

Corrosion action and passivation mechanism of magnesium alloy in fluoride solution

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Abstract: Corrosion action and passive mechanism of magnesium alloy in the fluoride solution were studied by means of scanning electron microscopy(SEM), energy dispersive X-ray spectroscopy(EDS), and electrochemistry methods. The results show that an insoluble MgF_2 film is generated on the surface of magnesium alloy activated in the hydrofluoric acid. And the mass of the deposited MgF_2 film may reach a constant value, when the mass ratio of Mg/F on the magnesium alloy surface is fixed at 11.3:1. The activated magnesium alloy gains a 'passivation state' in a mixture of sulfuric acid and hydrofluoric acid at a volume ratio of less than 1.2. At the same time the mass of magnesium alloy is maintained as a function of the time. When the ratio is above 1.4, the mass of magnesium alloy rapidly decreases. The passive film formed through adsorption of HF_2^- (or H_2F_3^- , H_3F_4^-) ions by the deposited MgF_2 film can protect the magnesium alloy from corrosion in fluoride solution, but not in non-fluoride solutions. The passive state is maintained for activated magnesium alloy in an acidic sulfuric nickel solution with added fluoride. If fluoride and carbonate are added to the acidic sulfuric nickel solution, a replacement reaction between magnesium alloy and solution takes place.

Key words: magnesium alloy; passive film; corrosion; fluoride; nickel sulfate

1 Introduction

The use of magnesium alloy, in a variety of applications, particularly in aerospace, automobile, and mechanical and electronic component industries, has increased steadily in recent years as magnesium alloys exhibit an attractive combination of low density, high specific strength, excellent castability, and good mechanical and damping characteristics. The driving force also lies in the greatly improved affordability of commercial magnesium alloy. Thus magnesium alloys show great potential. However, magnesium is intrinsically highly reactive and its alloys usually have relatively poor corrosion resistance, which is one of the main obstacles to the application of magnesium alloys in practical environments[1–3].

Hence, the application of surface engineering technique is the most appropriate method to further enhance corrosion resistance of magnesium alloy. Among the various surface engineering techniques that are available for this purpose, coating by electroless plating nickel is of special interest especially in the

electronics industry due to the combination of properties associated with this type of coating. These advantageous properties include good corrosion and wear resistance, deposit uniformity, electrical and thermal conductivity, and solderability, etc[4–7]. But the application of fluoride is mostly relevant to the pre-treatment process or electroless plating solution. Fluoride not only needs more stringent requirements for the containers or equipments, but does serious harm to the environment and the operators. However, why does fluoride have to be used during the process of electroless plating on magnesium alloy? Some researchers[8–11] reported the possibility of magnesium fluoride improving the corrosion resistance of a magnesium alloy. But there are few reports on the mechanism of action of corrosion resistance for fluoride deposited on magnesium alloys. In this work, the corrosion action and passive mechanism of magnesium alloy in the fluoride solution are investigated in detail.

2 Experimental

The substrate material used was ingot-cast AZ91D alloy. The chemical composition of the alloy is given in

Table 1. Specimens with size of 50 mm×40 mm×20 mm were used. The substrates were mechanically polished with emery papers up to 1000 grit to ensure similar surface roughness.

Table 1 Chemical composition of AZ91D (mass fraction, %)

Al	Mn	Ni	Cu	Zn
9.1	0.17	0.001	0.001	0.64
Ca	Si	K	Fe	Mg
<0.01	<0.01	<0.01	<0.001	Bal.

According to the mass change of specimens, the chemical reaction mechanism of magnesium alloy in different concentration HF solutions was studied. The treating process is as follows: oil removal→treating in HF solutions for 2 min (10%, 30%, 50% and 70% HF, respectively) → rinsing with acetone → air-drying → weighing. The operation was repeated until the mass of specimen reaches a constant value.

After activation with 70% HF solution for 20 min, the magnesium alloy specimens were chemically treated with solutions A, B, C and D for a period of time, respectively. After rinsed with acetone, the mass change of the air-dried substrate was measured using an electro-balance. Depending on the mass change, the corrosion of substrate was investigated under different treatment conditions. Table 2 shows the compositions of solutions A, B, C and D and the processing conditions.

The pH values of solution were monitored using a PHS-25C model PHS acidometer. The morphology of the substrates was analyzed by scanning electron microscope. The energy dispersive X-ray spectroscopy analysis was used to determine the composition of treated substrate surface. The mass change of the substrate was measured with an electro- balance with precision of 0.1 mg. Corrosion potential measurements in 3.5% (mass fraction) NaCl solution were carried out in order to compare the corrosion behaviors of the untreated and treated substrates[12]. The electrochemical cell used for corrosion potential measurements consisted of the bare substrate or the treated substrate as the working electrode (exposed area of 1 cm²), a saturated calomel electrode(SCE), and a platinum-foil counter electrode.

The scanning rate was 0.2 mV/s.

3 Results and discussion

3.1 Effect of acid solution on corrosion of magnesium alloy

At room temperature, the mass change of the magnesium alloy treated in different concentrations of hydrofluoric acid as a function of time is shown in Fig.1. The mass gain increases with increasing the treating time. However, after a certain time the mass gain reaches a constant value. When the concentration of hydrofluoric acid is low, the mass gain of magnesium alloy increases slowly, and when the concentration increases, the rate of mass gain increases. When the mass gain reaches a constant value, the mass ratio of Mg/F on the substrate surface is about 11.3:1, according to the EDS analysis. The surface morphology of magnesium alloy treated in 70% HF solution for 20 min, is presented in Fig.2. The surface morphology of magnesium alloy treated in 10%, 30% and 50% HF solutions is similar to Fig.2. From Fig.2, it is indicated that the surface of magnesium alloy treated with hydrofluoric acid has a nested structure[13] consisting of grey and black species, whose compositions are 90.5% Mg, 8.0% F, 1.5% Al (mass fraction). According to the EDS results, the grey species consists of F and Mg, and the black species contains Mg and Al. This proves that the surface is not entirely covered with deposit of MgF₂. The results can be explained as follows. The insoluble magnesium fluoride deposited on the magnesium alloy surface increases the mass of magnesium alloys, and retards the reaction between magnesium alloy and hydrofluoric acid. The reaction interface, as a function of treatment time, then decreases. At the same time, a passive film forms on the surface and gradually grows to a perfect layer, as an obstacle of the reaction. In addition, F⁻ ions in the hydrofluoric acid solution may form associated ions such as HF₂⁻, H₂F₃⁻, H₃F₄⁻, with the non-ionized HF molecules. The HF₂⁻ ions are weakly alkaline, and are more stable than F⁻ ions and H₂O[14]. This leads to

Table 2 Compositions of solutions A, B, C and D and processing conditions

Solution	Composition	Processing condition
A	Mixed solution of 98% H ₂ SO ₄ and 70% HF	Room temperature; 10 min interval; H ₂ SO ₄ to HF volume ratio of 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0
B	25 g/L NiSO ₄ solution	90 °C; 1 h interval; pH values of 3, 4, 5, adjusted with dilute sulfuric acid and ammonia
C	10 g/L NH ₄ HF ₂ and 25 g/L NiSO ₄	90 °C; 1 h interval; pH value of 4
D	10 g/L NH ₄ HF ₂ , 20 g/L Na ₂ CO ₃ and 25 g/L NiSO ₄	90 °C; 1 h interval; pH value of 4

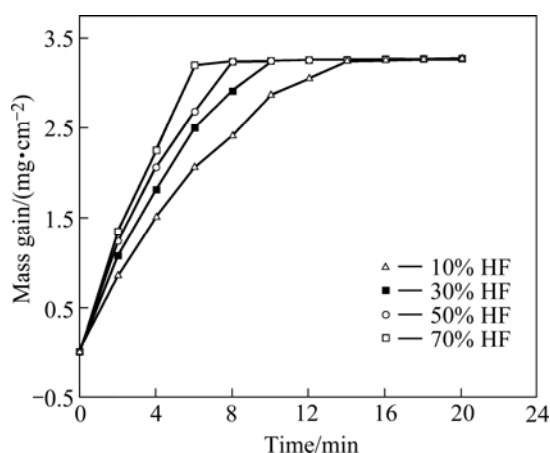


Fig.1 Mass change of magnesium alloy as function of time

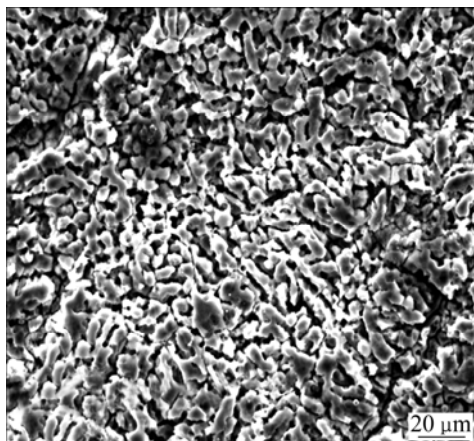


Fig.2 Surface morphology of magnesium alloy treated in 70% HF solution for 20 min

the improvement in the ionization of hydrofluoric acid. Hydrofluoric acid is a strong acid at concentrations above 5 mol/L. Thus the reaction rate between magnesium alloy and hydrofluoric acid increases with the concentration of hydrofluoric acid increasing. The higher concentration of hydrofluoric acid may promote the growth of passive film.

Fig.3 illustrates the mass change of magnesium alloy treated with different volume ratios of sulfuric acid to hydrofluoric acid at room temperature following activation with hydrofluoric acid. The mass of magnesium alloy is virtually unchanged in 10 min when the ratio of acids is below 1.2. When the ratio is above 1.4, the mass of magnesium alloy decreases quickly and the alloy becomes badly eroded over a large area. This indicates that the corrosion of magnesium alloy in the mixed acid is not directly related to the pH value. The results can be explained by the fact that F^- ions are strongly alkaline because of their high electronegativity. Thus, many acidic compounds in an aqueous solution demonstrate alkaline or amphoteric properties when they are exposed to a HF solution.

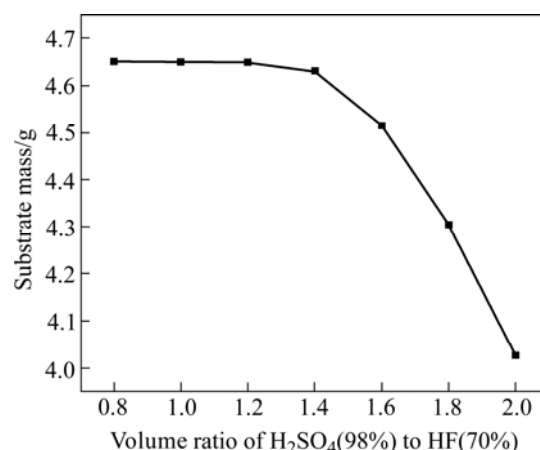
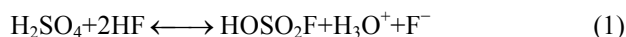


Fig.3 Mass change of magnesium alloy treated in mixed acid solution

Therefore, sulfuric acid, for example, will show alkaline properties in a HF solution as a result of the following chemical reaction[14]:



When the volume ratio of sulfuric acid to hydrofluoric acid is below 1.2, the mixed acid will not erode the substrate because the number of H^+ ions is reduced, as a result, the reverse reaction of reaction (1) takes place through the formation of HF_2^- (or $H_2F_3^-$, $H_3F_4^-$) from reaction between HF and F^- . When the volume ratio is above 1.4, HF reacts with the sulfate ions, thus increasing the concentration of H^+ ions. This then leads to the breakdown of the passive film and severe erosion of the substrate.

Meanwhile, magnesium alloy is also chemically treated with hydrofluoric acid (70%) until the mass change of substrate reaches a constant value. However, the treated substrate is severely eroded by dilute sulfuric acid.

3.2 Effect of $NiSO_4$ solution on corrosion of magnesium alloy

After activation with HF, the magnesium alloy was immersed in a solution of NH_4HF_2 (10 g/L) and $NiSO_4$ (25 g/L) at pH 4 and 90 °C. After 1 h, there was no remarkable change in the alloy mass. The surface morphology of the treated magnesium alloy is shown in Fig.4. Compared with Fig.2, it is clear that there is no obvious change in the surface morphology of the treated substrates. The EDS analysis on the surface of magnesium alloy indicates that the composition of surface is similar to that of the activated substrate, and that no nickel is detected on the surface. This demonstrates that there is a 'passivation state' between the nickel ions in the solution and the surface of magnesium alloy, thus indicating that the replacement

reaction does not take place. The results can be explained as follows. According to the chemistry of solid surfaces, activated magnesium alloy surfaces with high free energy are easily wetted in solution. F atoms in MgF_2 film adsorb H^+ ions in solution with strong binding energy, leading to electronic HF_2^- (or H_2F_3^- , H_3F_4^-) film formation through $\text{H}-\text{F}$ chemical bonds. The passive film protects the surface and retards the reaction between the hydrogen ions and the substrate.

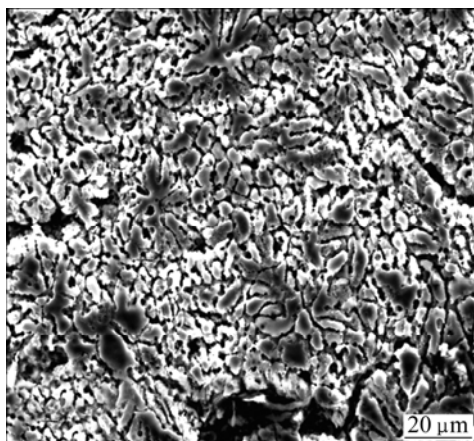


Fig.4 Surface morphology of magnesium alloy treated in mixed acid solution

After activation with HF at 90 °C, the magnesium alloy specimens were treated with solutions of NiSO_4 (25 g/L) whose pH values were 3, 4 and 5, respectively. After 1 h, the mass loss was observed, which was decreased as the pH increased. This suggests that the magnesium alloy is eroded by the NiSO_4 solution. The results can be explained by the fact that MgF_2 may not form in NiSO_4 solutions lacking fluoride and no passive film can form. So the activated substrate is easily eroded by H^+ ions in acidic NiSO_4 solution.

The magnesium alloy was also treated with a mixture (pH=4) of NH_4HF_2 (10 g/L), Na_2CO_3 (20 g/L) and NiSO_4 (25g/L) for 1 h at 90 °C. The surface morphology of the treated specimen is shown in Fig.5. The compositions are 86.3% Mg, 5.0% F, 7.6% Ni and 1.1% Al, according to the EDS analysis. Compared with Fig.2, some small off-white particles are generated on the substrate surface. EDS analysis indicates that these particles consist of nickel. They are generated by the replacement reaction between the substrate and the Ni^{2+} ions. CO_3^{2-} ions can capture H^+ ions from HF_2^- (or H_2F_3^- , H_3F_4^-) ions to form HCO_3^- ions, thus preventing the adsorption reactions from occurring and leading to disruption of the protective passive film. In addition, most of the free H^+ ions combine with CO_3^{2-} to form HCO_3^- ions, which have buffering properties and therefore limit the corrosion of the substrate[15–16]. Ni^{2+} ions can therefore diffuse to the surface and a replace-

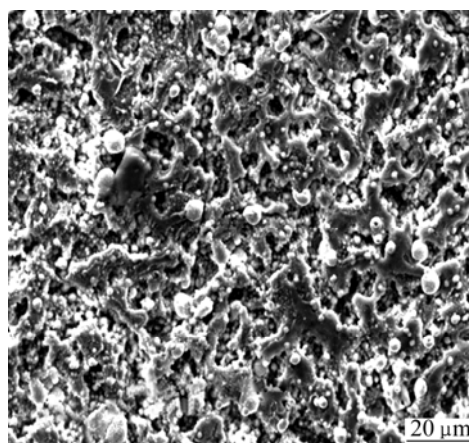


Fig.5 Surface morphology of magnesium alloy treated with mixture of NH_4HF_2 , Na_2CO_3 and NiSO_4

ment reaction can occur without electroless plating nickel because of the absence of reducing agents.

The electrochemical behavior of the specimens before and after treatment was investigated using the polarization test and the results are shown in Fig.6. The measurements were carried out in a 3.5% NaCl solution at room temperature. It can be seen from Fig.6 that the interesting turning point of the anodic and cathodic curves (φ_{corr}) of the activated magnesium alloy (or the substrate after treatment in $\text{NaCO}_3+\text{NiSO}_4+\text{NH}_4\text{HF}_2$ solutions) shows a small shift to the negative direction compared with that of the substrate, but the corrosion current density increases for the activated magnesium alloys (or the substrate after treatment in $\text{NaCO}_3+\text{NiSO}_4+\text{NH}_4\text{HF}_2$ solutions). These results show that the fluoride film deposited on the magnesium alloy does not improve its corrosion resistance in the 3.5% NaCl solution. This is because the fluoride on the magnesium alloy surface only improves its reactivity at the active site, so that the active sites enhance the corrosion reaction of the substrate.

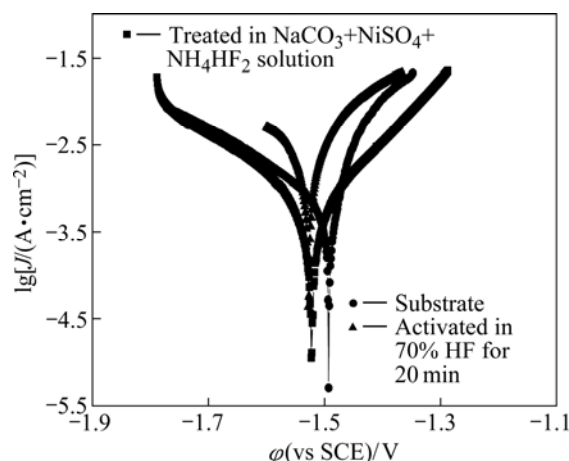


Fig.6 Electrochemical behavior of specimens before and after treatment

4 Conclusions

1) An insoluble MgF_2 film was generated on the surface of magnesium alloy activated in the hydrofluoric acid. The mass of the deposited MgF_2 film may reach a constant value, when the mass ratio of Mg/F on the magnesium alloy surface was fixed at 11.3:1.

2) The activated magnesium alloy gained a 'passivation state' in a mixture acid of sulfuric acid and hydrofluoric acid whose volume ratio was below 1.2. At the same time, the mass of magnesium alloy was maintained as a function of time. When the ratio was above 1.4, the mass of magnesium alloy rapidly decreased.

3) The passive film formed by the deposited MgF_2 film can protect the magnesium alloy from corrosion in fluoride solution (or H_2F_3^- , H_3F_4^-) ions through the adsorption of HF_2^- . However, no such film can protect the substrate in non-fluoride solution as no passive film can be formed in the absence of fluoride ions. The addition of fluoride and carbonate to nickel sulfate will result in the activated magnesium alloy undergoing a replacement reaction with nickel ions.

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