz to 100 kHz at open circuit potential with an ac perturbation of 5 mV. All measurements were conducted at room temperature.

3. RESULTS AND DISCUSSION

The obtained OM images of extruded Mg-7Li-3Al-1Si alloy was shown in Fig. 1. It was obvious that the alloy is distributed in a strip shape along the extrusion direction and the alloy is composed of α - Mg and β - Li phases. Xu et al. [4] reported that the corrosion resistance of the β -Li phase is significantly better than that of the α -Mg phase, indicating that the corrosion potential of the structure is heterogeneous. This potential difference will form a micro corrosion cell and accelerating the localized corrosion of the alloy.

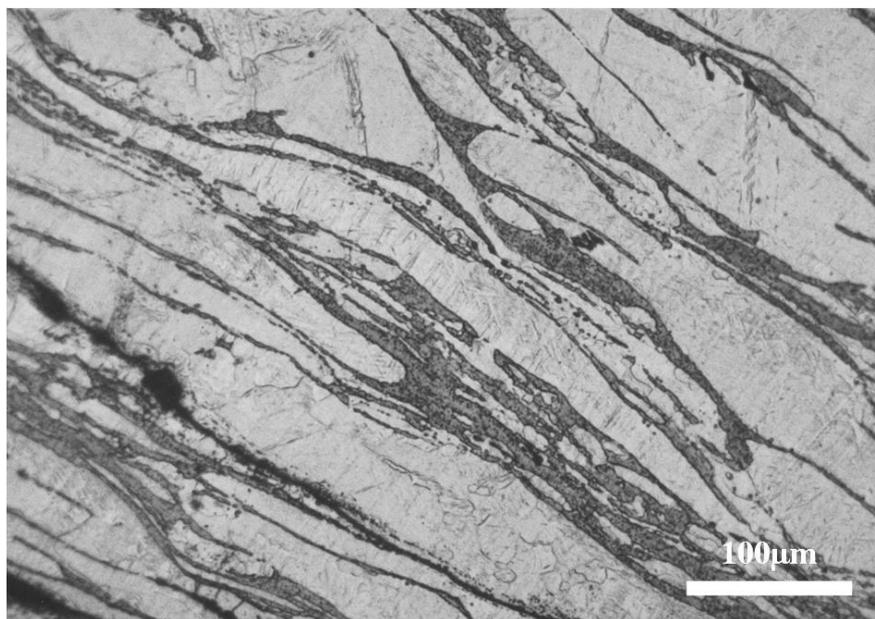


Figure 1. OM images of extruded Mg-7Li-3Al-1Si alloy

Fig. 2 shows the potentiodynamic polarization curves and EIS plots of the bare alloy and coated alloy in 3.5 wt%. It can be seen that the corrosion potential of the prepared sample with coating is -1.2 V/SCE, which is slightly lower than that of the bare alloy. It is mainly due to the inhomogeneity of the coating surface. However, the corrosion current of the coating is shifted negatively which is much lower than that of the bare alloy. It can be seen from EIS curve that the resistance of coated Mg alloy is much higher than that of bare sample, which is consistent with the result of polarization curves.

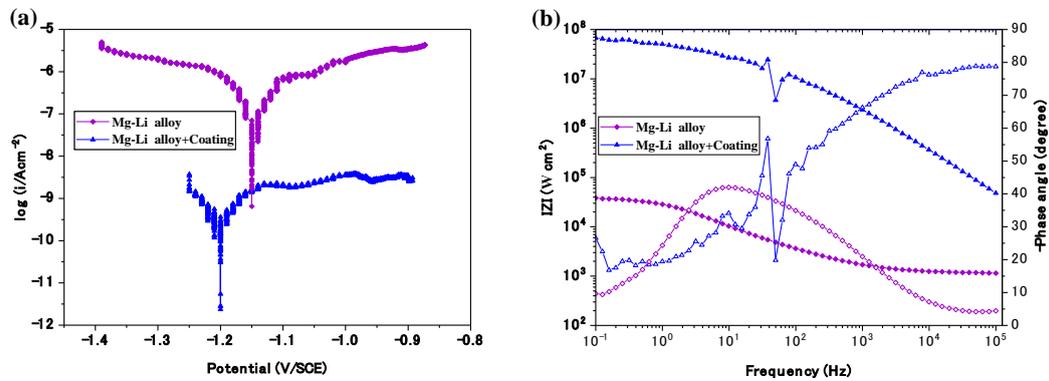


Figure 2. Potentiodynamic polarization curves and EIS plots of the bare and coated samples in 3.5 wt% NaCl solution: (a) potentiodynamic polarization curves, (b) EIS plots.

Fig. 3 shows the surface morphologies of various samples in 3.5 wt% NaCl solution. Fig. 3 (a) shows lots of corrosion pits, indicating that the localized corrosion of bare alloy is serious. Fig. 3 (b) shows that as the corrosion further intensifies, Cl ions will accumulate around the corrosion pits, which will destroy the structure of the passivation film. It can be clearly observed in Fig. 3 (c) that the coating is successfully coated on the surface of Mg-Li alloy by one-step method. The color of the coating is reddish brown, which indicates that the coating contains Fe ion. Combined with Fig. 3 (d), it can be observed that the coating effectively blocks the contact between the base metal and corrosive ions, thus slowing down the corrosion of the metal.

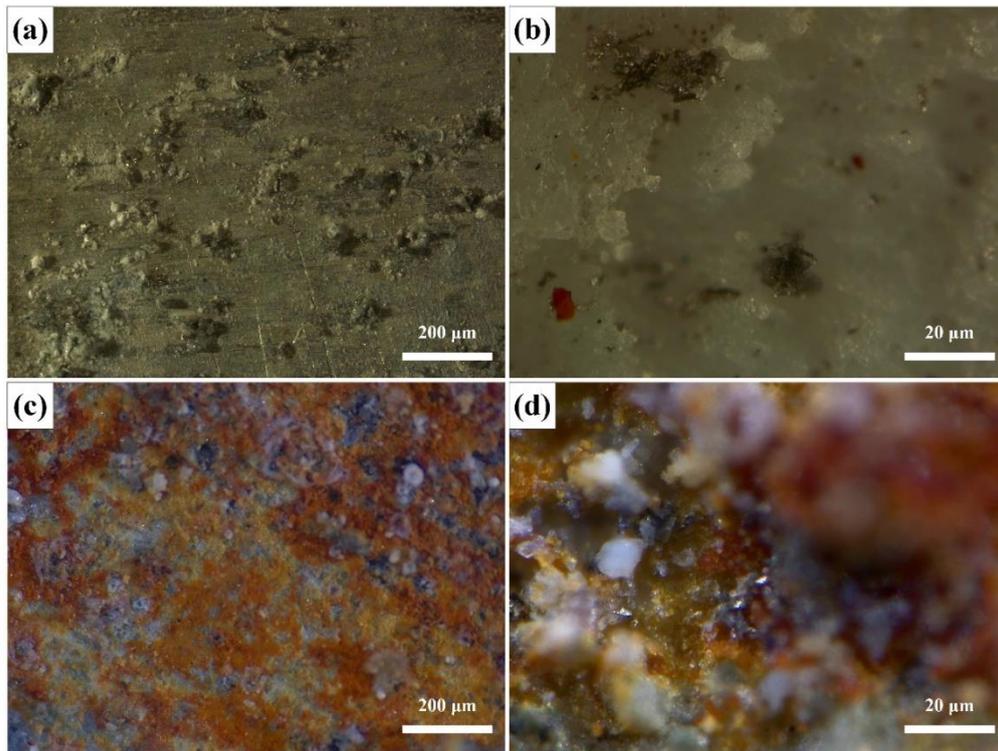


Figure 3. OM images in 3.5 wt% NaCl solution of bare alloy((a) and (b)) and coated samples ((c) and (d)).

Fig. 4 shows 3D-OM images in 3.5 wt% NaCl solution of substrate, and coating/substrate. Comparison of Fig. 4 (a) and Fig. 4 (b), the magnesium alloy is easily corroded than the coated Mg alloy. The corrosion of Mg-Li alloy is mainly caused by pitting corrosion, which is a kind of local corrosion with hidden appearance and great damage [11, 14]. Although the weight of the metal lost by pitting corrosion is very small, the pitting corrosion geometry constitutes the structure of large cathodes and small anodes[15], resulting in a considerable dissolution rate of pore corrosion. In addition, the development of pitting corrosion has the characteristics of automatic acceleration. Therefore, if the corrosion holes continue to develop, it is likely to cause corrosion perforation damage.

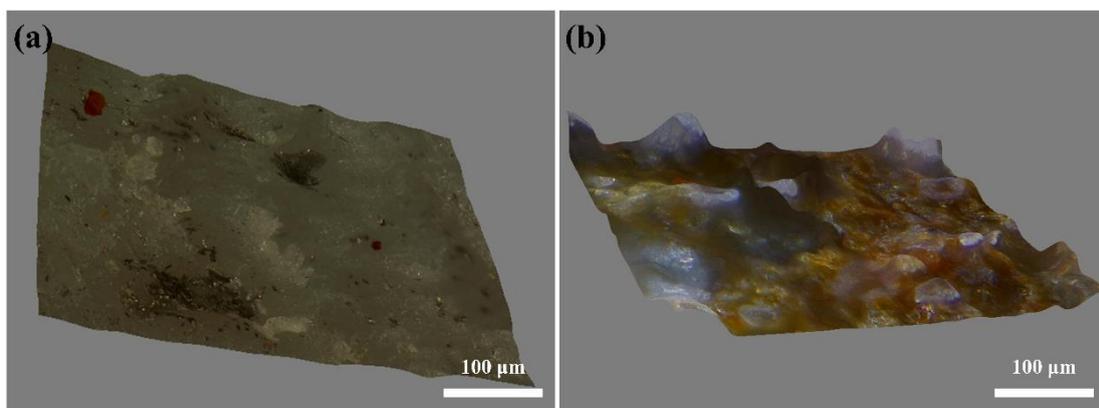


Figure 4. images in 3.5 wt% NaCl solution of bare alloy (a) and coated samples (b).

Figure 5 shows SEM and EDS images in 3.5 wt% NaCl solution of coating/substrate. It can be seen from that a dense protective film is formed on the surface of the coating to prevent the occurrence of pitting corrosion[15-17]. The results of EDS show that the coating is mainly composed of C, O, Mg, and Fe, which is consistent with the analysis results of Fig. 3 and Fig. 4. It also shows that the organic-inorganic hybrid coating is one of the important ways to solve the corrosion resistance of Mg-Li alloy.

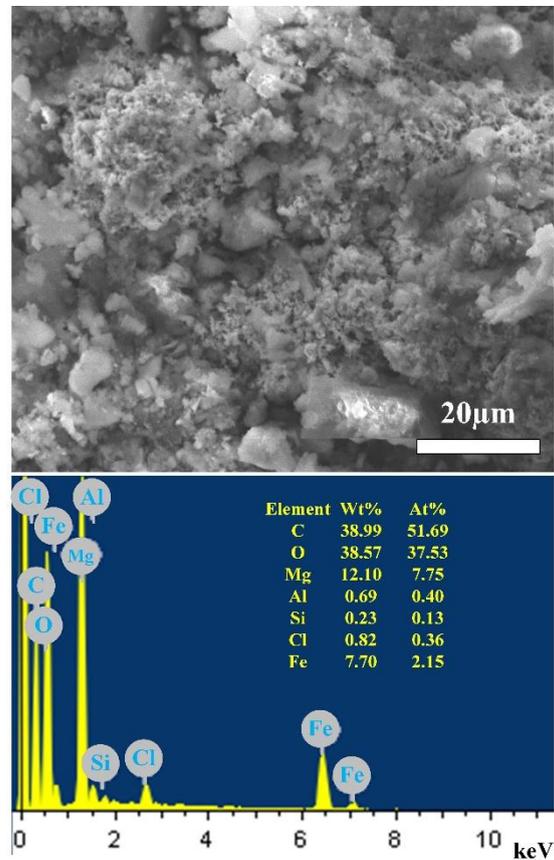


Figure 5. SEM images and EDS of bare alloy (a) and coated samples (b).

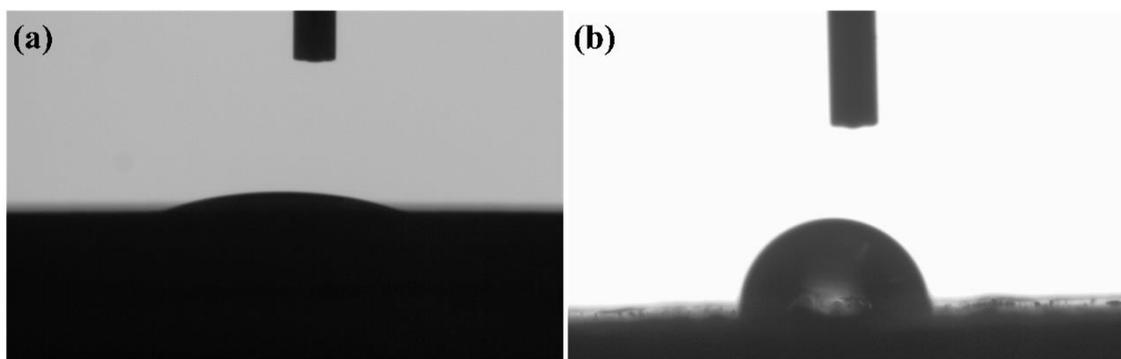


Figure 6. Contact angles of substrate, and coating/substrate

The contact angle is an important index to measure the corrosion resistance of metals[18]. The

matrix magnesium lithium alloy has strong hydrophilicity and the contact angle is less than 10° as illustrated in Fig. 6 (a). The alloy contact angle of the prepared coating increased to 80° significantly, which further improved the corrosion resistance of Mg-Li alloy.

4. CONCLUSIONS

(1) The corrosion potential of the alloy after coating is -1.2 V/SCE which is slightly lower than that of the base alloy, mainly due to the unevenness of the coating surface. However, the corrosion current of the Mg alloy for preparing the coating is much lower than that of the base alloy. The EIS curve shows that the resistance of the Mg alloy for preparing the coating is much higher than that of the base alloy.

(2) The main components of the coating are C, O, Mg, and Fe, which indicates that the organic-inorganic hybrid coating is one of the important ways to solve the corrosion resistance of Mg-Li alloy.

(3) The matrix Mg-Li alloy is hydrophilic, and the contact angle is less than 10° . The alloy contact angle of the prepared coating is up to 80° , thereby further improving the corrosion resistance of the magnesium-lithium alloy.

ACKNOWLEDGEMENTS

This work was supported by the Natural Science Foundation of China (No. 51773106, 51701029 and 51778088), Guangdong Basic and Applied Basic Research Foundation (No.2020A1515011274) and Natural Science Foundation of Inner Mongolia, China (No.2018MS05038).

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