Galvanic corrosion behaviour of carbon fibre reinforced polymer/magnesium alloys coupling

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The galvanic corrosion behaviour of carbon fibre reinforced polymer (CFRP, T300/648) in contact with different magnesium alloys (AZ31, LZ91 and LZ141) in a sodium chloride solution and the influence of micro-arc oxidation (MAO) film on the corrosion behaviour of CFRP/magnesium alloys coupling were investigated using the electrochemical method. The results showed that the galvanic activity of CFRP/magnesium alloys coupling increased with the increase of lithium concentrations. The duration of the inhibitory effect of MAO film on the corrosion of CFRP/Mg–Li coupling is longer than that of CFRP/Mg–Al coupling due to its double-layer structure.

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1. Introduction
Fibre metal laminates (FMLs), consisting of alternative layers of thin metal sheets and composite layers, have great potential to use in aerospace applications due to their exceptionally light weight, superior fatigue behaviour and high impact resistance [1]. Normally, the densities of FMLs based on aluminium and titanium alloys sheets are about 2.29–3.66 g/cm³ [2,3]. In order to further reduce the FMLs materials weight, many investigations were carried out by replacing the aluminium alloys with Mg–Al alloys (AZ31) [4,5], saving of around 24% materials weight. It is well-known that Mg–Li alloys are one of the lightest magnesium alloys with density of around 1.30–1.60 g/cm³. Hence, it is highly expected that the application of Mg–Li alloys sheets in the FMLs can further reduce the material density to around 1.50 g/cm³ and also improve the electromagnetic shielding capability as well as damping performance of the FMLs.

Nevertheless, the use of metal sheet and carbon fibre in FMLs may cause the galvanic corrosion which degrades the overall performance of FMLs materials [6]. In order to improve the galvanic corrosion resistance of carbon fibre in contact with metals, some pre-treatment techniques, such as anodizing and epoxy coating, were used to modify the metal surface [6,7]. There are an extensive amount of analytical work reported in literature to investigate the galvanic corrosion behaviour of CFRP coupled with aluminium alloys, titanium alloys and carbon steels [8–11]. However, the galvanic corrosion behaviour of CFRP/Mg–Li coupling and the influence of the MAO film on the corrosion properties of CFRP/magnesium alloys coupling have been overlooked.

In this paper, the open circuit potentials (OCP) of three magnesium alloys (AZ31, LZ91 and LZ141) and CFRP (T300/648) in a 3.5 wt.% sodium chloride solution were analyzed using the open circuit technique in the electrochemical station. Besides, the galvanic corrosion current densities of galvanic couplings of CFRP/magnesium alloys with and without MAO coatings were also analyzed using the galvanic corrosion technique in the electrochemical station. The aims of this work are to evaluate the galvanic activity of CFRP in contact with different magnesium alloys, and also to study the influence of MAO film on the galvanic corrosion of CFRP/magnesium alloys coupling.

2. Material and methods

2.1. Materials

The magnesium alloys (AZ31) sheets with 2 mm thickness are used in this study (produced by Luoyang Shengte Corp. Henan, China). The magnesium lithium alloys (LZ91 and LZ141) sheets.
were prepared by firstly stir-casting in a resistance furnace under argon atmosphere, then forged and rolled to make the slab. The chemical compositions of these three alloys are shown in Table 1. The 2 mm carbon fibre reinforced polymer (CFRP) composites sheets, consisting of unidirectional carbon fibre (55 Vol.% type T300) and epoxy (type 648), are produced by the System Design Institute of Mechanical-Electrical Engineering in Beijing, China. The magnesium alloys and CFRP specimens were cut into pieces (20 mm × 20 mm × 2 mm). Before the test, the surfaces of the magnesium alloys were ground using 1200 mesh papers and the CFRP surface were also sufficiently ground to expose the carbon fibre (around 55% surface area, see Fig. 1). At last, all the samples were ultrasonically cleaned.

### 2.2. Micro-arc oxidation process

Micro-arc oxidation (MAO) process was carried out by using an inverter pulsed power supply (Type GGMF25/600-A). The magnesium alloy specimens were used as anode, and two AISI 316L panels cathodes (50 mm × 20 mm × 3 mm) were positioned on both sides to ensure a homogeneous coating over the entire surface. The distance between both electrodes amounts to 4 cm. During treatment, the voltage used is 120 V, and the coating time is 25 min with a fixed frequency of 500 Hz and duty ratio of 45%. The electrolyte contains 50 g/L sodium hydroxide (NaOH) + 40 g/L sodium metasilicate nonahydrate (Na2SiO3 9H2O) + 20 g/L sodium borate dehydrate (Na2B4O7 10H2O) + 40 g/L citric acid trisodium salt dehydrate (C6H5Na3O7 2H2O) [12]. After MAO treatment, the coated samples were rinsed with distilled water and dried in air.

### 2.3. Electrochemical measurements

The electrochemical measurements of open circuit potential and galvanic current were conducted separately on a Versa STAT MC-4 electrochemical station. Beeswax was used to mask the surfaces of the alloy and the composites, leaving an exposed area of around 1 cm². The open circuit potential measurements were carried out in a conventional three-electrode cell for 2 h with the data acquisition rate of one point per one-second. The magnesium alloys and CFRP specimens were used as a working electrode, platinum plate as a counter electrode and a saturated calomel electrode (SCE) (Hg/Hg2Cl2 in saturated KCl) as a reference electrode (Fig. 2a). The galvanic current densities of bare and coated alloys coupled with CFRP were measured using the galvanic corrosion technique in the electrochemical station, and their current densities were recorded for 8 h with the data acquisition rate of one point per 15 s. The distance between both electrodes is around 3 cm (Fig. 2b). All measurements were carried out in a 3.5 wt.% sodium chloride solution (pH 6.5, 25 ± 2 °C) open to air and not to be stirred.

### 2.4. Microstructure characterization

The surface morphology, cross-section microstructure and chemical composition of the coatings were examined using the scanning electron microscopy (SEM, Phenom™ Pro) with energy dispersive analysis of X-rays (EDX). Phase composition in coatings was analysed using the X-ray diffraction (XRD, D/MAX-2000) with a Cu Kα source.

### 3. Results

#### 3.1. Open circuit potential measurements

Fig. 3 shows the open circuit potentials (OCP) of the CFRP and three magnesium alloys at different testing times. As can be seen, the OCP of CFRP composite (T300/648) is around +0.28 V_SCE with small dispersion, and for the AZ31 alloy is about −1.575 V_SCE. The LZ91 and LZ141 alloys are around −1.645 V_SCE and −1.648 V_SCE, respectively, which are more negative than the potential of AZ31 alloy. M. Schneider reported that [13], when the potential difference between two materials is less than 0.05 V, the galvanic
corrosion can be ignored. In this study, the potential difference between the CFRP and Mg–Al alloys is about 1.855 V, and the potential difference between the CFRP and Mg–Li alloys is more than 1.9 V, which means the galvanic corrosion could take place when the magnesium alloys coupled to CFRP composite. In addition, it also elucidated that the CFRP/Mg–Li alloys coupling has a higher driving force for galvanic corrosion than the CFRP/Mg–Al alloys coupling.

Similar to LZ141 alloy, LZ91 alloy starts from a small OCP, and then the OCP increase rapidly after a few minutes and finally stable at around $-1.65$ V. However, for AZ31 alloy, the OCP continuous increases within the first 1.2 h and then gradually stable at around $-1.68$ V. The time required for AZ31 alloy to reach the steady value of OCP is considerably longer than that of LZ91 and LZ141 alloys.

3.2. The galvanic corrosion current density measurements

Fig. 4 shows the galvanic corrosion current density curves of CFRP (T300/648) in contact with bare magnesium alloys. From Fig. 4, it can be seen that the CFRP/AZ31, CFRP/LZ91 and CFRP/LZ141 couplings starts with a high current density, and then the current density decreases rapidly with fluctuations within a few seconds. With the increase of testing time, the current densities of CFRP/AZ31, CFRP/LZ91 and CFRP/LZ141 are stabilized at around 58 $\mu$A/cm$^2$, 73 $\mu$A/cm$^2$ and 84 $\mu$A/cm$^2$, respectively. The required time for CFRP/AZ31, CFRP/LZ91 and CFRP/LZ141 to reach the steady current densities is 2.5 h, 4.5 h and 6.0 h, respectively. The steady values of current density and the stabilizing time in these three coupling systems follow the order: CFRP/AZ31 < CFRP/LZ91 < CFRP/LZ141.

The repeatedly measured galvanic corrosion current density curves of CFRP (T300/648) in contact with magnesium alloys with MAO film are shown in Fig. 5. It can be seen that the current densities have slightly fluctuations at each run, however, they show a same trend for the same coupling. The current densities of both CFRP/LZ91 (MAO) and CFRP/LZ141 (MAO) decline quickly at the initial stage, and finally stabilize at around 25 $\mu$A/cm$^2$ and 23 $\mu$A/cm$^2$, respectively.
respectively (Fig. 5b and c). Comparing to the current densities of CFRP/LZ91 and CFRP/LZ141 (Fig. 4), the current densities of CFRP/LZ91 (MAO) and CFRP/LZ141 (MAO) reduce by 66% and 72%, respectively. However, in the case of the CFRP/AZ31 (MAO) galvanic coupling, the galvanic corrosion current density first decreases rapidly to the minimum value, then increases slowly to the values similar to that of galvanic coupling in CFRP/AZ31 after 7 h (Fig. 5a). These results indicate that the MAO film can greatly inhibit the galvanic corrosion of CFRP/Mg–Li coupling, but for Mg–Al (AZ31) alloy, the increase of test time could cause a gradual loss of inhibition effect of MAO film.

4. Discussion

The different features of the OCP curves of Mg–Al and Mg–Li alloys are caused by the formation rate and chemical stability of the oxide film [14]. A dense oxide layer with high stability is introduced in AZ31 alloy due to the presence of Al elements [15], while for the LZ91 and LZ141 alloys, they are absent of Al elements but contains high amount of Li. As it was known, Li can promote the formation of oxide film on Mg alloy surface but with loose and low stability [16], hence the OCP of Mg–Li alloys move towards to positive direction is faster and stabilized at a lower value than Mg–Al alloys Although L921 alloy has low lithium concentrations than LZ141 alloy, the dual phase structure of the L921 alloy is unfavourable to stabilize the oxide film due to the presence of micro-galvanic corrosion between the α-Mg phase and the β-Li phase [17], hence, the value of OCP of L921 alloy is almost equal to that of LZ141 alloy. The carbon fibre in CFRP is an inert material, which behaves electrochemically like a noble metal such as gold or platinum [18], so the OCP of CFRP is more positive than the potential of magnesium alloys in sodium chloride solution.

Essentially, the change of galvanic current is a process of the formation and dissolution of passivation film [19]. The value of galvanic corrosion current density depends on the protection effect of the film. For the CFRP/AZ31 coupling, the main anodic reaction is shown in following (Eq. (1)):

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \]  

The corrosion of magnesium alloys will lead to an increase in pH value of the solution [19], and the oxidation of Al in an alkaline solution occurs (Eq. (2)) [20]:

\[ \text{Al} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \downarrow + 3\text{e}^- \]

Introduction of Al(OH)₃ leads to ennoblement of density and stability of passivation layer, suggesting an increasing corrosion resistance of the alloys [21]. For the galvanic corrosion of CFRP/Mg–Li alloys, due to the fact that the lithium had a relatively smaller potential of −3.02 V_SHE in comparison with the magnesium (−2.83 V_SHE), the lithium was preferentially oxidized in the environment of 3.5% chloride sodium (Eq. (3)) [17]:

\[ \text{Li} \rightarrow \text{Li}^+ + \text{e}^- \]

The lithium-containing compounds are detrimental to the corrosion resistance of alloys due to its loose structure and low chemical stability [16]. Thus, on the one hand, before the CFRP/magnesium coupling reach the corresponding galvanic corrosion current density, the duration of the current density instability increases with the increase of lithium concentrations in the magnesium alloys. On the other hand, the steady galvanic current density of CFRP/magnesium coupling increases with the increase of lithium concentrations.

Bennie A. Miller Jr et al. [10] reported the values of galvanic corrosion current density for CFRP (+0.16 V_SCE)/titanium alloys coupling were less than 0.5 μA/cm², and for CFRP (+0.16 V_SCE)/aluminium alloys coupling, in the range of 5.2–21.7 μA/cm². However, in present study, the values of galvanic corrosion current density for CFRP (+0.28 V_SCE)/Mg–Li alloys coupling are over 70 μA/cm², which means that the galvanic corrosion of CFRP/Mg–Li alloys coupling is more serious than that of CFRP/aluminium alloys and CFRP/titanium alloys coupling.

The protective effect of MAO film against the galvanic corrosion can be explained in the following two aspects: high insulation performance and anti-permeability. The MAO coatings are mainly composed of MgO phase (Fig. 6) while possibility contains other ceramic phases such as SiO₂, MgSiO₃ and MgAl₂O₄, see Table 2. Due to the high insulation ability of ceramics, the galvanic coupling between the CFRP and the MAO film as well as between the MAO film and the substrate material are hardly formed [22], which is beneficial to the protective of MAO film against the galvanic corrosion. From Fig. 7a, c and e, some micro-pores and micro-cracks were appeared in ceramic coatings, which may decrease the inhibition ability of ceramic film. However, the MAO film, different thickness and density, can act as a barrier layer to hinder the reaction (1), (2) and (3). The thickness of MAO film layer on AZ31 alloy surface is very thin, only about 7 μm, and some interconnected micro-pores and micro-defects are found in its microstructures (Fig. 7b), which facilitates the penetration of corrosive ions into magnesium alloy substrates. The thicknesses of MAO film on L921 and L141 alloys surfaces are approximately 15 μm and 14 μm with an inner density layer and an outer porous layer dual layer structure (Fig. 7d and f), which largely strengthening the barrier effect of the MAO film in CFRP/Mg–Li coupling. Therefore, the duration of the inhibitory effect of MAO film on the corrosion of CFRP/Mg–Li coupling is longer than that of CFRP/Mg–Al coupling.

| Table 2 Chemical compositions (in wt.%) of MAO films coated magnesium alloys by spot scanning of EDS. |
|---|---|---|---|---|---|
| Mg | O | Si | Na | Al |
| AZ31 | 50.3 | 40.9 | 5.0 | 2.5 | 1.3 |
| LZ91 | 50.4 | 41.0 | 5.2 | 3.4 | – |
| LZ141 | 54.7 | 38.1 | 4.2 | 3.0 | – |

Fig. 6 XRD patterns of the AZ31, L921 and L141 alloys treated by MAO.
5. Conclusions

(1) The open circuit potentials (OCP) of LZ91 and LZ141 alloys are more negative than the AZ31 alloy, and showing a high driving force for galvanic corrosion in the CFRP/Mg–Li alloys coupling.

(2) The galvanic activity of CFRP/Mg–Li alloys coupling is higher than CFRP/Mg–Al alloys, and the galvanic activity of CFRP/Mg–Li alloys coupling increases with the increase of lithium concentrations in Mg–Li alloys.

(3) Before the CFRP/magnesium alloys coupling reach the corresponding galvanic corrosion current density, the duration of the current density instability increases with the increase of lithium concentrations in the magnesium alloys.

(4) The micro arc oxidation (MAO) technique on the surface of the magnesium alloys can retard the galvanic corrosion of CFRP/magnesium alloys, and the duration of the inhibitory effect of MAO film on the corrosion of CFRP/Mg–Li coupling is longer than that of CFRP/Mg–Al coupling due to its double-layer structure.

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References


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