



# Article Microstructure and Corrosion Resistance of Two-Dimensional TiO<sub>2</sub>/MoS<sub>2</sub> Hydrophobic Coating on AZ31B Magnesium Alloy

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**Abstract:** The corrosion resistance of magnesium alloys can be effectively improved by surface treatment. In this study, a hydrophobic two-dimensional (2D) TiO<sub>2</sub>/MoS<sub>2</sub> nanocomposite coating was fabricated on AZ31B magnesium alloy by an electrophoretic deposition method. The corrosion resistance of the coating was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy analyses. After being modified by a silane coupling agent (KH570), the TiO<sub>2</sub>/MoS<sub>2</sub> coating changed from hydrophilic to hydrophobic, and the static water contact angle increased to 131.53°. The corrosion experiment results indicated that the hydrophobic 2D TiO<sub>2</sub>/MoS<sub>2</sub> coating had excellent anticorrosion performance (corrosion potential:  $E_{corr} = -0.85 V_{Ag/AgCl}$ , and corrosion current density:  $I_{corr} = 6.73 \times 10^{-8} \text{ A} \cdot \text{cm}^{-2}$ ). TiO<sub>2</sub>/MoS<sub>2</sub> films have promising applications in magnesium alloy corrosion protection.

Keywords: magnesium alloys; electrophoretic deposition; TiO<sub>2</sub>/MoS<sub>2</sub>; corrosion resistance

## 1. Introduction

Magnesium alloys, widely used in the aerospace and automotive industries, have the advantages of high specific strength, low density, good manufacturability and recyclability, and abundant resources [1–4]. However, due to the relatively active chemical properties of magnesium, low standard electrode potential, and poor protection ability of natural oxide film, the corrosion resistance of magnesium alloys is poor [5–7], which limits their wider application. Therefore, improving the corrosion resistance of magnesium alloys can greatly expand their practical application. The commonly used methods to improve the corrosion resistance of magnesium alloys include chemical conversion coating [8], plasma electrolytic oxidation [9], laser surface melting [10], shot peening [11], cold spraying [12], etc. These methods can improve the corrosion resistance of magnesium alloys, but the process is complex, costly, energy-intensive, and poses various environmental issues. On the other hand, constructing a thin film on the surface of magnesium alloys by electrodeposition can effectively slow down the corrosion rate of materials and has the advantages of low cost, convenient operation, rapid film formation, and ease of control [13,14].

Two-dimensional materials have attracted more attention for their potential applications in optics, electrochemical energy storage, biosensing, and other fields due to their special physical properties [15–20]. The 2D materials are also used as coatings to form protective layers, which can act as physical barriers to prevent contact between the corrosive medium and the substrate and avoid corrosion [21,22]. Since graphene was discovered, it has been widely used in the field of corrosion resistance due to its good chemical stability, high strength, and low friction coefficient [23–25]. Single-layer defect-free graphene can



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). prevent the permeation of molecules. However, defective graphene will accelerate galvanic corrosion [26,27]. In recent years, an increasing number of graphene-like 2D materials have been discovered, such as MoS<sub>2</sub>, TiO<sub>2</sub>, boron nitride, C<sub>3</sub>N<sub>4</sub>, and MXene [28–32]. TiO<sub>2</sub> and MoS<sub>2</sub> are two promising two-dimensional materials that have great development potential in the field of anticorrosion. TiO<sub>2</sub> has good chemical and thermal stability. At the same time, due to the lack of interconnected pores in  $TiO_2$ , the corrosion resistance of  $TiO_2$  is higher than that of other metal oxides [33–37]. For instance, Devikala et al. [38] showed that with the increase in  $TiO_2$  concentration the corrosion resistance efficiency of composites increased. Rostami et al. [39] demonstrated that the addition of TiO<sub>2</sub> improved the corrosion resistance of the pure cobalt film. Shams Anwar et al. [40] indicated that the addition of TiO<sub>2</sub> nanoparticles improved the corrosion resistance of Zn-Ni alloys. MoS<sub>2</sub> has attracted extensive attention in the field of corrosion protection because of its special (S-Mo-S) three-atomic-layer structure and excellent chemical stability [41,42]. For example, Xia et al. [43] prepared SiO<sub>2</sub> nanoparticles modified by  $MoS_2$  nanosheets, which showed robust corrosion resistance. Hu et al. [44] demonstrated that nano-MoS<sub>2</sub> on a zinc phosphate coating effectively promoted the phosphating process, which improved the corrosion resistance of Q235 low-carbon steel. Chen et al. [45] loaded nano-MoS<sub>2</sub> on the surface of graphene oxide flakes, which endowed the composite coating with excellent barrier properties and significantly improved the corrosion resistance of the coating.

In this work, we describe our recent progress in the synthesis of the hydrophobic nanocomposite coating, which is 2D  $TiO_2/MoS_2$  modified by a silane coupling agent, KH570. This was synthesized to enhance the corrosion resistance of AZ31B magnesium alloy. Because 2D  $TiO_2$  and  $MoS_2$  have similar electronegativity,  $MoS_2$  was added to  $TiO_2$  dispersion to obtain an electrophoretic solution. Then, a  $TiO_2/MoS_2$  thin film was prepared on the surface of the magnesium alloy by electrophoretic deposition. The prepared 2D  $TiO_2/MoS_2$  thin film was modified by KH570. The as-prepared thin film has hydrophobic properties and excellent corrosion resistance, which satisfies the demands of society and has broad application prospects.

#### 2. Materials and Methods

#### 2.1. Materials

AZ31B magnesium alloy (thickness of 1 mm, composition: 2.5–3.5 wt % Al, 0.6–1.4 wt % Zn, 0.2–1.0 wt % Mn, 0.04 wt % Ca, 0.003 wt % Fe, 0.001 wt % Ni, 0.08 wt % Si, 0.01 wt % Cu) was purchased from Dongguan Hongdi Metal Materials Co., Ltd. (Dongguan, China). Silane coupling agent KH570 was purchased from Jinan Xingfeilong Chemical Co., Ltd. (Jinan, China).

#### 2.2. Preparation of TiO<sub>2</sub>/MoS<sub>2</sub> Films

The TiO<sub>2</sub> colloid and MoS<sub>2</sub> were synthesized according to previous studies [46,47]. We added 0.7 mL of 1.0 mg/mL MoS<sub>2</sub> aqueous solution to 100 mL of 70% ethanol solution containing 1 mL of TiO<sub>2</sub> colloid. The two magnesium alloy substrates were kept at a distance of 15–20 mm in 5 mL of electrophoresis solution and electrophoresed for 90 s at a constant voltage of 20 V. After electrophoresis, the excess precipitates on the surface were washed with deionized water, dried at room temperature for 48 h, and heated at 150 °C for 60 min to obtain TiO<sub>2</sub>/MoS<sub>2</sub> coating.

#### 2.3. Preparation of $TiO_2/MoS_2$ Films Modified by KH570

The prepared samples were immersed in a beaker containing silane coupling agent, KH570 solution, for 30 min. After repeated rinsing with anhydrous ethanol, the silane-modified  $TiO_2/MoS_2$  surface layer was obtained. The resultant product was denoted as  $TiO_2/MoS_2$ -K.

The zeta potential of  $TiO_2$  and  $MoS_2$  was determined by Nanometrics (Malvern Zetasizer Nano ZS90, malvernpanalytical). Figure 1 shows the zeta potential diagrams of  $TiO_2$  and  $MoS_2$  measured at 25 °C. The measured electronegativity results are shown in Table 1. On the basis of Figure 1 and Table 1, it is shown that  $TiO_2$  and  $MoS_2$  have similar electronegativity. Therefore,  $MoS_2$  was added to the  $TiO_2$  dispersion, and both were deposited on the anode during electrophoresis deposition.



Figure 1. Zeta potential diagram of TiO<sub>2</sub> and MoS<sub>2</sub>.

**Table 1.** Electronegativity of  $TiO_2$  and  $MoS_2$ .

Sample	Zeta Potential/mV			
TiO <sub>2</sub>	-0.511			
MoS <sub>2</sub>	-0.356			

# 2.5. Characteristics of Morphology, Chemical Composition, and Hydrophobic and Anticorrosion *Properties*

The surface morphology of the samples was observed using an S-4800 scanning electron microscope (SEM, S-4800, Japan Hitachi Corporation, Tokyo, Japan). The phase structure of the samples was characterized by a D-8 X-ray diffractometer (XRD, D8, Beijing Brook Technology Co., Ltd., Beijing, China). The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo ESCALAB 250XI. Fourier transform infrared spectroscopy (FTIR, IRPrestige-21, Shanghai Yixiang Instrument Co., Ltd., Shanghai, China) was carried out for TiO<sub>2</sub>/MoS<sub>2</sub> and TiO<sub>2</sub>/MoS<sub>2</sub>-K. Measurement of the static water contact angle on the sample surface was performed using a contact angle measuring instrument (SDC-100S, Dongguan Shengding Precision Instrument Co., Ltd., Dongguan, China); 6 µL was set as the drip volume in the test, and multiple measurements were performed at different positions on the surface of each sample, with the average value of multiple measurements taken for analysis. Metal corrosion in the atmosphere was simulated by a salt spray corrosion test box (DF-YWX/Q-150, Nanjing Defu Test Equipment Co., Ltd., Nanjing, China); 5 wt % NaCl solution was prepared as the test solution. The experimental temperature was controlled at  $35 \pm 2$  °C, and the pressure of the atomized salt solution was maintained in the range of 69~172 kPa. The sample size was  $10 \times 10 \times 1$  mm. An electrochemical workstation (CHI760E, Shanghai Chenhua, Shanghai, China) was used to test the corrosion polarization curve of the magnesium alloy samples. A 3.5% NaCl solution was used as the electrolyte, and a three-electrode system was adopted, in which AgCl was used as the reference electrode and Pt was used as the counter electrode, and the scanning speed was 5 mV/s. The determination of  $E_{corr}$  is the abscissa corresponding to

the intersection of the cathode zone and the anode zone, and  $I_{coor}$  is the intersection of the tangent of the cathode zone and the vertical line corresponding to  $E_{corr}$ .

#### 3. Results and Discussion

#### 3.1. Morphology Analysis of TiO<sub>2</sub>/MoS<sub>2</sub> Films

The surface morphology of the films deposited on the magnesium alloy substrate at different magnifications is presented in Figure 2. According to Figure 2a,b, a layer of a fog-like film composed of nanosheets is evenly spread on the surface of AZ31B. The bright white point is due to the tiny residual particles of titanate when it is exfoliated into TiO<sub>2</sub>. In Figure 2c,d, the cracks are clearly displayed, which are caused by the accumulation of large amounts of MoS<sub>2</sub> in the substrate surface solution during electrophoretic deposition. Figure 2d shows the microscopic magnification of the relatively flat area. The nanosheets are stacked together to form large particles. The surface roughness was increased, and obvious cracks could be observed. As shown in Figure 2e, the surface layer completely and uniformly covers the surface of AZ31B, and there is no honeycomb connection between the nanosheets, which becomes very dense. The contact between the surface of AZ31B and air or corrosive substances is completely isolated, and a good protective barrier is formed [48,49]. Figure 2f shows that the coating becomes denser after KH570 modification.



Figure 2. SEM images of films deposited on AZ31B: (a,b)  $TiO_2$ , (c,d)  $MoS_2$ , (e)  $TiO_2/MoS_2$ , (f)  $TiO_2/MoS_2$ -K.

#### 3.2. Compositional Analysis of TiO<sub>2</sub>/MoS<sub>2</sub> Films

Figure 3 shows the XRD patterns of the AZ31B substrate,  $TiO_2$  and  $MoS_2$  powder and  $TiO_2/MoS_2$  film. The difference in peak position represents the difference in  $TiO_2$  layer spacing, which proves that  $TiO_2$  with random layer spacing is prepared [50,51]. The peaks of  $MoS_2$  powder correspond to the hexagonal  $MoS_2$  standard card (JCPDS No. 37-1492). Notably, after preparing  $TiO_2/MoS_2$  film on the surface of the magnesium alloy, the peaks of  $TiO_2$  and  $MoS_2$  are not obvious due to the strong peak of the AZ31B substrate. Combined

with the results of the energy spectrum analysis of the corrosion products of the samples,  $TiO_2/MoS_2$  films were successfully prepared.



Figure 3. XRD patterns of magnesium alloy, TiO<sub>2</sub>, MoS<sub>2</sub>, and TiO<sub>2</sub>/MoS<sub>2</sub> films.

#### 3.3. XPS of TiO<sub>2</sub>/MoS<sub>2</sub> Coating

XPS measurements were conducted to characterize the surface compositions. As shown in Figure 4, TiO<sub>2</sub> features two characteristic peaks at around 463.9 and 458.2 eV, corresponding to the Ti  $2p^{1/2}$  and Ti  $2p^{3/2}$  components, respectively. In Figure 4c, two peaks at 233.1 and 229.9 eV are assigned to Mo  $3d^{3/2}$  and Mo  $d^{5/2}$ , which suggests that the majority of Mo at the surface is Mo<sup>4+</sup>. Simultaneously, the peak at 227.1 eV belongs to the S 2s orbital of MoS<sub>2</sub>. The S 2p XPS spectrum shows that two peaks located at 163.9 and 162.9 eV correspond to S  $2p^{1/2}$  and S  $2p^{3/2}$ , which is consistent with the -2 oxidation state of sulfur. This confirms the successful synthesis of TiO<sub>2</sub>/MoS<sub>2</sub>.



Figure 4. XPS spectra of  $TiO_2/MoS_2$ : (a) Ti 2p, (b) O 1s, (c) Mo 3d, (d) S 2p.

### 3.4. Hydrophilicity Test of TiO<sub>2</sub>/MoS<sub>2</sub> Films

The wettability of the material surface also has an important influence on the corrosion resistance of the material. It is generally believed that the hydrophobic surface makes it more difficult for water molecules or chloride ions to penetrate the metal surface due to the isolation effect, thereby inhibiting the corrosion of the metal [52–54]. The contact angles (CA) of the magnesium alloy and the  $TiO_2/MoS_2$  and  $TiO_2/MoS_2$ -K films are presented in Figure 5a. As shown in Figure 5a, the CA of the magnesium alloy is  $36.08^{\circ}$ , indicating that the surface of the AZ31B substrate without coatings is hydrophilic. When the  $TiO_2/MoS_2$  surface layer was electrophoretically deposited on the surface of the AZ31B substrate, the CA increased to 65.43°. When the TiO<sub>2</sub>/MoS<sub>2</sub> film was modified by KH570, the CA value was 131.53°. Another important observation is that the surface of the alloy changes from hydrophilic to hydrophobic. This is because the silane coupling agent KH570 is hydrolyzed into silanol in the solution, and the silanol is condensed with -OH on the  $TiO_2/MoS_2$  film [55]. The hydrophilic functional group (-OH) of the  $TiO_2/MoS_2$  coating was replaced by the organic functional group in silanol, and the reaction process is shown in Formulas (1)–(3). Figure 5b shows the FTIR spectra of TiO<sub>2</sub>/MoS<sub>2</sub> and TiO<sub>2</sub>/MoS<sub>2</sub>-K. Two new peaks of TiO<sub>2</sub>/MoS<sub>2</sub>-K at about 1240 and 1280 cm<sup>-1</sup> are attributed to stretching vibrations of C-O-C. Meanwhile, the absorption peak at 1710  $\text{cm}^{-1}$  is assigned to the stretching vibration of C=O. The intensity of  $TiO_2/MoS_2$ -K is weaker than that of  $TiO_2/MoS_2$  because the organic functional groups in silanol replace -OH on the surface of silane-modified  $TiO_2/MoS_2$ . These results indicate that the surface of the  $TiO_2/MoS_2$  surface layer is modified by KH570, thereby enhancing the surface hydrophobicity of  $TiO_2/MOS_2$  [56]. This effectively isolates the magnesium alloy from making contact with liquid, making it more difficult for water molecules or chloride ions to penetrate the metal surface and effectively enhancing the corrosion resistance of the magnesium alloy [57].

 $CH_2 = C(CH_3)COO(CH_2)_3Si(OCH_3)_3 + 3H_2O \rightarrow CH_2 = C(CH_3)COO(CH_2)_3Si(OH)_3 + 3CH_3OH$ (1)

 $CH_2 = C(CH_3)COO(CH_2)_3Si(OH)_3 + HO-(TiO_2)_n \rightarrow CH_2 = C(CH_3)COO(CH_2)_3Si-O-(TiO_2)_n + H_2O + 2OH^-$ (2)

 $CH_2 = C(CH_3)COO(CH_2)_3Si(OH)_3 + HO-(MoS_2)_n \rightarrow CH_2 = C(CH_3)COO(CH_2)_3Si-O-(MoS_2)_n + H_2O + 2OH^-$ (3)



**Figure 5.** (a) Contact angles of magnesium alloy,  $TiO_2/MoS_2$ , and  $TiO_2/MoS_2$ -K; (b) FT-IR spectra of  $TiO_2/MoS_2$  and  $TiO_2/MoS_2$ -K.

#### 3.5. Electrochemical Test of TiO<sub>2</sub>/MoS<sub>2</sub> Films

Figure 6 shows the potentiodynamic polarization curves of all the samples in 3.5 wt % NaCl aqueous solution. The results of the test are summarized in Table 2. On the basis of Figure 6 and Table 2, it is shown that the corrosion current density ( $I_{corr}$ ) of the magnesium alloy decreases after electrophoresis. The polarization curve shape of the sample after deposition is similar to that of the magnesium alloy substrate, indicating that the 2D films

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do not change the corrosion kinetics process of the magnesium alloy. The contact between the substrate and the corrosion medium is isolated by the surface thin film, which improves the corrosion resistance of the magnesium alloy to a certain extent. The corrosion potential (E<sub>corr</sub>) of the AZ31B magnesium alloy is -1.47 V and the I<sub>corr</sub> is  $6.81 \times 10^{-4}$  A·cm<sup>-2</sup>, indicating that the corrosion resistance of the magnesium alloy matrix is poor [58]. The results show that the  $E_{corr}$  of TiO<sub>2</sub>/MoS<sub>2</sub>-K has a higher potential compared with TiO<sub>2</sub>, MoS<sub>2</sub>, and  $TiO_2/MoS_2$  composite coatings. Among them,  $TiO_2/MoS_2$ -K has the lowest I<sub>corr</sub>. The  $I_{corr}$  values for the TiO<sub>2</sub> and MoS<sub>2</sub> surface layer are  $5.13 \times 10^{-6}$  and  $2.19 \times 10^{-5}$  A·cm<sup>-2</sup>, respectively, whereas that of the TiO<sub>2</sub>/MoS<sub>2</sub> film is  $3.69 \times 10^{-7}$  A·cm<sup>-2</sup>. The I<sub>corr</sub> of the  $TiO_2/MOS_2$  film decreases by two orders of magnitude compared to the MoS<sub>2</sub> film, which is due to the dense state of the  $TiO_2/MoS_2$  coating. The  $E_{corr}$  of the  $TiO_2/MoS_2$ -K film is -0.85 V, and the I<sub>corr</sub> is  $6.73 \times 10^{-8}$  A·cm<sup>-2</sup>. Compared with the TiO<sub>2</sub>/MoS<sub>2</sub> film, the  $E_{corr}$  of the TiO<sub>2</sub>/MoS<sub>2</sub>-K film shifted positively by 0.15 V, and the I<sub>corr</sub> decreased by six times. This indicates that the KH570 modification improved the corrosion resistance of the  $TiO_2/MoS_2$  protective layer, which is ascribed to its effectively isolating the magnesium alloy from contacting the corrosive liquid.



Figure 6. Polarization curves of magnesium alloy, TiO<sub>2</sub>, MoS<sub>2</sub>, TiO<sub>2</sub>/MoS<sub>2</sub>, TiO<sub>2</sub>/MoS<sub>2</sub>-K.

Table 2. Potentiodynamic pol	larization curves of samples	; in 3.5 wt % NaCl aqueous sol	ution.
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Sample	$E_{corr}/(V_{Ag/AgCl})$	$I_{corr}/(A \cdot cm^{-2})$
Magnesium alloy	-1.47	$6.81 imes10^{-4}$
TiO <sub>2</sub>	-1.34	$5.31  imes 10^{-6}$
$MoS_2$	-1.11	$2.19 imes10^{-5}$
$TiO_2/MoS_2$	-1.00	$3.69 imes10^{-7}$
TiO <sub>2</sub> /MoS <sub>2</sub> -K	-0.85	$6.73 imes10^{-8}$

To further characterize corrosion resistance, we used EIS to analyze the anticorrosion of the sample. Figure 7 shows the electrochemical impedance spectroscopy of magnesium alloy,  $TiO_2$ ,  $TiO_2/MoS_2$ -K. The electrochemical impedance spectroscopy data are described in detail by the numerical fitting of experimental data. The corresponding equivalent circuit was selected to fit the impedance data, as shown in Figure 8. The fitting circuit of the magnesium alloy substrate is shown in Figure 8a, and the fitting circuit of the samples with  $TiO_2$  film and those with  $TiO_2/MoS_2$ -K films is shown in Figure 8b [59]. The results are shown in Table 3. The circuit involves the solution resistance ( $R_s$ ), the charge transfer

resistance ( $R_{ct}$ ) of the Mg particles, and the electric double-layer capacitance (CPE<sub>dl</sub>) at the interface between the electrolyte and magnesium particles.  $R_p$  is the inductance resistance, and CPL<sub>film</sub> is the inductance, corresponding to the electrode reaction between the film layer and the electrolyte interface. It is reported that  $R_{ct}$  is closely related to the corrosion process, that is, the higher the  $R_{ct}$ , the better the corrosion resistance. It can be seen from the results that the impedance radius of the TiO<sub>2</sub>/MoS<sub>2</sub>-K sample is the largest, and the  $R_{ct}$  value is the largest at 871.9  $\Omega \cdot cm^2$ , which is significantly higher than that of the magnesium alloy sample and the sample with the TiO<sub>2</sub> film. It shows that the corrosion resistance of TiO<sub>2</sub>/MoS<sub>2</sub>-K is the highest, which is consistent with the results of the polarization curve.



Figure 7. Electrochemical impedance spectroscopy of magnesium alloy, TiO<sub>2</sub>, TiO<sub>2</sub>/MoS<sub>2</sub>-K.



**Figure 8.** Equivalent circuits for EIS spectra: (**a**) magnesium alloy, (**b**)  $TiO_2$  thin film and  $TiO_2/MoS_2$ -K thin film.

Table 3. Electrochemical data extracted from ECs fitting of the EIS curves.

Sample	$R_s$ ( $\Omega \cdot cm^2$ )	CPE <sub>film</sub> (F/cm <sup>2</sup> )	$R_p$ ( $\Omega \cdot cm^2$ )	CPE <sub>d1</sub> -T (F/cm <sup>2</sup> )	CPE <sub>dl</sub> -P (F/cm <sup>2</sup> )	$\frac{R_{ct}}{(\Omega \cdot cm^2)}$
Magnesium alloy	10.2	-	-	$7.11  imes 10^{-6}$	-	111.9
TiO <sub>2</sub>	8.97	$1.27  imes 10^{-6}$	16.96	$1.66 imes10^{-6}$	0.98	659.6
TiO <sub>2</sub> /MoS <sub>2</sub> -K	9.25	$8.92  imes 10^{-6}$	19.29	$1.87  imes 10^{-6}$	0.95	871.9

#### 3.6. Salt Spray Corrosion Experiment of TiO<sub>2</sub>/MoS<sub>2</sub> Films

Figure 9 shows the comparison of the surface morphology of the magnesium alloy samples, electrophoretically deposited  $TiO_2$ , and  $TiO_2/MoS_2$ -K after the neutral salt spray test for 24, 48, and 72 h. Table 4 shows the results of the energy spectrum analysis of the corrosion products of the samples. It can be seen from the data in Table 4 that, in addition to the original elements, Na and Cl elements were also added to all the corrosion products

of the samples, indicating that the chemical corrosion process occurred in the samples and salt spray. Combined with the SEM images, it can be seen that pitting corrosion occurred on the samples with  $TiO_2/MoS_2$ -K film, which is similar to that on the samples with  $TiO_2$  coating. With increasing time, the corrosion area increased gradually, but it was smaller than that on the surface of the magnesium alloy and the samples with the  $TiO_2$  layer. This was mainly due to the good chemical stability of  $TiO_2$  and  $MoS_2$  and the formation of the dense protective layer after electrophoresis. The hydrophobic thin film modified by KH570 further delayed the corrosion of the magnesium alloy.



**Figure 9.** The microstructure of the sample surface after salt spray test at different times. Magnesium alloy: (a) 24 h, (b) 48 h, (c) 72 h;  $TiO_2$  film: (e) 24 h, (f) 48 h, (g) 72 h;  $TiO_2/MoS_2$ -K film: (i) 24 h, (j) 48 h, (k) 72 h. The (d,h,l) insets are partial enlargements of (c,g,k), respectively.

Point	0	Mg	Mn	Ti	Na	Cl	Мо	S
А	57.64	26.18	12.02	0	2.79	1.37	0	0
В	59.23	25.43	11.08	0	2.51	1.75	0	0
С	55.38	25.28	12.60	2.40	3.15	1.19	0	0
D	53.85	25.32	11.06	3.99	3.98	1.80	0	0
E	55.62	25.16	11.10	3.69	2.17	1.12	0.22	0.92
F	56.38	25.09	11.20	2.57	2.23	1.33	0.19	1.01

Table 4. Energy spectrum analysis of neutral salt spray test products (at. %).

Figure 10 shows the salt spray corrosion weight gain of the magnesium alloy samples after electrophoretic deposition of  $TiO_2$  and  $TiO_2/MoS_2$ -K films. The weight gain rate of the sample with  $TiO_2/MoS_2$ -K is higher at the beginning of the test than that of the magnesium alloy sample and the sample with  $TiO_2$  coating. With increasing salt spray corrosion time, the weight gain rate of the sample gradually slows down because the corrosion products on the surface of the sample increase, which hinders the continuous reaction of chloride ion contact with the magnesium alloy surface. In addition, the weight gain of the sample with the  $TiO_2/MoS_2$ -K film is significantly lower than that of the former two samples, and the corrosion rate is the lowest. This result indicates that the  $TiO_2/MoS_2$ -K protective layer delayed the corrosion of the magnesium alloy to a greater extent and had the best corrosion resistance.



Figure 10. Salt spray corrosion weight gain diagram.

#### 4. Conclusions

The TiO<sub>2</sub>/MoS<sub>2</sub> coating was successfully prepared on the surface of the magnesium alloy by adding MoS<sub>2</sub> in the electrophoretic deposition of TiO<sub>2</sub>. After the TiO<sub>2</sub>/MoS<sub>2</sub> layer was modified by the silane coupling agent KH570, the wettability of the magnesium alloy surface was changed from hydrophilic to hydrophobic. The as-prepared TiO<sub>2</sub>/MoS<sub>2</sub>-K film had a contact angle of 131.53°. Combined with the electrochemical test and salt spray corrosion analysis, it can be seen that the TiO<sub>2</sub>/MoS<sub>2</sub>-K film developed a significantly improved anticorrosion property compared to the magnesium alloy. In addition, we anticipate a promising potential to transfer this technology to other metal substrates for important applications.

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