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Comparison of the Inhibition Effect of Four Inhibitors on the Corrosion Behaviour of AM60 Magnesium Alloy

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The inhibition effect of four inhibitors of sodium citrate (SC), sodium dodecylbenzenesulphonate (SDBS), diammonium phosphate ($(NH_4)_2HPO_4$) and sodium vanadate ($NaVO_3$) on the corrosion behaviour of AM60 magnesium alloy in 0.1 M sodium chloride (NaCl) solution was investigated by immersion and electrochemical tests, surface morphology and chemical composition analyses. The results show that AM60 suffers severe attack in NaCl solution in long-term immersion. When inhibitors are added, its corrosion resistance is improved. All these inhibitors can form a barrier to inhibit the corrosion process. Especially, the barrier becomes more protective after longer immersion. All the inhibitors except (NH_4)₂HPO₄ can prevent the localized corrosion of AM60. The inhibitor is SDBS with efficiency up to 93% measured by hydrogen evolution.

Keywords: Magnesium alloys; Inhibitors; Inhibition efficiency; Corrosion resistance; Product films

1. INTRODUCTION

Magnesium alloys, as the lightest metallic structure materials, are one of the most promising "green metals" in transportation, electronic and aerospace industries [1]. However, the corrosion resistance of magnesium alloys is poor [2, 3]. Protective coatings are widely used to improve their corrosion resistance [4, 5]. In aqueous environments, the use of inhibitor is one of the most practical methods to prolong the lifetime of alloy parts. Although magnesium alloys are seldom used in aqueous environments, liquids are prone to accumulate in magnesium alloy parts due to the high-low temperature difference or humid environments. Therefore, inhibitors are often doped into coatings to

inhibit the corrosion of naked Mg substrate where coatings are damaged by some inevitable reasons [6-8].

Up to now, many kinds of inhibitors have been investigated in different Mg alloys to replace the toxic typical inhibitor of chromate [9-13] Generally, these chromate-free inhibitors can retard corrosion by precipitation, oxidation, chelation and absorption reactions with Mg substrates, respectively. Thus, the typical inhibitors which work with the four reaction mechanisms are selected in this investigation. Phosphate is a typical inter-phase inhibitor and its inhibition efficiency can match chromate [12]. Neutral phosphate (NH₄)₂HPO₄ inhibits magnesium alloys by forming compact barrier of $Mg_3(PO_4)_2$ [13], which is the same with alkaline Na_3PO_4 [12]. Moreover, phosphate conversion coating not only acts as the efficient replacement of chromate conversion coating [14], but also shows self-healing ability in some cases [15]. Vanadium is the neighbor of chrome in periodic table of elements, so vanadate may be similar to chromate. Vanadium is used as an oxidant inhibitor of AZ91 magnesium alloy in acidic phosphate medium with inhibition efficiency of 25% by forming MgO, Al_2O_3 and V_2O_3 [16]. Furthermore, vanadate can also be used to prepare self-healing conversion coatings for most magnesium alloys [17. 18], except Elektron 21 alloy [19]. Dodecylbenzenesulphonate anion is a typical inter-face inhibitor by forming an adsorption film on the surface especially in the defect of films [20, 21], while many researchers think that dodecylbenzenesulphonate anion inhibits the corrosion of magnesium by forming insoluble substance [10, 22]. On the one hand, citrate can chelate with magnesium, making magnesium alloys corrode heavier [23], on the other hand, the chelates may be adsorbed on the surface of Mg alloys because it contains abundant absorption atoms. Thus, it's hard to say whether SC is an inhibitor for Mg alloys.

Despite these inhibitors for magnesium alloys have already been reported, they are investigated on different magnesium alloys in different electrolytes. The comparison of the inhibition effect of different inhibitors on the same magnesium substrate, especially on the widely used AM60 magnesium alloy, is far away from sufficient, which cannot provide overall information for selecting the most suitable inhibitors during the actual applications of a certain magnesium alloy parts. Also, there are contradictions in the inhibition mechanisms and efficiency of various inhibitors, which is necessary to be clarified by using the same magnesium substrate. Thus, it is significant to compare the inhibition effect of different inhibitors on AM60 Mg alloy.

Therefore, the aim of this investigation is to compare the inhibition effect of the four possible inhibitors on the corrosion behaviour of AM60 magnesium alloy in sodium chloride solution. Also, the possible inhibition mechanisms are suggested. These results can give valuable reference to the industrial applications and scientific research.

2. EXPERIMENTAL

2.1. Sample preparation

The experimental material used in this investigation was AM60 magnesium alloy (nominal chemical composition by weight: 6% Al; 0.27–0.3% Mn, and balance Mg). The samples were cut from

cast ingot which was purchased from Shanxi Yinguang Huasheng Magnesium Co., Ltd., PR China. For electrochemical tests, the samples were sealed by epoxy with an exposed area of 1 cm². For immersion tests, the samples were cut to 30mm×30mm×10mm. All the exposed surface was mechanically ground to 2000# SiC paper, washed with distilled water, degreased with ethanol in an ultrasonic bath for 5 min, dried in cold flowing air.

The organic inhibitors of SC and SDBS, and inorganic inhibitors of $(NH_4)_2HPO_4$ and $NaVO_3$ were chosen. 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors were used in this investigation. All reagents were analytical grade. The solutions were not updated during immersion to simulate the possible service condition. The molecular structures of SC and SDBS are showed in Fig. 1.



Figure 1. Molecular structures of SC (a) and SDBS (b)

2.2 Immersion tests

The immersion tests were sustained for 10 days. Corrosion rate was evaluated by measuring the volumes of hydrogen evolution, collected by a funnel and burette above the samples [24]. The overall magnesium corrosion reaction is

 $Mg + 2H_2O = Mg(OH)_2 + H_2\uparrow$

(1)

(2)

One milliliter (1 ml) H_2 was evolved when one milligram (1.07 mg) magnesium was dissolved. Therefore, the evolved hydrogen was a direct measurement of the corrosion rate [25]. And the inhibition efficiency was calculated as:

 $\eta_{\rm H} = (V_0 - V) / V_0 \times 100\%$

where η_H was inhibition efficiency calculated by hydrogen evolution, V_0 and V were the hydrogen evolution volumes of blank samples and inhibited samples in per unit area, respectively. During the immersion tests, 2 L solution for each sample was used, and pH values of the solutions were measured directly by pH meter (PHB-1, shanghai San-Xin instrumentation. Inc, PR China).

The samples before immersion were weighed as W_0 . After immersion for 10 days, the samples were removed from the solutions, rinsed with distilled water and ethanol, dried and weighted as W_1 . The increase of sample weight was attributed to the product films on the sample surface. The weight variation in per unit area, ΔW_1 (with products) was evaluated as:

 $\Delta W_1 = (W_1 - W_0) / \text{ sample areas}$

(3)

After the optical photos of the immersion samples were taken (PC1743, Canon Inc, Japan), samples were immersed in a chromic acid solution consisting of CrO_3 180 g/L at room temperature (RT) for approximately 10 min to remove the products [24]. Then the samples were washed, dried and weighted as W₂. The weight variation in per unit area, ΔW_2 (without products) was evaluated as:

 $\Delta W_2 = (W_2 - W_0) / \text{ sample areas}$ (4)

the inhibition efficiency was calculated as:

$$\eta_{\rm w}$$
=-($\Delta W_2^{\rm blank}$ - $\Delta W_2^{\rm inh}$)/ $\Delta W_2^{\rm blank} \times 100\%$

where η_w was inhibition efficiency calculated by weight loss, ΔW_2^{blank} and ΔW_2^{inh} were the weight loss of blank samples and inhibited samples in per unit area, respectively.

2.3 Electrochemical tests

Potentiodynamic polarization curves and electrochemical impedance spectra (EIS) were measured (after immersion for 1 d and 10 d, respectively) in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors using PARSTAT4000 electrochemistry test system (Princeton Applied Research USA). A classical three-electrode cell was used with a saturated calomel electrode (SCE) (+0.242 V vs. standard hydrogen electrode) as the reference electrode, platinum sheet as counter electrode, and the sample with an exposed area of 1 cm² as work electrode.

Open circuit potential (OCP) was measured for 1 d. Cathodic and anodic polarization curves were recorded respectively from the quasi-steady OCP with the scan rate of 1 mV/s. The cathodic polarization curves were terminated at the potential of -250 mV vs. OCP and the anodic polarization curves were terminated at the current density approximately 2 mA/cm². Corrosion current densities (*i*_{corr}) were fitted using cathodic polarization curves at the potential range of -100 to -70 mV vs. OCP by using origin software. EIS spectra were recorded at OCP using a single sinusoidal excitation signal of 20 mV amplitude with the frequency scope of 100 kHz to 10 mHz. All impedance data were fitted according to the appropriate equivalent circuits using ZsimpWin software.

The surface morphologies of AM60 magnesium alloy after immersion in various solutions for 1 d were observed using a Phillips XL30FEG scanning electron microscope equipped with an energy–dispersive X–ray spectroscope (EDX) with an acceleration voltage of 14 kV. The structures of product films formed in 0.1 M NaCl and 0.1 M NaCl + inorganic inhibitors of $(NH_4)_2HPO_4$ and NaVO₃ were probed using a Philips PW1700 XRD instrument with a Cu target ($\lambda = 0.154$ nm), and the XRD patterns were analyzed by MDI Jade software. The solid Fourier transform infrared (FT-IR) spectra of product films formed in 0.1 M NaCl+ 0.01 M organic inhibitors of SC and SDBS were recorded with an Agilent Cary 650 over the wavelength range 400–4000 cm⁻¹.

3. RESULTS

3.1. Surface morphologies and chemical composition of AM60 after immersion in the NaCl solutions containing various inhibitors

The optical images of AM60 after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 10 d are shown in Fig. 2. It can be seen that AM60 Mg alloy suffers the severest attack in the NaCl solution without inhibitor. Most of the surface is damaged and abundant white corrosion products are visible (Fig. 2a). When $(NH_4)_2HPO_4$ is added as inhibitor, AM60 is covered by thick film (Fig. 2d) and suffers some attack (Fig. 2e). When SC, SDBS and NaVO₃ are added as inhibitor, AM60 is well protected (Fig. 2b, c and f). Even after immersion for 10 d, the surface of AM60 is still smooth

(5)

with little metallic luster in the solution containing SC or SDBS. AM60 is covered by black film when inhibited by NaVO₃. From the comparison of surface morphologies, it can be seen that SC, SDBS and NaVO₃ are efficient inhibitors for AM60, but (NH₄)₂HPO₄ is weaker.



Figure 2. Optical images of AM60 Mg alloy after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 10 d: (a) 0.1 M NaCl; (b) 0.1 M NaCl + 0.01 M SC; (c) 0.1 M NaCl + 0.01 M SDBS; (d) 0.1 M NaCl + 0.01 M (NH₄)₂HPO₄; (e) 0.1 M NaCl + 0.01 M (NH₄)₂HPO₄ after removal of corrosion products; (f) 0.1 M NaCl + 0.01 M NaVO₃.

The SEM surface morphologies of AM60 after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 1 d are shown in Fig. 3. AM60 suffers severe attack in the uninhibited NaCl solution (Fig. 3a) with loose corrosion products in the locally corroded areas, and there is still some initiation of localized corrosion in the smooth areas (Point A in Fig. 3a). When SC is added into NaCl solution, AM60 is covered by a thin film (Fig. 3b), although most of the film flakes away due to dehydration during the drying and vacuumizing processes [26]. When SDBS is chosen as inhibitor (Fig. 3c), AM60 seems to be naked with little crack. Therefore, SDBS may be an inter-face inhibitor absorbing on the surface of metal during immersion for 1 d. Crystalloid thick film with compact and loose parts is formed when $(NH_4)_2HPO_4$ is added to the electrolyte (Fig. 3d), which indicates that $(NH_4)_2HPO_4$ is a typical inter-phase inhibitor. AM60 is covered by a crack film in NaCl solution inhibited by NaVO₃. EDX shows that the top layer consists of 16 at.% Mg and 19 at.% V, and the ratio of Mg and V is also ca. 1:1 in the inner layer. The crack should be formed during drying and vacuumizing processes [26].



Figure 3. SEM surface morphologies of AM60 after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 1 d, and the insert figures are the magnified morphologies of each sample: (a) 0.1 M NaCl; (b) 0.1 M NaCl + 0.01 M SC; (c) 0.1 M NaCl + 0.01 M SDBS; (d) 0.1 M NaCl + 0.01 M (NH₄)₂HPO₄; (e) 0.1 M NaCl + 0.01 M NaVO₃. Point A in (a) is the initiation of localized corrosion.

The XRD patterns of AM60 after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inorganic inhibitors for 1 d are shown in Fig. 4. The blank sample consists of α -Mg, β -Al₁₂Mg₁₇, Al_xMn_y, and a little Mg(OH)₂. When (NH₄)₂HPO₄ acts as inhibitor, the film contains Mg₃(PO₄)₂ and MgNH₄PO₄. For NaVO₃ sample, the film contains MgVO₃ and Mg₃(VO₄)₂.



Figure 4. XRD patterns of AM60 after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inorganic inhibitors for 1 d.

The FT-IR spectra of surface product films formed on AM60 after immersion in 0.1 M NaCl + 0.01 M organic inhibitors are shown in Fig. 5. The infrared spectrum of SC sample shows the characteristic absorption bands of citrate, particularly a strong peak at 1567 cm⁻¹ (due to the asymmetric stretching vibration of C=O) and a weak peak in 1261 cm⁻¹ (due to the C-H rocking and twisting vibration of CH₂ groups). The strong peak near 1400 cm⁻¹ can be assigned to the O-H in-plane deformation. The peak in 1081 cm⁻¹ can be assigned to the C-OH stretching vibration (1070 cm⁻¹ blueshifted because of carboxyl). The bands in the range of $500-700 \text{ cm}^{-1}$ are attributed to metaloxygen-metal stretching [27]. The peak at 463 cm⁻¹ is assigned to the Mg-O band [28]. The infrared spectrum of SDBS sample shows the characteristic absorption bands of dodecylbenzenesulphonate, particularly a peak near 1620 cm⁻¹ (1, 4-disubstituted benzene, C-C stretching) and peaks at 1777 cm⁻¹ (S=O asymmetric stretching), 1089 cm⁻¹, 1037 cm⁻¹ (S=O symmetric stretching), and 620 cm⁻¹ (C-S stretching vibration). The strong peak near 1400 cm⁻¹ can be assigned to the O-H in-plane deformation. The peak at 855 cm⁻¹ can be assigned to C-H deformation vibration of CH₂ wagging. The FT-IR results confirm the adsorption of citrate and dodecylbenzenesulphonate on the surface of AM60. The stronger characteristic peaks near 1400 cm⁻¹ indicate that they are more likely to cooperate with $Mg(OH)_2$.



Figure 5. FT-IR spectra of AM60 after immersion in 0.1 M NaCl + 0.01 M organic inhibitors for 1 d.

3.2 Comparison of corrosion rates by immersion measurements

The hydrogen evolution volumes of two samples for each solution as a function of immersion time are shown in Fig. 6. The duplicate samples show similar hydrogen evolution except the blank samples. Although the duplicate blank samples show large error and different corrosion rate, they exhibit the same trend of the hydrogen evolution volume and the corrosion rate maintains almost steady for each one (Fig. 6a). When SC is added as inhibitor, H₂ is evolved slower after immersion for about 12 h (Fig. 6b). When SDBS is added as inhibitor, the hydrogen evolution volume is very little, and the rate slows down with increasing immersion time even after immersion for 10 d (Fig. 6c). When $(NH_4)_2HPO_4$ is added, H₂ is evolved very quickly in the initial period (about 4 h), then the rate slows down and stays steady (Fig. 6d). When NaVO₃ is added, the hydrogen evolution rate becomes slower after immersion for 12 h and then reaches a steady state (Fig. 6e) as well. These trends can be attributed to the reaction between inhibitor and substrate to form barriers to reduce the corrosion areas.

A comparison of the average hydrogen evolution volumes for each inhibitor is shown in Fig. 6f. The blank samples exhibit the most hydrogen evolution volume, while the inhibited samples exhibit much lower ones. The hydrogen evolution volumes of $(NH_4)_2HPO_4$ samples show a special trend of high rate (faster than the blank sample) in the initial stage and a quick decrease after immersion for 12 h (slower than NaVO₃ samples). It indicates that the reaction between $(NH_4)_2HPO_4$ and magnesium is quick in the initial stage and then a protective barrier is formed. The inhibition efficiency η_H of SC, SDBS, $(NH_4)_2HPO_4$ and NaVO₃ is 85%, 93%, 79% and 77%, respectively.



Figure 6. Hydrogen evolution volumes of two specimens for each inhibitor as a function of immersion time: (a) 0.1 M NaCl; (b) 0.1 M NaCl + 0.01 M SC; (c) 0.1 M NaCl + 0.01 M SDBS; (d) 0.1 M NaCl + 0.01 M (NH₄)₂HPO₄; (e) 0.1 M NaCl + 0.01 M NaVO₃; (f) Average hydrogen evolution volume for AM60 during immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 10 d.

Samples are weighted after immersion for 10 d. The average weight variations are listed in Table 1. The weights of the blank samples and the inorganic inhibited samples increase while the weights of the organic inhibited samples decrease. It's due to that magnesium is dissolved in the initial immersion. When $(NH_4)_2HPO_4$ and NaVO₃ are used as inhibitors, thick insoluble product films are formed making the weight increase. Differently, SC and SDBS inhibit the corrosion of Mg by chelation or absorption reactions. The weight gain by chelation or absorption of SC or SDBS is less than the dissolution of Mg, resulting in a decrease of weight. The weight variations of the samples after removal of product films are in consistent with the inhibition efficiency evaluated by hydrogen evolution measurements, with the efficiency η_W of 78%, 90%, 70%, and 64% for SC, SDBS, $(NH_4)_2HPO_4$ and NaVO₃, respectively.

Table 1. Average weight variations of AM60 after immersion in 0.1 M NaCl without or with different0.01 M inhibitors for 10 d

Inhibitors	With product films (W_1 - W_0) (mg/cm^2)	Without product films (W_2 - W_0) (mg/cm ²)
Blank	1.00	-6.00
SC	-0.33	-1.34
SDBS	-0.05	-0.58
$(NH_4)_2HPO_4$	3.90	-1.79
NaVO ₃	0.44	-2.14

3.3 Comparison of inhibition effect by electrochemical measurements

OCP curves of AM60 Mg alloy immersed in 0.1 M NaCl and 0.1 M NaCl+0.01 M inhibitors for 1 d are shown in Fig. 7. All the OCP curves exhibit a similar trend, namely, the potentials increase rapidly in the initial immersion, and then increase slowly toward a quasi-steady value. The positive shift of potentials can be attributed to the deposition of surface films and absorption of inhibitors on the anodic sites of alloy [29]. When the growth and dissolution of surface films reach a stable status, the OCP becomes steady.



Figure 7. OCP of AM60 as a function of immersion time, during immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 1 d.

Generally speaking, the increase of OCP value suggests the enhancement of passivation properties and the weakening of the electrochemical corrosion tendency [23], but the cathodic corrosion inhibitors will make OCP more negative than the blank sample by inhibiting the cathodic processes more than the anodic ones. In this study, all the quasi-steady values of OCP in NaCl solutions with different inhibitors are more negative than the blank one during immersion for 1 d. This means that SC, SDBS, (NH₄)₂HPO₄ and NaVO₃ are cathodic corrosion inhibitors. SDBS and NaVO₃ samples show the most negative OCP values, which means they inhibit the cathodic process obviously. The zigzagged OCP curve of (NH₄)₂HPO₄ indicates the competition between the active dissolution process and passivation process during the localized corrosion. The OCP curve of the blank sample also presents a zigzagged trend, which can be attributed to the competition between the propagation of localized corrosion and deposition of corrosion products.

The potentiodynamic polarization curves (*E*-log *i*) of AM60 after immersion for different durations are shown in Fig. 8. It is obvious that the shapes of the cathodic branches of polarization curves follow the Tafel behavior. Therefore, the cathodic branches are used to fit. The fitted corrosion current density (i_{corr}), corrosion potential (E_{corr}), and anodic breakdown potential (E_{bd}) are summarized in Table 2.



Figure 8. Polarization curves of AM60 in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 1 d (a) and 10 d (b).

Table 2. Fitting results of polarization curves of AM60 after immersion in 0.1 M NaCl without or withdifferent 0.01 M inhibitors for 1 d and 10 d

Inhibitora	<i>b</i> _c -1d	$i_{\rm corr}$ -1d	<i>E</i> _{corr} -1d	$E_{\rm bd}$ -1d	<i>b</i> _c -10d	$i_{\rm corr}$ -10d	$E_{\rm corr}$ -10d	$E_{\rm bd}$ -10d
minutors	(mV/dec)	(A/cm^2)	(V_{SCE})	(V_{SCE})	(mV/dec)	(A/cm^2)	(V _{SCE})	(V_{SCE})
Blank	-120	2.24×10^{-5}	-1.583		-151	5.38×10 ⁻⁵	-1.557	
SC	-111	1.46×10^{-5}	-1.621	-1.413	-114	6.46×10 ⁻⁶	-1.562	-1.39
SDBS	-92	4.00×10^{-6}	-1.692	-1.051	-143	1.44×10^{-6}	-1.579	-0.77
$(NH_4)_2HPO_4$	-159	1.00×10^{-5}	-1.604		-151	5.43×10 ⁻⁶	-1.527	
NaVO ₃	-180	2.05×10^{-5}	-1.667	-1.393	-161	8.05×10^{-6}	-1.610	-1.365

The shapes of the anodic branches of polarization curves present two types: (a) for blank and $(NH_4)_2HPO_4$ samples, the current densities increase with increasing anodic potentials without obvious plateau, and (b) for NaVO₃, SC and SDBS samples, a well-defined current plateau between E_{corr} and breakdown potential (E_{bd}) is found. The localized corrosion usually starts from the breakdown of passive film in its defective sites. Therefore, it means that the more positive E_{bd} is, the more stable the passive film is [29]. From the results of Fig. 8 and Table 2, it can be seen that SDBS samples show the most positive E_{bd} up to -1.051 and -0.77 V (vs. SCE) after immersion for 1 d and 10 d, respectively. The shapes of those curves are consistent with the results in immersion tests in Fig. 2 where localized corrosion is observed in the blank and $(NH_4)_2HPO_4$ samples while others are general corrosion. They are consistent with the results of OCP curves as well, where blank and $(NH_4)_2HPO_4$ samples present a zigzagged OCP trend. In long-term immersion, the i_{corr} of blank sample increase while that of the inhibited samples decrease and E_{bd} of the inhibited samples move positively, which means that more protective films are formed in the inhibited solution after longer immersion.

For AM60 in blank solution, defective $Mg(OH)_2$ is deposited, which cannot resist corrosion [30]. Despite the chelation between SC and Mg, SC is still an effective inhibitor in the given condition, which not only decreases the i_{corr} , but also causes a current plateau (Fig. 8). Obviously, SDBS is the most efficient inhibitor which can inhibit the anodic processes as well as cathodic processes (Fig. 8). The anodic branch of $(NH_4)_2$ HPO₄ sample is almost the same as the blank sample, but the cathodic

current density of $(NH_4)_2HPO_4$ sample is significantly lower than that of blank sample. Thus, $(NH_4)_2HPO_4$ is cathodic corrosion inhibitor after immersion for 1 d. Similarly, SC and NaVO₃ are cathodic corrosion inhibitors as well.

The Nyquist plots of AM60 alloy in 0.1 M NaCl solution containing 0.01 M different inhibitors for 1 d and 10 d are presented in Fig. 9. The measured data are shown as symbols and the fitted data are shown as lines. These plots present three types: (a) for blank and NaVO₃ samples, Nyquist plots consist of a large high-frequency capacitance loop and a low-frequency inductance loop, (b) for SC and SDBS samples, Nyquist plots consist of a large high-frequency capacitance loop and a mediumfrequency capacitance loop, and (c) for $(NH_4)_2HPO_4$ samples, a low-frequency inductance loop appears and the high-frequency capacitance loop is much smaller than the medium-frequency capacitance loop. The high-frequency capacitance loops are due to the electric double layer at the interface of the Mg substrate and solution; the medium-frequency capacitance loops are related to the surface films, and the low-frequency inductance loops indicate the initiation of corrosion [24]. With a longer immersion time, the dimension of the Nyquist plot of the blank sample decreases while that of the inhibited samples increases, which indicates that the corrosion resistance of the inhibited samples increases with increasing immersion time. This result is consistent with the potentiodynamic polarization curves.

Bode plots of AM60 immersed in different solutions for 10 d are presented in Fig. 9f. The low frequency impedance modulus |Z| (at 0.01 Hz) is one of the parameters used to evaluate the corrosion resistance of different samples [31]. A larger |Z| indicates a better protection performance. |Z| shows that all these selected inhibitors can improve the corrosion resistance, and SDBS is the most efficient one.



Figure 9. Electrochemical impedance spectra of AM60 alloy after immersion in 0.1 M NaCl and 0.1 M NaCl + 0.01 M inhibitors for 1 d and 10 d: (a) 0.1 M NaCl; (b) 0.1 M NaCl + 0.01 M SC; (c) 0.1 M NaCl + 0.01 M SDBS; (d) 0.1 M NaCl + 0.01 M (NH₄)₂HPO₄; (e) 0.1 M NaCl + 0.01 M NaVO₃; (f) bode plots after immersion for 10 d.

Equivalent circuits (EC) for fitting EIS plots are shown in Fig. 10. The fitting results are shown in Table. 3. Because the film on $(NH_4)_2$ HPO₄ sample is partly loose (Fig. 2, 3), (RQ) and (RQ) in parallel is chosen. Conversely, the film in SC and SDBS samples are even, so (RQ) and (RQ) in series are chosen. In these circuit models, R_s is the solution resistance between the reference electrode and the surface of work electrode, R_t is the charge transfer resistance which depends on the dissolution rate of the Mg substrate, R_f is the film resistance which depends mainly on the film porosity and the solution conductivity in the pores of surface film [7]. R_L and L are the resistance and inductance associated with inductive impedance. C_{dl} and C_f are the capacitances associated with electric double layer and film, respectively. In this study, a constant phase element (CPE) is introduced in the fitting procedure to replace the ideal capacitance element because of the inhomogeneity caused by second phases and films [7]. According to the fitting results, SDBS shows the maximum R_t and R_f , meaning the minimum metallic dissolution rate and the most protective film.



Figure 10. Equivalent circuits used for fitting EIS results: (a) when immersed in 0.1 M NaCl or 0.1 M NaCl + 0.01 M NaVO₃; (b) when immersed in 0.1 M NaCl + 0.01 M SC or 0.1 M NaCl + 0.01 M SDBS; (c) when immersed in 0.1 M NaCl + 0.01 M (NH₄)₂HPO₄.

Table 3. Fitting results of EIS of AM60 after immersion in 0.1 M NaCl without or with different 0.01M inhibitors for 10 d

Inhibitors	$R_{\rm s}$ ($\Omega {\rm cm}^2$)	$Q_{\rm dl}$ (µS cm ⁻² s ⁻ⁿ)	n	$R_{\rm t}$ ($\Omega {\rm cm}^2$)	$Q_{\rm f}$ (µS cm ⁻² s ⁻ⁿ)	n _f	$R_{\rm f}$ ($\Omega {\rm cm}^2$)	L (H cm ²)	$R_{\rm L}$ ($\Omega {\rm cm}^2$)
Blank	39.41	57.18	0.8182	710.9				2137	2044
SC	39.89	1137	0.5235	3158	12.67	0.9595	2148		
SDBS	35.25	279.8	0.5500	16400	8.964	0.9886	13130		
$(NH_4)_2HPO_4$	220.0	0.6099	0.6226	375.2	48.56	0.6078	6289	6289	10740
NaVO ₃	28.16	97.31	0.8464	4501				14960	18570

4. DISCUSSION

Five sketch maps (Fig. 11) are used to explain the possible inhibition mechanisms. For the blank samples (Fig. 11a), $Mg(OH)_2$ film can be formed after AM60 is immersed into NaCl. However, the presence of Cl⁻ will accelerate the damage of Mg(OH)₂ film by forming soluble $5Mg(OH)_2 \cdot MgCl_2$, $Mg_3(OH)_5$ Cl and further MgCl₂ [13]. Therefore, the protection of the naturally formed Mg(OH)₂ is highly limited, and electrolyte easily permeates into the film leading to the localized corrosion (Fig. 2a and 3a).



Figure 11. Sketch maps of corrosion and inhibition mechanisms: (a) blank; (b) SC; (c) SDBS; (d) (NH₄)₂HPO₄; and (e) NaVO₃

When SC is added as inhibitor (Fig. 11b), SC chelates with Mg^{2+} [23]. Although the chelate is soluble, it can be absorbed on the surface of AM60 (Fig. 5) by oxygen atom, hindering the adsorption of Cl⁻. Electrolyte permeates into the film homogeneously, making the EC in series connection (Fig. 10b). When samples are taken out of electrolyte, some residual Mg-SC is retained on the surface of samples to form a protective film. This film is very easy to fall off in the process of drying and vacuumizing.

SDBS can be absorbed on the porous $Mg(OH)_2$ film or naked matrix [20, 21] (Fig. 5) by sulfur and oxygen atoms, Mg-SDBS is insoluble, so SDBS shows high inhibition efficiency. Because of the strong binding force between mental and S, the coverage areas of SDBS increase gradually along the immersion time. Therefore, the rate of hydrogen evolution decreases gradually even after immersion for 10 d.

When $(NH_4)_2HPO_4$ is added as inhibitor, the solution displays the minimal pH and maximal ionic concentration among all the given solutions. Therefore, AM60 is quickly dissolved in the initial period (Fig. 6d), making the H₂ evolved very quickly, and then the product film is grown by the reactions of Mg and $(NH_4)_2HPO_4$,

$$Mg + (NH_4)_2 HPO_4 = MgNH_4PO_4 + H_2\uparrow + NH_3\uparrow$$
(6)

 $Mg + (NH_4)_2 HPO_4 = Mg_3(PO_4)_2 + 3H_2 \uparrow + 4NH_3 \uparrow$ (7)

The formation of NH_3 can explain the negligible decrease in Fig. 6d. Because the solubility of ammonia in water is about 700:1 in volume [32], the evolved gas most is H_2 . When the film is protective enough, the hydrogen evolution rate decreases and stays steady.

When $NaVO_3$ is added as inhibitor, a black film containing $MgVO_3$ and $Mg_3(VO_4)_2$ is formed on AM60 Mg alloy by the reactions of $NaVO_3$ and Mg,

$$2Mg + 2NaVO_3 + 2H_2O = 2MgVO_3 + 2NaOH + H_2\uparrow$$
(8)

 $3Mg + 2NaVO_3 + 4H_2O = Mg_3(VO_4)_2 + 2NaOH + 3H_2\uparrow$ (9)

Solution can permeate through the film, resulting in the dissolution of Mg substrate slightly. Then the inner layer film can be formed. Also, the low-frequency inductance loop can appear in Nyquist plot.

Based on the inhibition mechanisms of four inhibitors, there are two questions to clarify: (1) why is the inhibition efficiency of SDBS the best? (2) why cannot $(NH_4)_2HPO_4$ prevent the localized corrosion of AM60 while the others can? These reasons have still not been clarified in previous work [13].

For the question one, it is well-known that lone pair electrons, π -bone or any other bones which contain higher electron cloud densities can be absorbed on atoms with electron vacancy like Mg and Mg²⁺. The adsorption ability is determined by many aspects especially the following three: (1) electron cloud densities, (2) quantity of adsorption sites, and (3) radius difference between absorbing atom and absorbed atom. SDBS owns the sulfonic group with the adsorbents of S and O, so it can adsorb on Mg to form Mg-SDBS complexes [13] (Fig. 5). In comparison of Mg-SC and Mg-SDBS (Fig. 1), citrate has more adsorption sites (7 sites for Mg-SC while 4 sites for Mg-SDBS) but Mg-SDBS has greater electron cloud densities, especially the radius difference between Mg^{2+} (72 pm) and S (88 pm) is smaller than the radius difference between Mg²⁺ (72 pm) and O (48 pm) [23, 33]. Therefore, the adsorption of SDBS and Mg-SDBS is more efficient, and the adsorption film is more compact. The second reason is that SDBS has a long chain of hydrophobic group in the opposite direction of S and O atoms (Fig. 1b), hindering the permeation of corrosive electrolyte, and also hindering the adsorption of more SDBS. The third reason is that Mg-SDBS is insoluble while Mg-SC is soluble. Actually, the difference between Mn^{2+} (83 pm) and S is much smaller than that of Mg^{2+} and S, and the difference between Al^{3+} (54 pm) and O is much smaller than that of Mg²⁺ and O [33]. Therefore, SDBS is prone to be absorbed on the Al_xMn_y and $Al_{12}Mg_{17}$ phases, especially in the initial period when the insoluble Mg-SDBS has not been formed. The BSE-SEM morphology of AM60 and the EDS results of different sites after immersion in 0.1 M NaCl + 0.01 M SDBS for 10 d are presented in Fig. 12. During the corrosion of AM60, β -Al₁₂Mg₁₇ and Al_xMn_y act as cathodes [29]. It is obvious that more S is detected on the sites where the contents of Al and Mn are higher (site B and C). This result well proves the speculation above.



Figure 12. BSE-SEM morphology and EDS results of different sites on AM60 after immersion in 0.1 M NaCl + 0.01 M SDBS for 10 d: (a) BSE-SEM morphology; (b) EDS result of area A; (c) EDS result of area B; (d) EDS result of point C.

2.

For the question two, according to the hydrolytic equilibrium of acids and bases, monohydrogen phosphate (HPO₄²⁻) is the dominant constituent at pH 7-12, but the solubility product of MgHPO₄ (6×10^{-5} mol² dm⁻⁶) is too high in comparison with Mg₃(PO₄)₂ and MgNH₄PO₄ [12]. As a result, HPO₄²⁻ only plays a relatively minor role in this test condition. The concentration of PO₄³⁻ can be calculated as [12,33],

$$[PO_{4}^{3-}] = \frac{[PO_{4}^{3-}]_{tot}}{_{1+10}^{(-pH+12.5)} + 10^{(-2pH+12.5+6.9)} + 10^{(-3pH+12.5+6.9+2)}}$$
(10)
Similarly [33],
$$[NH_{4}^{+}] = \frac{[NH_{4}^{+}]_{tot}}{_{1+10}^{pH-14+4.8}}$$
(11)

In the present phosphate system of pH \approx 7.5, it can be calculated that the concentration of [PQ₄³⁻] is 8×10⁻⁸ mol/L and [NH₄⁺] is 0.0196 mol/L in bulk solution. [PO₄³⁻] will become more and [NH₄⁺] will become less near to the sample surface due to the larger pH value, no matter it's anode or cathode because of the dissolution of Mg and negative difference effect (NDE) [29]. The solubility product constants of some low solubility inorganic solutes and relating calculated required [Mg²⁺] in given pH are presented in Table 4. It can be seen that when [Mg²⁺] \ge 1.6×10⁻⁴ or 5.4×10⁻⁴ in bulk solution, MgNH₄PO₄ and Mg₃(PO₄)₂ can be precipitated, respectively. According to the reference [12], the concentration of [Mg²⁺] is approximately 2.9×10⁻³ M in the vicinity of metallic surface when pure Mg is immersed into 5 wt.% NaCl solution with 10⁻³ M Na₃PO₄, which is much higher than the required concentration of MgNH₄PO₄ and Mg₃(PO₄)₂ deposition in bulk solution. Hence, the precipitation films are loose, especially in anodic areas where the concentration of [Mg²⁺] is higher. That is why (NH₄)₂HPO₄ acts as cathodic corrosion inhibitor when immersion for 1 d.

Table 4. Solubility product constants of some low solubility inorganic solutes and relating calculated required [Mg²⁺] in given pH

Molecular	Temp.	pK _{sp}	Required [Mg ²⁺]	Required [Mg ²⁺]
formula	(°C)	[33, 34]	(pH=7.5) (M)	(pH=10) (M)
$Mg_3(PO_4)_2$	20	24.0	5.4×10^{-4}	1.0×10^{-5}
MgNH ₄ PO ₄	20	12.6	1.6×10^{-4}	2.7×10^{-6}
$Mg(OH)_2$	20	11.3	56.2	5.6×10 ⁻⁴

5. CONCLUSIONS

The selected four inhibitors can inhibit the corrosion processes. SDBS shows the best inhibition efficiency up to 93% because the perfect adsorption ability of S on Mg, the long chain alkyl and the insolubility of Mg-SDBS. The chelate by the reaction of SC and Mg is absorbed on AM60 to hinder the absorption of Cl⁻. The high concentration of NH_4^+ and PO_4^{3-} makes $(NH_4)_2HPO_4$ to form uneven product film which cannot prevent localized corrosion well. A black film is formed when $NaVO_3$ is used as inhibitor. All these inhibitors can inhibit the corrosion process by forming barriers on the Mg surface, and the barrier effect becomes stronger at a longer time immersion.

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