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# Inhibition mechanism of NaF on WE43 Mg alloy in NaCl solution

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**Abstract:** The influence of NaF on the microstructure, composition and corrosion performance of WE43 Mg alloy in 3.5 wt.% NaCl solution was systematically investigated by means of SEM, TEM, EPMA, XRD, XPS and electrochemical measurements. It was proved that NaF is an effective inhibitor for WE43 Mg alloy and the highest inhibition efficiency is 92.6% at its concentration of 40 mmol/L in neutral NaCl solution. The dissolution of WE43 alloy is inhibited by formation and deposition of a dense and protective double-layered corrosion film by chemical reaction between corrosion inhibitor and dissolved Mg<sup>2+</sup>. The microstructure and composition of this double-layered corrosion film were investigated by FIB and TEM. The outer layer of the corrosion film is found to be composed of NaMgF<sub>3</sub>, MgF<sub>2</sub> and MgO, while the inner layer mainly consists of MgO and MgF<sub>2</sub>.

**Key words:** Mg alloy; corrosion; corrosion film; inhibitor; inhibition mechanism

## 1 Introduction

Magnesium (Mg) has great potential as an engineering material for applications in industries due to its high specific strength [1–3]. Due to its biocompatibility and low density, Mg is utilized in the medical field [4–6]. In recent years, Mg has also been employed in the field of aqueous and secondary batteries due to the high conductivity and low cost [7–9]. Nevertheless, Mg alloy suffers severe corrosion attack due to its low standard potential (−2.37 V (vs SHE)) [10–13]. It was found that there is a large potential between the intermetallic phase and Mg matrix, promoting the micro-corrosion process [14,15]. Fe, Ni and other impurities inevitably enter the matrix during the smelting process, which further increase dissolution

rate of the substrate [16–18]. Additionally, the corrosion film is primarily composed of Mg(OH)<sub>2</sub>. The hydroxide layer is porous and has a minimal impact on limiting the corrosion process of the substrate [19–22]. Besides surface treatment processes, the introduction of corrosion inhibitors has been proved to be one of the most effective approaches to reduce the corrosion rate of Mg for industrial application [23–26]. It was reported that the adsorption of organic inhibitors onto the surface of Mg can greatly reduce the contact area between the matrix and electrolyte, leading to the enhanced corrosion resistance [27–30]. LU et al [31,32] found that sodium dodecyl sulfate (SDS) was adsorbed on the surface of AZ91 Mg alloy, which inhibited micro-galvanic corrosion and degradation process of the substrate. The inhibition efficiency of SDS on AZ91 Mg alloy was 88.8% after immersion

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for 48 h. YANG et al [33] studied the inhibition mechanism of carboxylic acids (2,5-PDCA and fumaric acid) on pure Mg. It was found that the adsorption of 2,5-PDCA and fumaric acid reduced the potential difference between the matrix and the secondary phase, which inhibited the micro-galvanic corrosion. XIAO et al [34] proved that sodium lignosulfonate (SLS) had a good corrosion inhibition effect on AZ31 Mg alloy and found that the adsorption of inhibitor on the sample surface was in line with Langmuir adsorption model. DINODI and SHETTY [35] found that the inhibition efficiency of 3 mmol/L stearate on ZE41 Mg alloy reached 88%. A compact and protective corrosion film was formed due to precipitation of adsorbed alkyl carboxylates on Mg alloy surface.

It was also found that inhibitors participate in the deposition of protective corrosion film on the sample surface by chemical reaction, which effectively influence the degradation process of the substrate [36–39]. POKHAREL et al [40] studied the influence of glycine on the corrosion performance of AZ31 Mg alloy in simulated body fluids. It was proved that glycine chelated with  $\text{Ca}^{2+}$  and deposited on Mg alloy surface after long-term immersion. KHARITONOV et al [41] found that 100 mmol/L  $\text{Na}_2\text{MoO}_4$  had significant corrosion inhibition effect on WE43 Mg alloy.  $\text{MoO}_4^{2-}$  leads to the formation of  $\text{MoO}(\text{OH})_3$ , which inhibits the dissolution process. PRINCE et al [42] concluded that passive film layer generated on AZ31 Mg alloy in the presence of 50 mmol/L  $\text{Na}_2\text{CO}_3$ . After 7 d of immersion, 80% of inhibition efficiency was achieved in this solution. HUANG et al [43] studied the synergistic effect of  $\text{Na}_3\text{PO}_4$  and sodium dodecyl benzene-sulfonic acid (SDBS) on GW103 Mg alloy. The chemical reaction between  $\text{Na}_3\text{PO}_4$  and Mg matrix resulted in the deposition of large amounts of  $\text{Mg}_3(\text{PO}_4)_2$  on the sample surface, which greatly improved the protective ability of the corrosion product layer. QIU et al [44] found that 94.1% of inhibition efficiency was achieved by using NaF and DL-malic acid as inhibitor in NaCl solution. In the presence of mixed inorganic and organic inhibitor, large cubic  $\text{NaMgF}_3$  particles were transformed into smaller and refined spheroidal particles, leading to superior corrosion performance.

In this work, NaF was selected as corrosion inhibitor to modify the degradation process and

improve the corrosion resistance of WE43 Mg alloy. The inhibition mechanism of NaF on WE43 Mg alloy was studied by means of analyzing the composition and microstructure of the corrosion film layer formed on the sample surface.

## 2 Experimental

### 2.1 Material and reagents

WE43 Mg alloy was used and cut (10 mm  $\times$  10 mm  $\times$  5 mm) as the substrate. The Mg alloy samples were ground by emery papers before performing electrochemical corrosion tests. Different concentrations of NaF solution (5, 40 and 80 mmol/L) were added into 3.5 wt.% NaCl solution to study the influence of inhibitor on Mg alloy. pH value of all electrolytes was adjusted to 6.8–7.2 by dropping diluted NaOH solution. The chemicals used in this study were provided by Sinopharm Chemical Reagent Company in analytical grade.

### 2.2 Electrochemical measurements

The electrochemical corrosion tests were measured in conventional three-electrode cell by using Princeton Instruments P4000 (Ametek, the United States). 1 cm<sup>2</sup> of WE43 Mg alloy was used as the working electrode, a saturated calomel electrode was used as the reference electrode, and a platinum sheet was used as the counter electrode. The open circuit potential (OCP) was measured for 1 h to achieve a steady state before corrosion measurements. The polarization curves were collected from -300 mV (vs OCP) until anodic current density reached 10 mA/cm<sup>2</sup> with a scanning rate of 0.333 mV/s. The corrosion current density of sample was calculated by Stern equation (Eq. (1)).  $J_{\text{corr}}$  is the corrosion current density,  $\beta_a$  represents anodic polarization slope,  $\beta_c$  presents cathodic polarization slope, and  $R_p$  is the polarization resistance.

$$J_{\text{corr}} = \frac{\beta_a \beta_c}{\beta_a + \beta_c} \cdot \frac{1}{R_p} \quad (1)$$

Let  $J_{\text{corr}}$  and  $J'_{\text{corr}}$  represent the corrosion current density of the samples in the blank and NaF-containing NaCl solutions, respectively. The inhibition efficiency ( $\eta$ ) was calculated based on Eq. (1) as follows:

$$\eta = \frac{J_{\text{corr}} - J'_{\text{corr}}}{J_{\text{corr}}} \times 100\% \quad (2)$$

The electrochemical impedance spectroscopy (EIS) measurement was performed with AC amplitude 10 mV sinusoidal perturbation in frequency range from  $10^{-2}$  to  $10^5$  Hz. The obtained EIS data were fitted using a ZsimpWin software. All the measurements were repeated at least three times to ensure reproducibility.

### 2.3 Microstructure and elemental composition measurements

The surface and cross-sectional morphologies of the corroded samples after immersion test for 72 h were studied by scanning electron microscope (SEM, JSM-7001 F, JEOL, Japan). The phase composition of corrosion products was determined by using X-ray diffraction (Smartlab, Rigaku, Japan) in  $2\theta$  range from  $15^\circ$  to  $80^\circ$  with a scan rate of  $4^\circ/\text{min}$ . X-ray photoelectron spectroscopy (Shimazu-Kratos Analytical, UK) was used to investigate the chemical composition of the corroded samples. Peak identification was performed using XPSpeak41 software as reference and the binding energy scale was calibrated to the C 1s peak (284.6 eV). The elemental composition and distribution of the corroded samples were investigated by electron probe microanalysis (EPMA, JXA-8530F JEOL, Japan). The microstructure and composition of the corrosion product layer after immersion for 72 h with addition of NaF were obtained by transmission electron microscopy (TEM, JEM-2100 F, Japan, 200 keV) to study the inhibition mechanism of the inhibitors. The TEM lamellae were milled from the corroded specimen with focused ion beam (FIB, Zeiss Crossbeam 350, Germany).

## 3 Results

### 3.1 Mass loss test

Mass loss test was carried out to study the influence of NaF concentrations on the corrosion behavior of Mg alloy in different solutions (Fig. 1). The addition of different concentrations of NaF reduces dissolution rate of the Mg alloy samples. After introduction of 40 mmol/L NaF into the electrolyte, the mass loss rate of the substrate is reduced to the lowest value (0.013 mm/a, 1 a=1 year). As a result, the highest inhibition efficiency

is found to be 87.37% after immersion for 72 h. It can be inferred that addition of NaF might contribute to deposition of corrosion product layer with enhanced barrier property, which effectively inhibits the degradation process of Mg alloy.

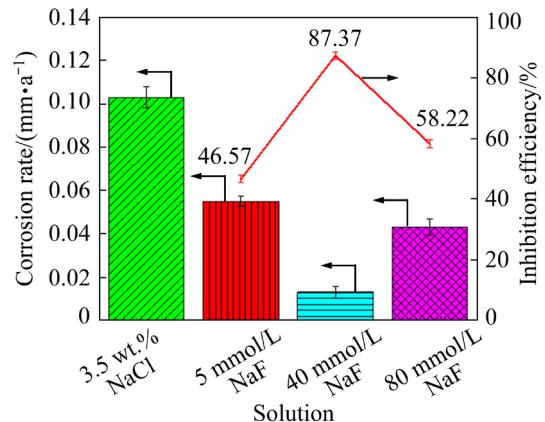
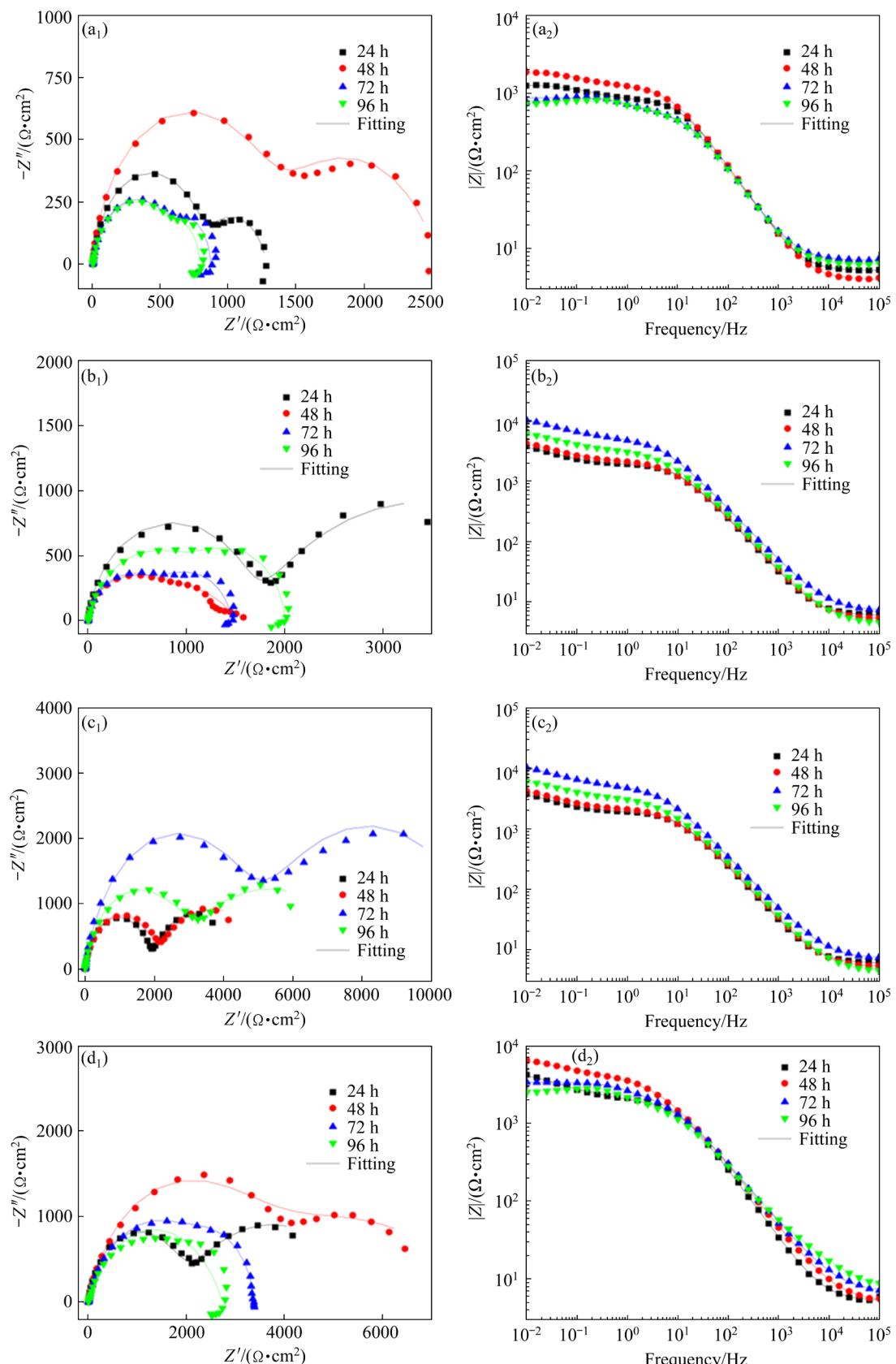


Fig. 1 Corrosion rate and inhibition efficiency of WE43 Mg alloy after immersion in various solutions for 72 h

### 3.2 Electrochemical behavior

#### 3.2.1 Electrochemical impedance spectroscopy

Figure 2 demonstrates the EIS data of sample immersed in different electrolytes. WE43 Mg alloy displays relatively low corrosion resistance during the immersion in 3.5 wt.% NaCl solution. The impedance of the sample starts to decrease after immersion for 24 h and an inductive loop appears since the beginning of the EIS measurement. Obviously, the presence of different concentrations of inhibitor significantly enhances the corrosion performance of the substrate. The sample shows the largest capacitive loop in the presence of 40 mmol/L NaF after soaking in the electrolyte for 72 h. The impedance value at low frequency sharply increases from  $611.2 \Omega \cdot \text{cm}^2$  (blank NaCl solution) to  $5091 \Omega \cdot \text{cm}^2$  (Table 1), suggesting that the protective capability of the corrosion product layer is greatly enhanced. As demonstrated in Table 1 and Fig. 3,  $R_s$  represents the solution resistance;  $R_f$  and  $\text{CPE}_f$  are related to the corrosion resistance and capacitance of the corrosion film formed on sample surface, respectively;  $R_{ct}$  corresponds to the charge transfer resistance, while  $\text{CPE}_{dl}$  is the capacitance of double layer at metal/electrolyte interface. The evolution of  $R_p$  ( $R_{ct}+R_f$ ) during immersion in different solutions is depicted in Fig. 3(b). The impedance of the samples immersed in 5 and 80 mmol/L NaF containing electrolyte increases firstly and decreases after 48 h

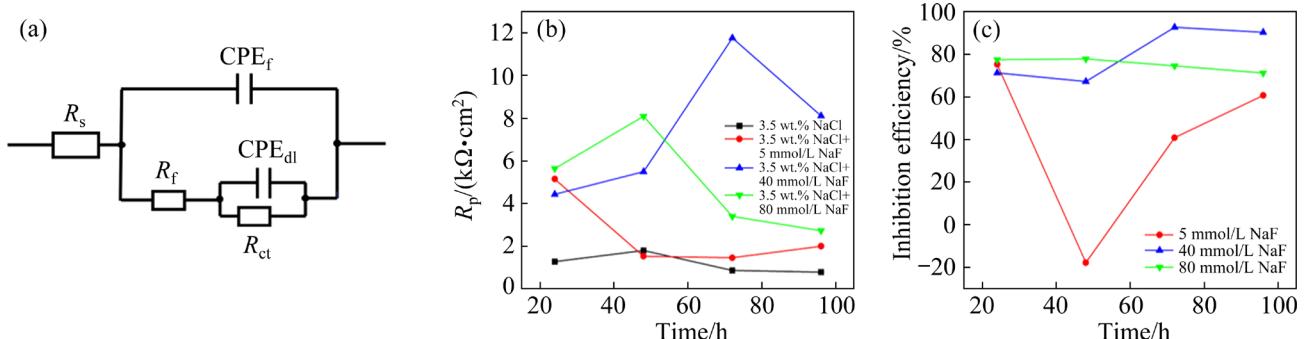


**Fig. 2** Electrochemical impedance spectra and fitting curves for WE43 Mg alloy immersed in 3.5 wt.% NaCl (a<sub>1</sub>, a<sub>2</sub>), 3.5 wt.% NaCl + 5 mmol/L NaF (b<sub>1</sub>, b<sub>2</sub>), 3.5 wt.% NaCl + 40 mmol/L NaF (c<sub>1</sub>, c<sub>2</sub>), and 3.5 wt.% NaCl + 80 mmol/L NaF (d<sub>1</sub>, d<sub>2</sub>) solutions for different time

**Table 1** Fitted results of impedance spectra

Solution	Time/h	$R_s/(\Omega \cdot \text{cm}^2)$	$\text{CPE}_f/(\mu\text{S} \cdot \text{s}^{-n} \cdot \text{cm}^{-2})$	$n_1$	$R_f/(\Omega \cdot \text{cm}^2)$	$\text{CPE}_{dl}/(\mu\text{S} \cdot \text{s}^{-n} \cdot \text{cm}^{-2})$	$n_2$	$R_{ct}/(\Omega \cdot \text{cm}^2)$
3.5 wt.% NaCl	24	5.2	23.43	0.92	838.8	2384	0.82	437.9
	48	5.16	27.09	0.90	991.8	1869	0.74	810.7
	72	7.04	31.11	0.88	611.2	597.1	0.95	255.8
	96	6.17	30.94	0.88	598.8	546.8	0.92	188.7
3.5 wt.% NaCl + 5 mmol/L NaF	24	5.84	12.74	0.92	1677	1851	0.61	3474
	48	5.15	14.62	0.92	595.2	406.8	0.51	934.8
	72	5.78	16.92	0.90	817.2	245.4	0.88	644.7
	96	8.12	25.23	0.87	1300	250.9	0.90	700.8
3.5 wt.% NaCl + 40 mmol/L NaF	24	5.98	13.18	0.89	1883	1890	0.74	2554
	48	5.25	13.54	0.88	1952	1149	0.60	3543
	72	7.28	11.36	0.86	5091	548.5	0.70	6673
	96	4.43	13.2	0.87	2791	638.1	0.53	5324
3.5 wt.% NaCl + 80 mmol/L NaF	24	5.28	12.88	0.89	1907	1008	0.56	3734
	48	5.11	17.66	0.81	3256	431.5	0.43	4837
	72	6.65	21.86	0.77	2674	229.5	0.91	724.1
	96	7.05	35.29	0.69	171.4	0.68	0.95	2556

$n_1$  and  $n_2$  are indexes ranging from 0 to 1, determining whether  $\text{CPE}_f$  or  $\text{CPE}_{dl}$  behaves as resistance ( $n_1$  or  $n_2=0$ ) or capacitance ( $n_1$  or  $n_2=1$ )



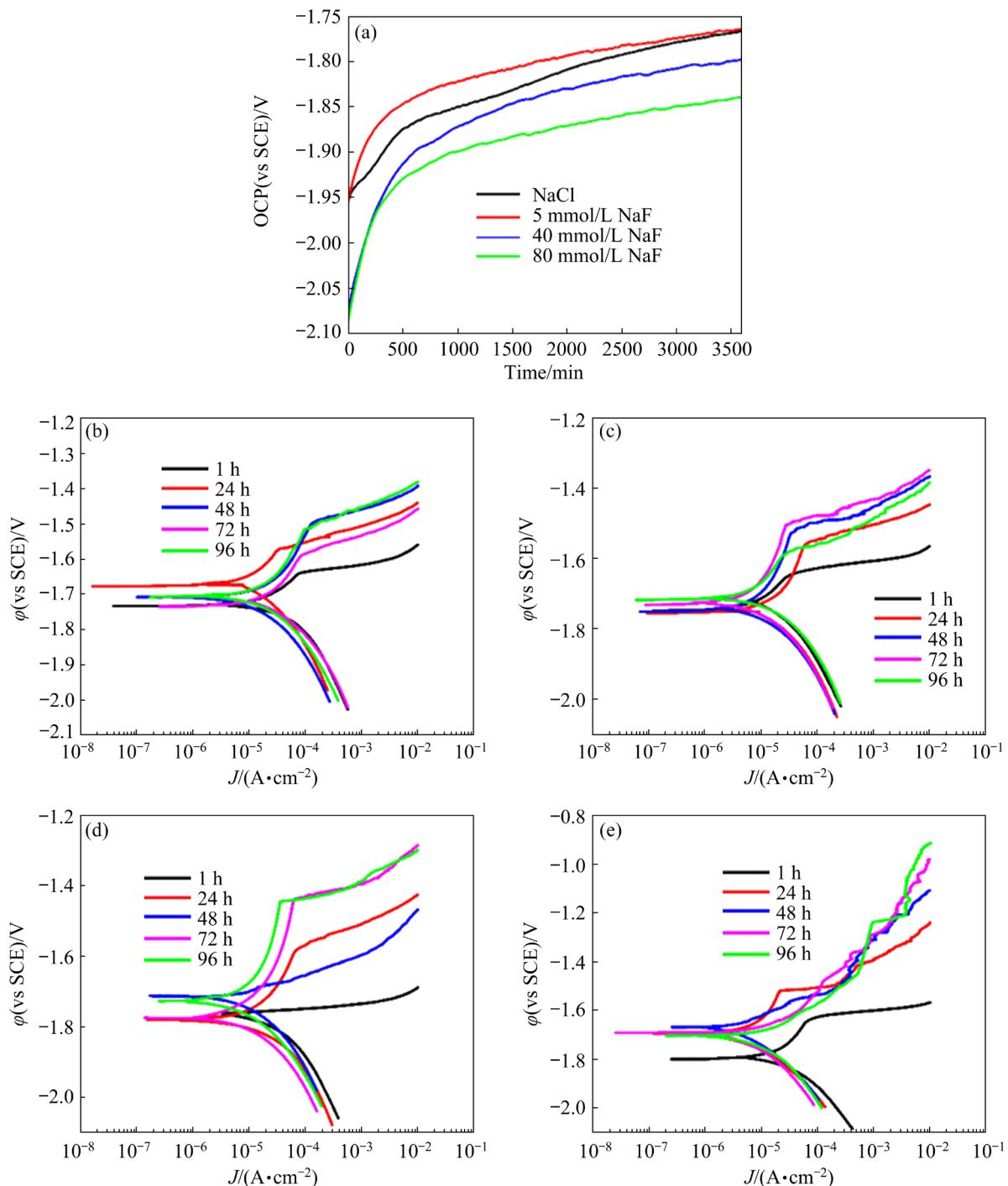
**Fig. 3** Equivalent circuit used to fit EIS data (a), evolution of  $R_p$  during immersion in various solutions (b), and inhibition efficiency of different concentrations of NaF solutions (c)

immersion. In contrast, the addition of 40 mmol/L NaF into the electrolyte demonstrates the highest corrosion resistance during the entire corrosion test.  $R_p$  of the sample is found to be  $11764 \Omega \cdot \text{cm}^2$  after EIS test for 72 h, which is more than 10 times compared to that in the blank electrolyte. The evolution of the inhibition efficiency during EIS measurement can be found in Fig. 3(c). It is clear that the inhibition efficiency of NaF increases with the increase of its concentration in the electrolyte.

### 3.2.2 Open circuit potential and polarization curves

The evolution of OCP and polarization curves of Mg samples after immersion in various solutions for different time is shown in Fig. 4. It is observable

that the OCP of the Mg alloy sample surface is reduced when immersed in the electrolyte in the presence of high concentration of inhibitor. This might be related to the dissolution and precipitation of corrosion products on the sample surface during corrosion test. In terms of blank electrolyte, the anodic branch of the polarized sample firstly moves to the left direction after immersion for 24 h and subsequently shifts to the right side until 96 h, indicating that the substrate degrades continually with the increase of immersion time. For samples immersed in inhibitor-containing solution, the anodic branch of the curves seems to show a passivation region after certain immersion time,



**Fig. 4** Evolution of OCP of samples during immersion in different solutions (a), and polarization curves of Mg alloy after immersion for different time in 3.5 wt.% NaCl (b), 3.5 wt.% NaCl + 5 mmol/L NaF (c), 3.5 wt.% NaCl + 40 mmol/L NaF (d), and 3.5 wt.% NaCl + 80 mmol/L NaF (e) solutions

indicating that the anodic dissolution kinetics is suppressed in the presence of NaF. The corrosion potential ( $\phi_{\text{corr}}$ ) and corrosion current density ( $J_{\text{corr}}$ ) of different samples were calculated from the cathodic polarization branch, as shown in Table 2. It can be found that higher concentration of inhibitor in the electrolyte results in lower corrosion current

density and the sample after immersion in 40 mmol/L inhibitor-containing solution for 72 h demonstrates the lowest  $J_{\text{corr}}$  ( $8.49 \mu\text{A}/\text{cm}^2$ ). The abovementioned results suggest that the presence of NaF facilitates the formation of corrosion product layer with enhanced barrier property on the sample surface.

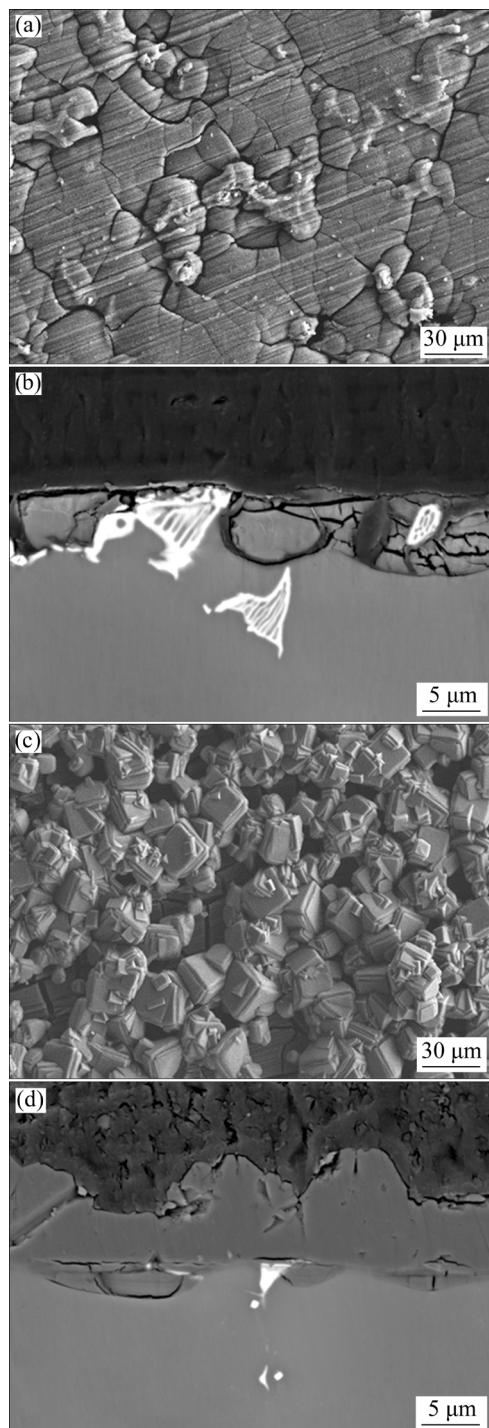
**Table 2** Corrosion performance of WE43 Mg alloy immersed in different solutions

Solution	Time/h	$\phi_{corr}$ (vs SCE)/V	$J_{corr}/(A \cdot cm^{-2})$
3.5 wt.% NaCl	1	-1.73	$4.42 \times 10^{-5}$
	24	-1.67	$1.41 \times 10^{-5}$
	48	-1.71	$1.24 \times 10^{-5}$
	72	-1.72	$2.90 \times 10^{-5}$
	96	-1.70	$1.44 \times 10^{-5}$
3.5 wt.% NaCl + 5 mmol/L NaF	1	-1.76	$3.01 \times 10^{-5}$
	24	-1.78	$1.22 \times 10^{-5}$
	48	-1.71	$2.25 \times 10^{-5}$
	72	-1.77	$1.24 \times 10^{-5}$
	96	-1.73	$1.16 \times 10^{-5}$
3.5 wt.% NaCl + 40 mmol/L NaF	1	-1.72	$1.50 \times 10^{-5}$
	24	-1.75	$1.57 \times 10^{-5}$
	48	-1.74	$1.00 \times 10^{-5}$
	72	-1.73	$8.49 \times 10^{-6}$
	96	-1.71	$1.27 \times 10^{-5}$
3.5 wt.% NaCl + 80 mmol/L NaF	1	-1.79	$2.83 \times 10^{-5}$
	24	-1.70	$1.13 \times 10^{-5}$
	48	-1.67	$8.99 \times 10^{-6}$
	72	-1.69	$1.01 \times 10^{-5}$
	96	-1.70	$1.23 \times 10^{-5}$

### 3.3 Characteristics of corroded samples

#### 3.3.1 Surface and cross-section morphologies

According to the electrochemical corrosion tests, the sample demonstrates superior corrosion performance in the presence of 40 mmol/L NaF. Therefore, the microstructure and composition of such corroded sample are investigated to further study the inhibition mechanism of NaF in NaCl solution, as shown in Fig. 5. After being immersed in 3.5 wt.% NaCl solution for 72 h (Fig. 5(a)), apparent corrosion products and large cracks can be observed on the sample surface. In terms of the cross-sectional morphology, the corrosion product layer is non-uniform and porous. Large chunks of corrosion products are found to be adjacent to the intermetallic phase (Fig. 5(b)), indicating that the matrix is preferentially dissolved due to micro-galvanic corrosion effect. It can be inferred that such a corrosion layer is not capable of providing sufficient protection for the substrate. As for the sample immersed in inhibitor-containing solution, a



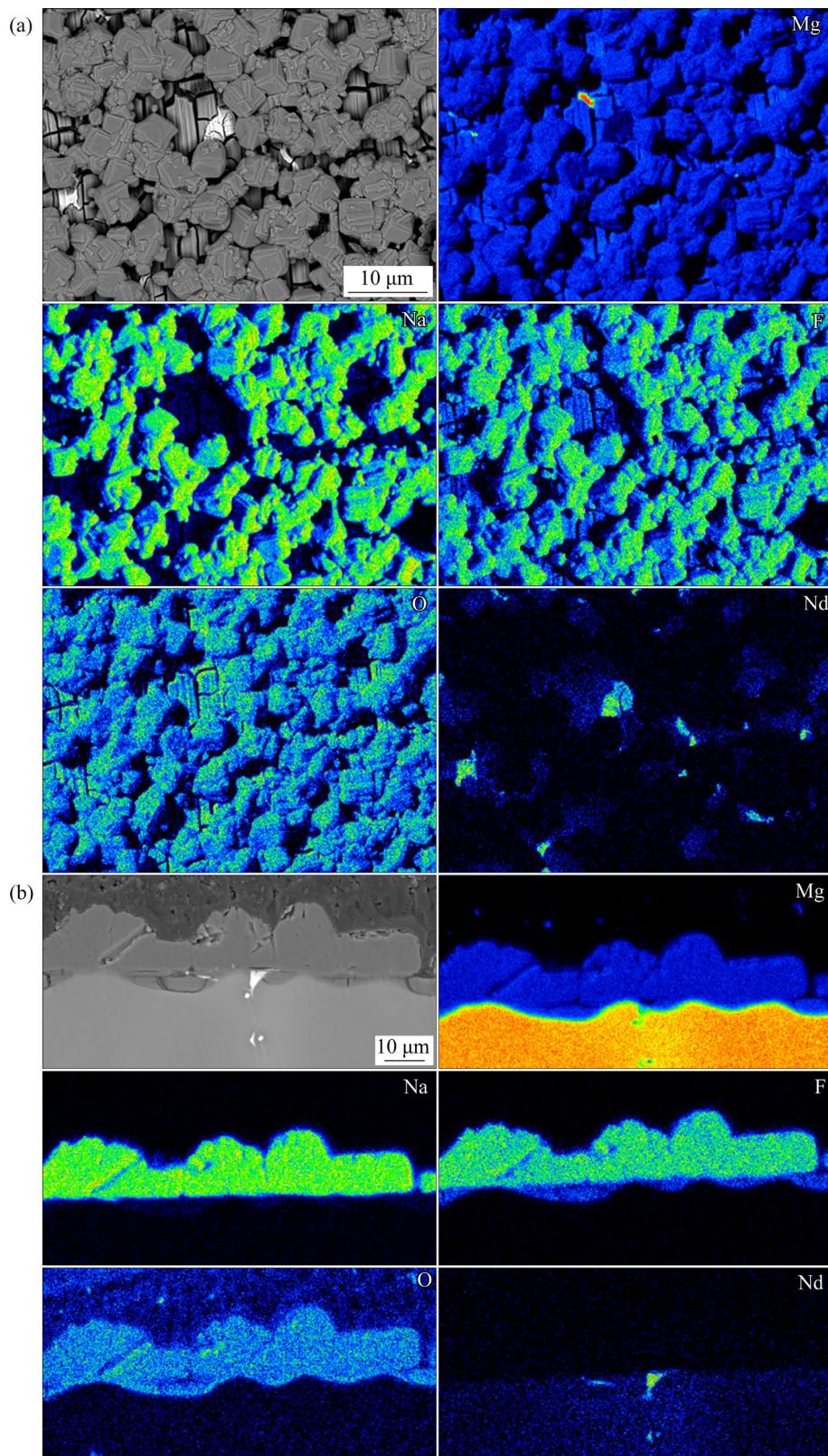
**Fig. 5** SEM images of Mg alloy after immersion in 3.5 wt.% NaCl (a, b) and 3.5 wt.% NaCl + 40 mmol/L NaF (c, d) solutions for 72 h

thick and dense corrosion product layer can be clearly visible on the Mg alloy surface (Figs. 5(c) and (d)). In particular, large and irregular particles are found on the sample surface, suggesting that large amounts of corrosion products are formed and deposited during immersion test.

### 3.3.2 Composition of corroded samples

EPMA is used to study the elemental distribution and composition of corroded samples after being immersed in NaF-containing electrolyte.

Different colors are employed to present various kinds of elements. Compared to dark places, the bright places indicate high density for each element. Figure 6(a) shows that the corrosion product layer



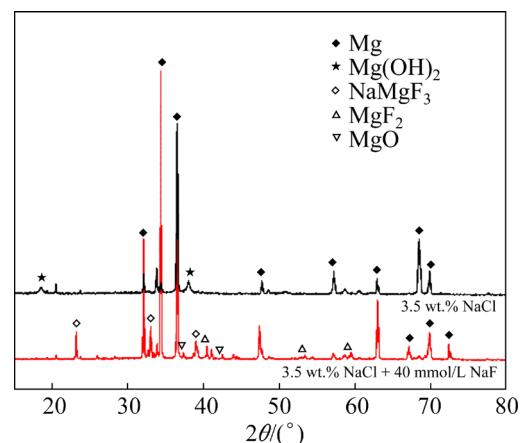
**Fig. 6** EPMA mappings of surface (a) and cross-section (b) of corroded sample after immersion in 3.5 wt.% NaCl + 40 mmol/L NaF solution for 72 h

is divided into two sub-layers. The main elements of the corrosion products are O, Mg, F and Na. The outer corrosion layer has large-sized and irregular corrosion products, while the inner layer seems to be denser with some cracks (Fig. 6(a)). In terms of chemical composition, Mg, Na, F and O can be detected in the outer corrosion product layer. As for the inner corrosion layer, Na is not detectable and the content of F is less than that in the outer layer. The bright particles underneath are most likely to be rare earth-containing secondary phase. Figure 6(b) demonstrates the elemental composition and distribution of the cross-section. A clear boundary can be found between the inner and outer corrosion layers. The distribution of the main elements in the cross-section of the corroded sample is consistent with the surface morphology. In other words, the composition of the corrosion products varies in the outer and inner corrosion films. Moreover, the inner layer appears to be denser and thinner in contrast with the outer corrosion layer.

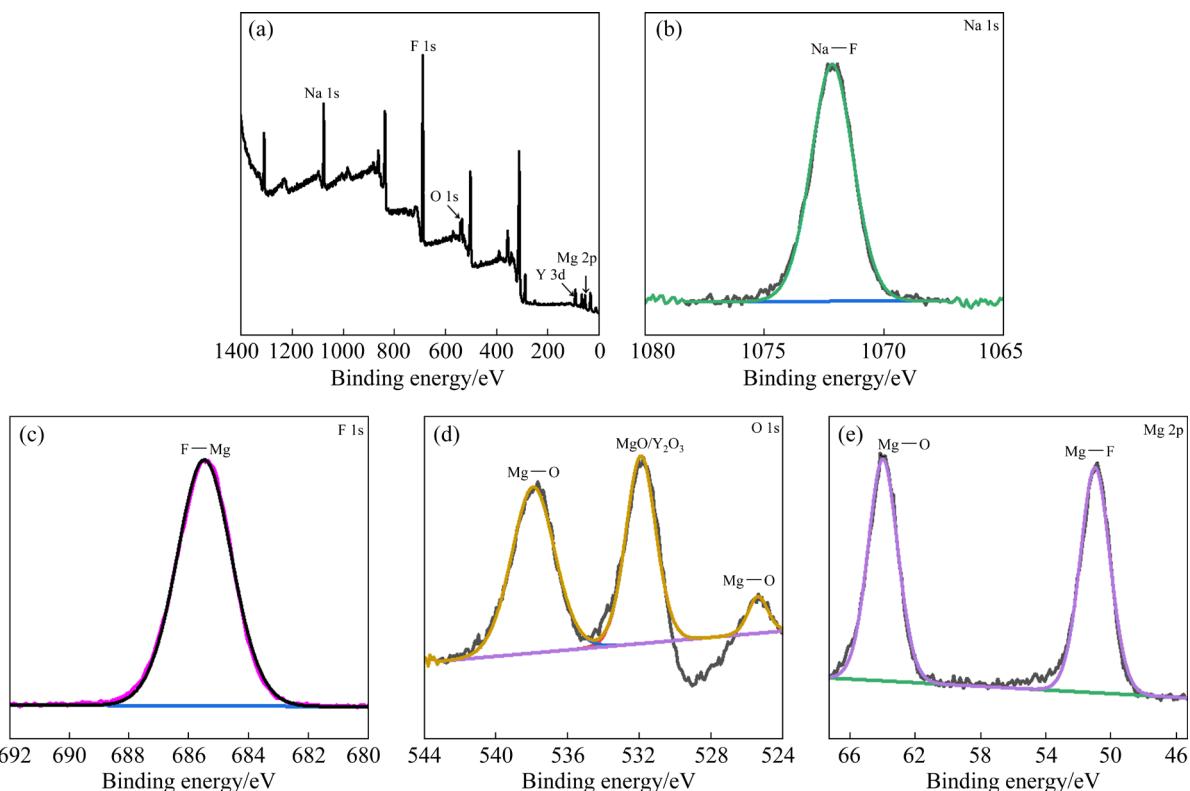
Figure 7 displays the XRD patterns of the corroded samples. The main corrosion product of samples is  $\text{Mg}(\text{OH})_2$  after being immersed in the blank solution. However,  $\text{Mg}(\text{OH})_2$  phase is hardly

to be detected in samples with the addition of corrosion inhibitor. It should be noticed that  $\text{NaMgF}_3$ ,  $\text{MgF}_2$  and small amount of  $\text{MgO}$  are detected in the corrosion product layer after soaking in NaF containing solution for 72 h, indicating that the inhibitor is involved in the formation and deposition of corrosion products.

The composition of the corroded sample is also measured by using the X-ray photoelectron spectroscopy (XPS), as shown in Fig. 8. In the XPS



**Fig. 7** XRD patterns of corroded samples immersed in 3.5 wt.% NaCl (a) and 3.5 wt.% NaCl + 40 mmol/L NaF (b) solutions



**Fig. 8** XPS (a) and high-resolution (b–e) spectra of sample after immersion in 3.5 wt.% NaCl + 40 mmol/L NaF solution for 72 h

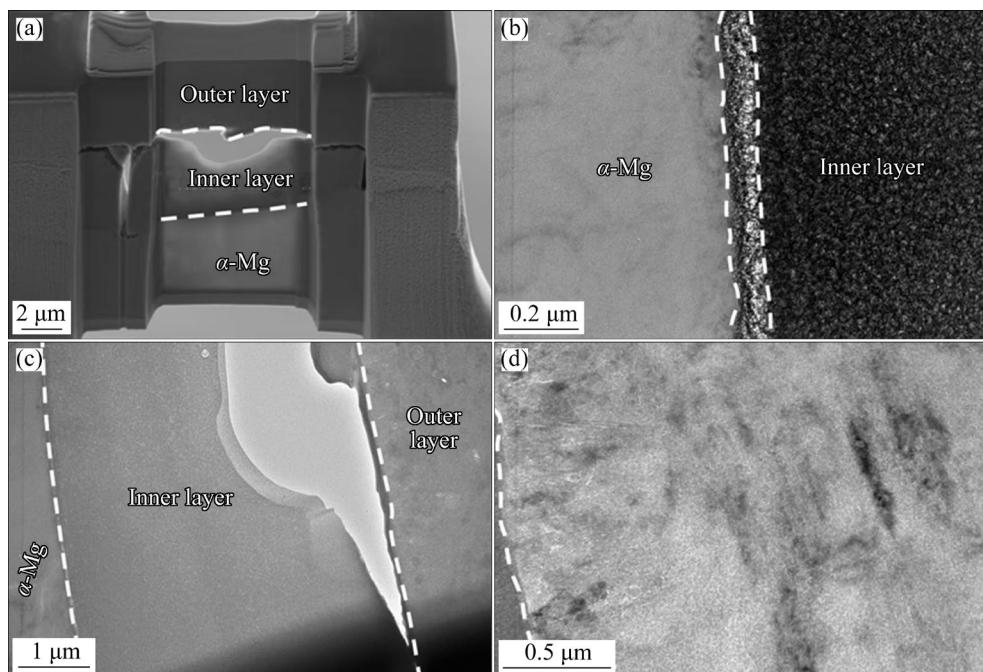
spectra of Na 1s and F 1s, peaks at 1072.2 and 685.5 eV are related to Na—F and F—Mg bonds, which can be associated with the presence of  $\text{NaMgF}_3$  and  $\text{MgF}_2$ , respectively. O 1s spectrum at 538.1, 531.9 and 525.8 eV is related to  $\text{MgO}$  and  $\text{Y}_2\text{O}_3$ . The Mg 2p spectrum can be fitted by two peaks at 50.9 and 63.9 eV, which represents F—Mg and  $\text{MgO}$ , respectively.

FIB and TEM tests are used to further investigate the microstructure and composition of the corrosion film with the addition of inhibitor. The corrosion product on top of  $\alpha$ -Mg is cut by means of FIB (Fig. 9(a)). The corrosion product layer is composed of two layers and a large crack is observed between the outer and inner corrosion layers. In addition, an ultrathin layer can be detected at the interface between Mg substrate and

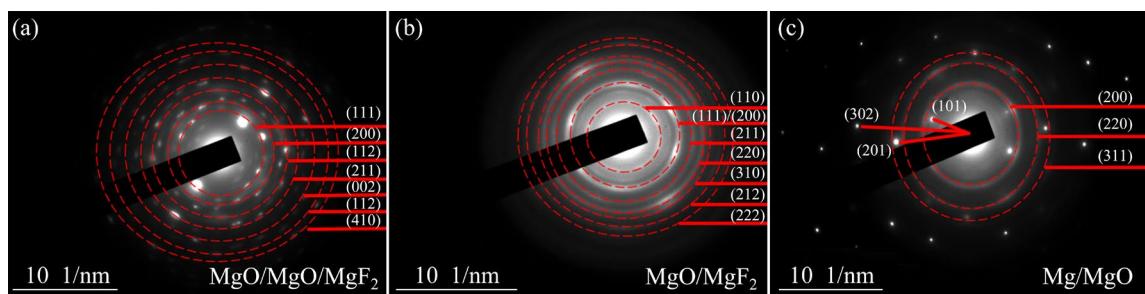
the inner corrosion layer, as shown in Fig. 9(b). Figure 10 shows the SAED ring and diffraction results of the selected regions in the corrosion product layer. It is apparent that the addition of NaF into the NaCl solution suppresses the formation and deposition of  $\text{Mg}(\text{OH})_2$ . The phase composition of the outer corrosion layer has been identified to be  $\text{NaMgF}_3$ ,  $\text{MgF}_2$  and  $\text{MgO}$ . As for the inner corrosion layer, it mainly consists of  $\text{MgF}_2$  and  $\text{MgO}$ . Additionally,  $\text{MgO}$  is found to be the main composition at the interface between Mg substrate and corrosion product layer.

#### 4 Discussion

The corrosion behavior of WE43 Mg alloy is greatly influenced after the addition of NaF into

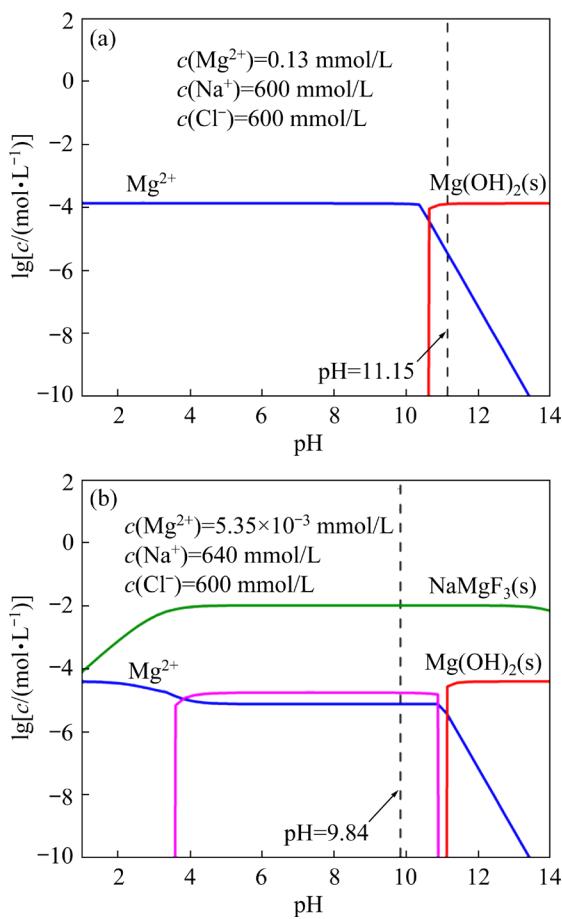


**Fig. 9** Overview TEM image of corrosion layer after FIB milling (a), and TEM images of corrosion product on top of  $\alpha$ -Mg (b–d)



**Fig. 10** SAED ring and diffraction results of corrosion products in different regions: (a) Interface layer in Fig. 9(b); (b) Inner corrosion layer in Fig. 9(c); (c) Outer corrosion layer in Fig. 9(d)

NaCl solution. On the one hand, the presence of NaF can suppress the formation of  $\text{Mg}(\text{OH})_2$  compared to the blank NaCl solution, which will in turn increase the densification of the corrosion film. The effect of inhibitor on the corrosion products is analyzed by using Hydra-Medusa software, as demonstrated in Fig. 11. It is clear that the formation and deposition of  $\text{Mg}(\text{OH})_2$  are inhibited in the presence of NaF. According to Fig. 11(b), the final pH of the electrolyte after performing corrosion test is 9.84, while formation of insoluble  $\text{Mg}(\text{OH})_2$  occurs when pH is 11.14. On the other hand, the addition of inhibitor into the electrolyte contributes to the deposition of a dense and thick corrosion product layer, which becomes a barrier to improve the corrosion resistance of the substrate.



**Fig. 11** Thermodynamic calculation of equilibrium composition of Mg alloy immersed in different electrolytes: (a) 3.5 wt.% NaCl solution; (b) 3.5 wt.% NaCl + 40 mmol/L NaF solution

As demonstrated by Figs. 6–11, the main composition of the corrosion products consists of  $\text{NaMgF}_3$ ,  $\text{MgF}_2$  and  $\text{MgO}$ . The formation of  $\text{MgF}_2$  and  $\text{NaMgF}_3$  can be explained by the following two

reactions:



Since the solubility of  $\text{MgF}_2$  ( $K_{\text{sp}}=5.16 \times 10^{-11}$ , 25 °C) is significantly larger compared to that of  $\text{Mg}(\text{OH})_2$  ( $K_{\text{sp}}=5.61 \times 10^{-12}$ , 25 °C), the dissolved  $\text{Mg}^{2+}$  ions preferentially react with  $\text{F}^-$ , which deposit directly on the Mg alloy surface. Afterwards, a large amounts of  $\text{F}^-$  and  $\text{Na}^+$  in the electrolyte will further take part in the formation and deposition of corrosion product, as verified by the appearance of  $\text{NaMgF}_3$  in the outermost layer of the corroded sample. Therefore, the presence of NaF facilitates the formation and deposition of stable and dense corrosion product layer on top of Mg alloy, and the inhibition efficiency is mainly related to the corrosion resistance of the inner barrier layer.

## 5 Conclusions

(1) NaF is an effective inhibitor for WE43 Mg alloy in 3.5 wt.% NaCl solution. After immersion in 40 mmol/L NaF containing solution, the highest inhibition efficiency of the inhibitor is found to be 92.6%.

(2) The formation and deposition of  $\text{Mg}(\text{OH})_2$  are suppressed after the addition of NaF, as the inhibitor contributes to the deposition of a double-layered corrosion product film on the sample surface.

(3) The inner layer appears to be thinner but denser compared to the outer corrosion layer. The main composition of the inner corrosion layer is  $\text{MgO}$  and  $\text{MgF}_2$ , which plays a key role in providing barrier property for the substrate.

(4) The outer corrosion layer consists of  $\text{NaMgF}_3$ ,  $\text{MgF}_2$  and  $\text{MgO}$ , which is porous and thicker compared to the inner layer.

## CRediT authorship contribution statement

**Yun-tian YANG** and **Yu-xin ZHOU**: Conceptualization, Methodology, Investigation, Writing – Original draft preparation; **Xiao-peng LU**: Conceptualization, Investigation, Writing – Reviewing and editing, Supervision, Funding acquisition; **Ji-ru MA**: Conceptualization, Writing – Reviewing and editing; **Jun-jie YANG**: Investigation, Supervision, Writing – Reviewing and editing; **Fu-hui WANG**: Conceptualization, Writing – Reviewing and editing,

Supervision, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## NaCl 溶液中 NaF 对 WE43 镁合金的缓蚀机制

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**摘要:** 采用 SEM、TEM、EPMA、XRD、XPS 和电化学测试等方法系统研究了 3.5% NaCl(质量分数)溶液中 NaF 对 WE43 镁合金显微组织、组成和腐蚀性能的影响。结果表明, NaF 是一种有效的 WE43 镁合金缓蚀剂。在中性 NaCl 溶液中, 当 NaF 浓度为 40 mmol/L 时, 抑制效率最高, 其值为 92.6%。缓蚀剂与溶解的 Mg<sup>2+</sup>发生反应, 形成并沉积双层致密且具有保护性的腐蚀膜层, 抑制了 WE43 合金的溶解。采用 FIB 和 TEM 分析了该双层腐蚀膜层的显微组织和组成。腐蚀膜外层主要由 NaMgF<sub>3</sub>、MgF<sub>2</sub> 和 MgO 组成, 内层主要由 MgO 和 MgF<sub>2</sub> 组成。

**关键词:** 镁合金; 腐蚀; 腐蚀膜层; 缓蚀剂; 缓蚀机制

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