Effect of CO$_2$ Saturation on the Corrosion Behaviour of AZ31B Magnesium Alloy in Na$_3$PO$_4$ Solutions

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Effect of CO$_2$ saturation on the corrosion behaviour of AZ31B magnesium alloy in the presence of different concentrations of Na$_3$PO$_4$ solution was investigated by open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). As it was expected, in solution without CO$_2$ the corrosion rate decreases with increasing Na$_3$PO$_4$ concentration and the passive behaviour of AZ31B magnesium alloy apparently occurs when the concentration of Na$_3$PO$_4$ is increased to $10^{-2}$ mol L$^{-1}$ after 2 h immersion. However, in solution saturated with CO$_2$ the corrosion rate decreases with increasing Na$_3$PO$_4$ after 2 h immersion. And the corrosion rate in Na$_3$PO$_4$ solution saturated with CO$_2$ is bigger than that in single Na$_3$PO$_4$ solution, showing that CO$_2$ obviously accelerates the corrosion of AZ31B magnesium alloy in Na$_3$PO$_4$ solutions. The corrosion rate is also observed with immersion time decreased in Na$_3$PO$_4$ solution saturated with CO$_2$ as a result of increase in pH value with time going on.

**Keywords:** Corrosion; AZ31B magnesium alloy; Na$_3$PO$_4$; CO$_2$

1. INTRODUCTION

Nowadays, magnesium alloys have received extensive application in the aerospace, automotive application and electronic industries because of their excellent physical properties, including low density, high strength to weight ratio, excellent electrical conductivity, high thermal conductivity and good electromagnetic shielding characteristics among others [1-3]. However, the magnesium alloy has a low corrosion potential and easily corrodes, which limits its extensive utilization in these fields. Therefore, corrosion behaviour of magnesium and its alloy have been widely investigated in various environments and is still a significant research field [4-11].
Many material and components made by magnesium alloy are usually exposed to atmosphere containing abundant vapor and CO$_2$. It is easy to form a thin film saturated with CO$_2$ on the surface of magnesium alloy in this environment where magnesium alloy is active and easily corroded. Therefore, CO$_2$-induced atmospheric corrosion of magnesium and its alloys has received the attention of many researchers [8-11]. It is also reported that CO$_2$ may play an important role in the corrosion of magnesium alloy. For examples, Baril et al [8] studied the corrosion of pure magnesium in Na$_2$SO$_4$ solution aerated and deaerated. Their results showed that O$_2$ did not influence the corrosion of magnesium and the corrosion rate of magnesium was controlled by HCO$_3^-$ concentration in the presence of CO$_2$. Lin et al [9] also studied the role of CO$_2$ in the initial atmospheric corrosion of AZ91 magnesium alloy in the presence of NaCl. NaCl was added by spraying the sample with saturated NaCl solution in 90% ethanol and the volume of CO$_2$ in mixed gas was 1%. They suggested NaCl-induced corrosion was inhibited in the presence of CO$_2$ by the formation of slightly soluble corrosion products containing hydroxy carbonates and hydroxy chlorides that provided a partly protective layer on the surface of the magnesium alloy. But it is unlikely to form a thin fluid film on magnesium alloy in their study. While Lindström et al. [10] made investigations of the influence of carbon dioxide on the atmospheric corrosion of magnesium; they concluded that in the presence of 350 ppm CO$_2$ the corrosion rate was only 25% of that registered in CO$_2$-free air. This was explained by the formation of a protective carbonate layer. Qu et al. [11] investigated the corrosion behaviour of AZ31B magnesium alloy in different concentrations of NaCl solution saturated with CO$_2$, they showed that the presence of CO$_2$ accelerated the anodic dissolution in NaCl solution. However, little has been studied about the corrosion mechanism of magnesium alloy in the presence of other salts saturated with CO$_2$.

Considering that metal phosphates are insolubility in neutral water and have high temperature resistance and chemical stability [12], phosphate chemical conversion may be a promising coating method for corrosion protection films of magnesium alloys. More and more researchers have interests in studying effect of phosphates on the corrosion of magnesium alloys [12-16]. Previous studies concerning the electrochemical performance of AZ91D alloy in phosphate electrolytes dealt mainly with producing a film by chemical [13] or electrochemical [14] oxidation to form protective coatings on AZ91D substrate. Niu et al. [15] succeeded in forming a zinc phosphate coating on AZ91D alloy with a typical phosphate microstructure having better corrosion resistance due to the presence of crystalline zinc in the coat. Heakal et al. [16] studied the influence of pH on the corrosion behavior of Mg-based AZ91D alloy in a constant composition phosphate medium, they suggested that pH value of phosphate medium have an important effect and spontaneously formed protective layers on the AZ91D surface greatly improve with increasing pH value of phosphate (over 8.1), which leads to partial blocking of the film pores; their results also showed the corrosion rate in NaH$_2$PO$_4$ solution is far larger than that in Na$_3$PO$_4$ solution. But literature available to date about effect of the concentration of phosphate on the corrosion of magnesium alloy with and without CO$_2$ is scare. Consequently, there is no clear understanding of the role of CO$_2$ in the corrosion kinetics of magnesium alloy in Na$_3$PO$_4$ solution saturated with CO$_2$.

The purpose of the present study is to study the detailed reaction sequence of AZ31B alloy in Na$_3$PO$_4$ solutions saturated with and without CO$_2$ by open circuit potential (OCP), potentiodynamic
polarization and electrochemical impedance spectroscopy (EIS) and is to discuss the effect of CO$_2$ saturation on the corrosion mechanism of magnesium alloy in Na$_3$PO$_4$ solutions.

2. EXPERIMENTAL METHODS

2.1 Materials

The experiments were performed with AZ31B magnesium alloy specimens with the following chemical composition (wt %): Al 3.05 %, Zn 0.99 %, Mn 0.28 %, Fe 0.003 %, Si 0.025 %, Cu 0.002 %, Ni 0.0049 % and Mg balance.

Sodium phosphate (Na$_3$PO$_4$) was of analytical grade. Different concentrations of Na$_3$PO$_4$ (0, 10$^{-5}$, 10$^{-4}$, 10$^{-3}$, 10$^{-2}$, 10$^{-1}$ mol L$^{-1}$) were prepared from distilled water. The experimental solution was aerated using a CO$_2$ gas generator. pH was surveyed by PHS-25 pH-metre.

2.2 Electrochemical measurements

The working electrode was embedded in a PVC holder using epoxy resin given an exposed surface of 4.0 cm$^2$. The exposed face was abraded with emery paper from 100 to 1200 grades, scoured with distilled water, degreased with acetone, washed again with distilled water, and dried with a blower.

A three-electrode system including a working electrode, an auxiliary electrode and a reference electrode was used for electrochemical measurements in 250 mL solution. Auxiliary electrode was a platinum foil and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary positioned close to the working electrode surface in order to minimize ohmic potential drop. The working electrodes were immersed in the test solution at 30°C for 2 h before measurement until a steady state appeared. All electrochemical measurements were carried out using a PAR 2263 Potentistat/Galvanostat (Princeton Applied Research). EIS was carried out in a frequency range of 2×10$^6$ Hz to 0.1 Hz using a 10 mV peak-to-peak voltage excitation. The potentiodynamic polarization scan was carried out by polarizing from -1.9 V to 1.0 V with respect to the free corrosion potential ($E_{corr}$ vs. SCE) at a scan rate of 1 mV s$^{-1}$. Each experiment was repeated at least three times to check the reproducibility.

3. EXPERIMENTAL RESULTS

3.1 Solution saturated with CO$_2$

It is generally agreed that the following reactions will occur in solution containing CO$_2$:

$$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{aq})$$  (1)
\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^- (\text{aq}) \]  
\[ \text{HCO}_3^- (\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{CO}_3^{2-} \]

When \( \text{CO}_2 \) is saturated in the solution, hydrogen ion \( (\text{H}^+) \) will be in equilibrium with \( \text{CO}_2 \), and pH will be steady. So pH value of the solution can be used to determine whether and when the solution is saturated with \( \text{CO}_2 \).

**Figure 1.** pH value of the solution with and without \( \text{Na}_3\text{PO}_4 \) as a function of the time aerated with \( \text{CO}_2 \)

Fig. 1 shows the pH value of the solution with and without \( \text{Na}_3\text{PO}_4 \) as a function of the time aerated with \( \text{CO}_2 \) at 30\(^\circ\)C. It is evident that, the pH value of the solution with and without \( \text{Na}_3\text{PO}_4 \) tends firstly towards negative direction quickly, and then it changes slowly until steady state is established after 10 minutes. Therefore, the solution saturated with \( \text{CO}_2 \) can be obtained after 10 minutes aerated with \( \text{CO}_2 \). So 10 minutes were chosen as the aeration time in this paper.

3.2 Electrochemical studies

3.2.1 Open circuit potential (OCP)

The OCP experiments of AZ31B in solution saturated with \( \text{CO}_2 \) without and with 0.01 mol L\(^{-1}\) \( \text{Na}_3\text{PO}_4 \) at 30\(^\circ\)C were recorded and plotted in Fig. 2. As it can be seen, the corrosion potentials \( (E_{\text{corr}} \text{ vs. SCE}) \) shift towards positive direction quickly during the initial 2000 s, then slightly increase with time and reach a steady state at 6000 s in solution saturated with \( \text{CO}_2 \) with and without \( \text{Na}_3\text{PO}_4 \). Both curves in solution saturated with \( \text{CO}_2 \) with and without \( \text{Na}_3\text{PO}_4 \) have similar shapes. Fig. 2 also shows that the corrosion potential in \( \text{Na}_3\text{PO}_4 \) solution saturated with \( \text{CO}_2 \) is higher than that measured in
solution without Na$_3$PO$_4$ saturated with CO$_2$ but lower than that in Na$_3$PO$_4$ solution in the absence of CO$_2$.

![Figure 2. Variation of the OCP of AZ31B in solution saturated with CO$_2$ without and with Na$_3$PO$_4$](image)

This indicates that Na$_3$PO$_4$ affects the kinetics of the anodic reaction of AZ31B magnesium alloy in solution saturated with CO$_2$ more strongly. Because the OCP does not change obviously with increasing immersion time after 2 h immersion, in this article 2 h was chosen as the immersion time in electrochemical studies.

### 3.2.2 Potentiodynamic polarization

To discuss the effect of Na$_3$PO$_4$ on the kinetics of the anodic reaction of AZ31B magnesium alloy in solution, the potentiodynamic polarization curves for the corrosion of AZ31B in solution without and with CO$_2$ containing different concentrations of Na$_3$PO$_4$ at 30 ºC were shown in Fig.3a and b, respectively. Fig.3a shows that, corrosion potentials ($E_{corr}$ vs. SCE) are shifted to noble direction with increasing Na$_3$PO$_4$ concentration in the absence of CO$_2$, the anodic branches are shifted to more positive potential direction while the cathodic branches do not change obviously, suggesting that Na$_3$PO$_4$ mainly retards the anodic reaction. And from Fig.3a it also can be seen that, when the concentration of Na$_3$PO$_4$ is higher than or equal to $10^{-2}$ mol L$^{-1}$, the anodic current densities become very low and do not change with increasing the applied potential (from corrosion potential to 1.5V). This domain corresponds to an apparent passivation zone. Over the potential region of the passive current zone a steady state is established between the rates of metal dissolution and passive film formation. Therefore, the anodic passive behaviour of AZ31B magnesium alloy apparently occurs when the concentration of Na$_3$PO$_4$ is increased to $10^{-2}$ mol L$^{-1}$ in the absence of CO$_2$. Whereas a reverse trend about the effect of Na$_3$PO$_4$ was observed in the presence of CO$_2$ from Fig.3b. Fig3b
shows that the corrosion potential decreases with increasing the concentration of Na₃PO₄ from 0 to 0.1 mol L⁻¹ in solution saturated with CO₂, and that the anodic current densities obviously increase with increasing the concentration of Na₃PO₄, suggesting that Na₃PO₄ accelerates the anodic dissolution of AZ31B alloy in solution saturated with CO₂.

Figure 3. Potentiodynamic polarization for magnesium alloy in solution without (a) and saturated with CO₂ (b) at different concentrations of Na₃PO₄
Table 1. Electrochemical parameters from potentiodynamic polarization and EIS in different concentration of Na$_3$PO$_4$ solution saturated with CO$_2$ at 30 °C

<table>
<thead>
<tr>
<th>CO$_2$</th>
<th>C$_{Na_3PO_4}$ (mol L$^{-1}$)</th>
<th>$E_{corr}$ vs. SCE (V)</th>
<th>$i_{corr}$ (μA cm$^{-2}$)</th>
<th>$R'_i$ (Ω cm$^2$)</th>
<th>$R_f$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (μF cm$^{-2}$)</th>
<th>$R_l$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (μF cm$^{-2}$)</th>
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<td>0</td>
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<td>112.1</td>
<td>256.7</td>
<td>1547</td>
<td>0.0002</td>
<td>1461</td>
<td>25.02</td>
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<tr>
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<td>56.3</td>
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<td>5307</td>
<td>0.0005</td>
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<td>24.82</td>
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<tr>
<td></td>
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<td>36.5</td>
<td>14120</td>
<td>0.0003</td>
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<td>19.9</td>
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<tr>
<td></td>
<td>$10^{10}$</td>
<td>-1.856</td>
<td>512.3</td>
<td>219.7</td>
<td>-</td>
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</tr>
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The corrosion potential $E_{corr}$ and corrosion current density $i_{corr}$ obtained from these curves were summarized in Table 1. Similar to the results obtained from OCP tests, the corrosion potential in Na$_3$PO$_4$ solution saturated with CO$_2$ is lower than that in Na$_3$PO$_4$ solution in the absence of CO$_2$, as shown in Table 1. It also can be seen from Table 1 that, with increasing concentration of Na$_3$PO$_4$ from 0 to 0.1 mol L$^{-1}$, the $i_{corr}$ values in the presence of saturation CO$_2$ increase from 125.6 to 512.3 μA cm$^{-2}$ while those in the absence of CO$_2$ only decrease from 112.1 to 19.9 μA cm$^{-2}$. The corrosion rate is much higher in solution saturated with CO$_2$ than without CO$_2$ at each same concentration of Na$_3$PO$_4$. That is to say, CO$_2$ significantly accelerates AZ31B alloy corrosion in Na$_3$PO$_4$ solutions, which can be attributed to the co-effect of CO$_2$ and Na$_3$PO$_4$.

3.2.3 EIS

![Figure 4](image_url). EIS of AZ31B at different concentrations of Na$_3$PO$_4$ solution without (a) and saturated with CO$_2$ (b).
In order to compare the corrosion behaviour of different solutions, Fig. 4a and b show the Nyquist diagrams of AZ31B for different concentrations of Na$_3$PO$_4$ without and saturated with CO$_2$ at 30°C. It is easy to see from these figures that all impedance spectra are rather complex when the concentration is lower than 10$^{-3}$ mol L$^{-1}$. In general, the EIS for AZ31B is quite similar to that of magnesium and AZ21 in NaCl solution [11,17,18], even though the data is much scattered, the trend is still clear that the EIS consists of three loops, one capacitive in the high frequency range (hf), one inductive loop in the intermediate-frequency range (mf) and another capacitive loop in the low frequency (lf) in low concentration of Na$_3$PO$_4$. However, the intermediate-frequency inductive loop and low frequency capacitive almost disappear when the concentration is higher than 10$^{-3}$ mol L$^{-1}$, correspondingly, the impedance spectra mainly exhibit one capacitive loop. Additionally, when the concentration is higher than 10$^{-3}$ mol L$^{-1}$, these capacitive loops in the absence of CO$_2$ only are part of depress semicircles and the diameters are very large comparing to that in solution saturated with CO$_2$. The larger values of impedance and the character of impedance diagrams in the absence of CO$_2$ suggest existence of a passive film on AZ31B magnesium alloy.

![Figure 5. Equivalent circuit of EIS in low (a) and high (b) concentration of Na$_3$PO$_4$](image)

It is generally agreed that the capacitive loop in the high frequency region is always related to the transient resistance ($R_t$) and the double layer capacitance ($C_{dl}$) of the electrode [8,18-21], and it is possible to obtain the oxide film resistance of AZ31B from these loops as presented in Fig.4. Comparing the semicircle of high frequency capacitive loop, it is easy to see that the loop of the
solution saturated with CO₂ is smaller than that without CO₂ at each concentration of Na₃PO₄. With increase of the concentration of Na₃PO₄ saturated with CO₂ the diameter decreases, meaning that the corrosion of AZ31B accelerates, whereas in the absence of CO₂ the corrosion rate decreases with increase of the concentration of Na₃PO₄. These results are consistent in potentiodynamic polarization curves.

According to Song et al. [17,18] the low frequency capacitive loop is related to Mg⁺ ion concentration within the face oxide broken area. The inductive loop in the intermediate-frequency range is generally attributed to the adsorbed species such as Mg(OH)⁺ or Mg(OH)₂ [17,18,22]. According to our observations, the rate of adsorption of these species is only significant in solution containing higher concentration of Na₃PO₄ saturated with and without CO₂, since there is no inductive loop appeared in higher concentration of Na₃PO₄ solutions.

The EIS results were simulated using the equivalent circuit shown in Fig.5a (low concentration) and b (high concentration) to pure electronic models that could verify or rule out mechanistic models and enable the calculation of numerical values corresponding to the electrochemical system under investigation [23]. In these circuits, Rₛ is solution resistance, Rₜ is charge transfer resistance and Ctdl is the double layer capacity associated to the oxidation film of AZ31B; Rf and Cfdl are associated to the adsorption film on the oxidation film of AZ31B. In high concentration of Na₃PO₄, the equivalent circuit contains inductance L and disturbs resistance; Q is the constant phase element comprising Ctdl and Rₛ, Rₜ, Rf and Q are all obtained from EIS in Fig. 4 via equivalent circuit in Fig. 5. And the solid lines in Fig.4 show the fit of the experimental data according to this model circuit. Cdl is accounted using the following equation [24]:

\[
C_{dl} = \frac{1}{2\pi f_{max} R}
\]

(4)

Where \( f_{max} \) represents the frequency at which imaginary value reaches a maximum in one capacitive loop in the Nyquist plot. R is the resistance (\( Rₛ, Rₜ \)) and \( C_{dl} \) the double layer capacity (\( C_{tdl}, C_{fdl} \)). The resistances and double layer capacity (\( C_{tdl}, C_{fdl} \)) are all listed in Table 1.

From Table 1 it can be found, with the increasing concentration of Na₃PO₄ without CO₂, that \( C_{tdl} \) value decreases and \( Rₜ \) values increase, which reveals that corrosion rate of AZ31B decreases with increasing concentration of Na₃PO₄; while with the increasing concentration of Na₃PO₄ saturated with CO₂, the results are the contrary. The \( Rₜ \) values are far smaller in solution saturated with CO₂ than single Na₃PO₄. But \( C_{tdl} \) values are just the opposite. That is, the corrosion rate increases markedly in the solution aerated with CO₂. These results are well in agreement with the results obtained from potentiodynamic polarization.

### 3.2.4 Effect of immersion time

To further investigate the effect of immersion time on the corrosion of AZ31B in Na₃PO₄ solution saturated with CO₂, the potentiodynamic polarization curves and EIS of 10⁻² mol L⁻¹ Na₃PO₄
solution saturated with CO$_2$ at different time are presented in Fig 6a and b, respectively. Fig 6a shows that the corrosion potentials shift to more positive direction with increasing immersion time, the anodic branches are shifted to more positive potential direction, indicating that the anodic dissolution is retarded with increasing immersion time.

Figure 6. Potentiodynamic polarization (a) and EIS (b) of AZ31B in solution saturated with CO$_2$ in the presence of 10$^{-2}$ mol L$^{-1}$ Na$_3$PO$_4$ at different times

As a result, the corrosion current also decreases with increasing immersion time. From these polarization curves, it is also clear passive behaviour will occur if the immersion time is longer than 32 h, and the passive range increases with increasing immersion time. It also can be seen from Fig. 6b
that, the immersion time increases significantly the size of the capacitive loop, when the time is raised to 32 h, the diameter of the capacitive loop becomes very large, and the capacitive loop increases more obviously than that before 32 h, the larger values of impedance and the character of impedance diagrams suggest existence of a corrosion film in Na$_3$PO$_4$ solution saturated with CO$_2$ after immersion for 32 h. And the film becomes more protective with increasing immersion time. This fact is consistent with the result from Baril et al. [8]. Baril also have reported that the concentration of HCO$_3^-$ is a main factor of corrosion rate and in aerated solution the magnesium surface is covered with a porous film (MgO, Mg(OH)$_2$) which became thicker with time and had a low protective action.

4 DISCUSSION

4.1 Corrosion in Na$_3$PO$_4$ solution without CO$_2$

It is well known that dissolution of magnesium in aqueous solutions proceeds by reduction of water molecules to produce magnesium oxide and/or hydroxide and hydrogen gas.

In Na$_3$PO$_4$ solution without CO$_2$, PO$_4^{3-}$ will hydrolyze and lead to increase in pH of the solution which brings into strongly alkaline solution. As shown in Fig.1 that pH value of 0.01 M Na$_3$PO$_4$ is higher than 11.

The anodic dissolution of magnesium in alkaline solution is

\[ \text{Mg(s)} \rightarrow \text{Mg}^+(l) + e^- \]  
(5)

\[ \text{Mg}^+(l) + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+}(l) + \text{OH}^-(l) \]  
(6)

\[ \text{Mg(s)} + 2\text{OH}^- (s) \rightarrow \text{Mg(OH)}_2(s) + 2e^- \]  
(7)

And the corresponding cathodic reaction is

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \]  
(8)

Therefore, countless electrochemical cells begin to form on the surface of AZ31B. Then cations, e.g. Na$^+$, Mg$^+$ will migrate towards to the cathodic areas, at the same time anions, e.g. PO$_4^{3-}$, OH$^-$ will migrate towards to the dissolution sites. Accordingly, insoluble Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) will form close to the anodic sites. The anodic dissolution is subsequently retarded. With increase in concentration of Na$_3$PO$_4$, pH becomes higher, and insoluble Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) come into being more easily. Thus the anodic dissolution becomes more difficult. When the concentration of PO$_4^{3-}$ is equal to or higher than 10$^{-2}$ mol L$^{-1}$, the insoluble film becomes thicker and more protective; it will exhibit existence of a passive film in electrochemical tests. The phenomena are well in agreement with the results obtained from potentiodynamic polarization and EIS.
However, when in solution saturated with CO$_2$, on the one hand, the formation of H$^+$ and CO$_3^{2-}$ will enhance the conductivity and acidity of the electrolyte rather quickly, the cathodic hydrogen evolution becomes more facile. Accordingly, the corrosion rate also increases in the presence of CO$_2$; on the other hand, just as can be seen from Fig.1, pH value of the solution in the absence of Na$_3$PO$_4$ is about 3.8 and that in the presence of $10^{-2}$ mol L$^{-1}$ Na$_3$PO$_4$ is about 4.4, which means that the exist formation of phosphate ion is H$_2$PO$_4^-$, furthermore, according to the pourbaix diagram of Mg, Mg(OH)$_2$ is unstable when pH value is lower than 8.5, thus insoluble Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) can not form in this solution, Heakal et al.[16] also pointed out that precipitation of Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) is impossible in acid solution. Therefore, here the role of phosphate ion is to act as electrolyte, with increasing the concentration of Na$_3$PO$_4$, the conductivity of solution increases, meaning that the anodic dissolution accelerates with increasing the concentration of Na$_3$PO$_4$. With hydrogen evolution going on, concentration of H$^+$ ions will decrease, and the pH value will increase. After the equilibrium pH value required for the precipitation of Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) meet the qualification, insoluble Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) will form on the anodic sites. In additional, the following reaction will take place:

$$2Mg^{2+}(aq)+2OH^-(aq)+CO_3^{2-}(aq)\rightarrow Mg_2(OH)_2CO_3(s)$$

(9)

So with immersion time increased, the insoluble corrosion product Mg$_2$(OH)$_2$CO$_3$(s), Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) also increase and accumulate on the surface of AZ31B, which become thicker with time and have a high protective action. The formation of Mg$_2$(OH)$_2$CO$_3$(s), Mg$_3$(PO$_4$)$_2$(s) and Mg(OH)$_2$(s) further restricts the transport of CO$_2$ and O$_2$ to the magnesium surface and thereby favors the inhibitive effect with time increased. This is in agreement with the result obtained from effect of immersion time.

5. CONCLUSIONS

(1) In solution without CO$_2$, Na$_3$PO$_4$ can inhibit the corrosion of AZ31B magnesium alloy, the corrosion decreases with increasing Na$_3$PO$_4$ concentration, the anodic dissolution will go into passive zone with increasing the applied potential when the concentration is equal to or higher than $10^{-2}$ mol L$^{-1}$. However, in solution saturated with CO$_2$, Na$_3$PO$_4$ will accelerate the corrosion of AZ31B magnesium alloy, and the corrosion rate increases with increasing Na$_3$PO$_4$ concentration.

(2) CO$_2$ plays an important role in the corrosion of AZ31B magnesium alloy in Na$_3$PO$_4$ solution. The corrosion of AZ31B is stronger in Na$_3$PO$_4$ solution saturated with CO$_2$ than without CO$_2$. EIS shows that the corrosion reaction is controlled by charge transfer resistance and film resistance. The results of potentiodynamic polarization and EIS are consistent.

(3) The inhibitive effect of CO$_2$ is also observed with time increased due to hydrogen evolution which results in increase of the pH value, showing that CO$_2$ reduces the average corrosion rate due to the formation of insoluble products. With increase in immersion time, the protective film becomes thicker, the $i_{corr}$ decrease and $R_t$ increase.
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