Study on Corrosion Behavior of as-forged AZ81 Mg alloy in different concentrations of NaCl solution

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Abstract: In this paper, the microstructure of as-forged AZ81 Mg alloy before and after heat treatment was analyzed by means of optical microscope and XRD, the corrosion behavior of as-forged AZ81 Mg alloy after heat treatment with different concentrations of NaCl solution was studied by static immersion weight loss method. The results show that: after solution aging heat treatment at 400℃×0.5h+200℃×20h, the grain size of the alloy is more uniform, but the effect on the average grain size is not obvious; when the corrosion time is fixed, the corrosion rate of as-forged AZ81 Mg alloy increases rapidly with the increase of NaCl concentration; with the extension of corrosion time, the corrosion rate of as-forged AZ81 magnesium alloy increases in a fluctuating manner, and then in a fluctuating decreases after reaching the peak value, and after 72h of etching, the corrosion rate of the alloy is basically unchanged; meanwhile, the corrosion in as-forged AZ81 magnesium alloy shows obvious filamentous propagation characteristics, and these filamentous corrosion characteristics basically extend and distribute along the grain boundary.

1. Introduction
Magnesium alloys are widely used in automobile, aerospace, military, electrical and electronic, medical and sports equipment fields due to its low density, high specific strength and specific stiffness, good damping and vibration absorption and cutting performance, excellent electromagnetic shielding and dimensional stability[1-3]. However, due to the close packed hexagonal structure, the plastic deformation ability of magnesium alloy at room temperature is poor, and the plastic processing temperature is generally in the middle and high temperature[4]. In addition, because of the negative electrode potential and high chemical activity of magnesium alloy, it will be electrochemically corrosion in humid air, sulfur and sea, and it is prone to general corrosion and pitting corrosion, etc., which seriously limits the magnesium alloys application and development[5-7].

The influence of different media on the corrosion performance of magnesium alloy was analyzed and studied. Huang Xiaomei et al. studied the corrosion behavior of pure Mg and Mg Li alloy in Neutral 3.5% NaCl solution by electrochemical method, the results showed that the electrochemical reaction resistance of pure Mg was higher than that of Mg Li alloy at the initial stage of corrosion; after 24h corrosion, the corrosion rate of pure Mg was higher than that of Mg Li alloy[5]. Zhang Xin et al. studied the corrosion performance of Mg-Y magnesium alloy in 3.5% NaCl aqueous solution by electrochemical test[8]. With the increase of Y content, the corrosion potential and corrosion rate of
Mg-Y alloy increased. Liang Chenghao and others studied the corrosion behavior of AZ31 magnesium alloy and industrial pure magnesium in the atmosphere, and found that the corrosion resistance of magnesium alloy was better than that of industrial pure magnesium\cite{9}. Li Lingjie et al. studied the dynamic electrochemical corrosion behavior of AZ31 magnesium alloy in NaCl medium\cite{10}. Wang Yajun et al. studied the corrosion behavior of extruded AZ80 Magnesium Alloy in simulated human body fluid\cite{11}. In this paper, the corrosion behavior of as-forged AZ81 magnesium alloy in different concentrations of NaCl solution is analyzed and studied, which provides some experimental reference for the further application of as-forged AZ81 magnesium alloy.

2. Experimental material and method

2.1. Experimental material

The composition of the alloy is Mg-Al(8.33%)-Zn(0.82%)-Mn(0.27%) (mass fraction), in which \(w(Fe)\leq0.005\), \(w(Si)\leq0.019\), \(w(Ni)\leq0.0007\), \(w(Cu)\leq0.0016\). The raw materials used are grade I single substance, and the alloy is melted in resistance furnace. At the same time, gas and a small amount of flux are used for continuous casting to obtain \(112(\pm0.2)mm\times250mm\) semi continuous ingot, which was protected by mixed gas of \(SO_2\) (1%, volume fraction) and \(CO_2\) (99%, volume fraction) mixed gas protection during continuous casting, and air cooled to room temperature after pouring; the semi continuous ingot was homogenized treatment at \(400^\circ C\times12h\) and air cooled, and then extruded by XJ–800 bedroom extruder at \(400^\circ C\). The extrusion ratio was 16, and the extrusion speed was \(13mm/s\), then, the blank with the same volume as the sample was cut from the extruded profile, and put into the cavity of the die-forging die, and then isothermal die forging was carried out on 200t forging press, which the temperature of die forging was \(400^\circ C\) and die forging speed of \(5.6 mm/s\), deformation degree of \(50%\) and holding time of \(8~10s\), and the air cooling is conducted after forging. Finally, the die forging samples were treated by solution aging at \(400^\circ C\times0.5h + 200^\circ C\times27h\), and then the \(6mm\times3.5mm\times6\) was prepared along the vertical extrusion direction by wire cutting, and the surface of each sample was pre-ground and polished.

![Fig.1 Preparation process of corrosion samples](image)

2.2. Experimental method

The microstructure of as-extruded AZ81 magnesium alloy with solution aging heat treatment was observed by optical microscope. Abrasive paper and polishing machine are used to pre grind and polish the samples to be corroded, so as to ensure the good surface finish of samples. The prepared samples were immersed in 1%, 2%, 3%, 4% and 5% NaCl solution at room temperature. Before immersion, the samples were cleaned with absolute ethanol, ultrasonic cleaned for at least three times, then dried, weighed and recorded. After immersion, the corrosion products on the surface of the samples were cleaned with 20%\(CrO_3\) + 1%\(AgNO_3\) (volume fraction) mixture, and then cleaned again with alcohol, then dried and weighed and recorded. The average corrosion rate is calculated by weight loss method. The calculation formula of corrosion rate is shown in (1)

\[
A = \frac{8.76\times10^7 \times (m_0 - m_1)}{St\rho}
\]
Where: \( A \) is the corrosion rate (mm/a); \( m_0 \) is the mass of the sample before immersion (g); \( m_1 \) is the mass of the sample after immersion (g); \( s \) is the total area of the sample (cm\(^2\)); \( t \) is the soaking time (H); \( \rho \) is the density of the material (kg/m\(^3\));

3. Result and discussion

3.1. Microstructure of as-forged AZ81 magnesium alloy before corrosion

Fig.2 shows the microstructure of as-forged AZ81 magnesium alloy. It can be seen from the figure that the alloy is composed of near equiaxed grains with different sizes, which are distributed along the deformation direction, and the grain sizes are uneven, as shown in Fig.2(a); after solution aging heat treatment, the grains of the alloy become uniform obviously, but the deformation streamline does not disappear during the forging process, and a large number of black fine phases are obviously precipitated, which is distributed at grain boundaries or within boundaries, as shown in Fig.2(b)~(c). The average grain size of as-forged AZ81 is about 2.92μm which measured by the cross-section method, and the average grain size of longitudinal and transverse sections after heat treatment is 2.84μm and 3.43μm respectively, and the grain size changes little.

According to Fig.3 and related literature\(^{[12]}\), after solution aging heat treatment, a large number of small black phases precipitated in AZ81 magnesium alloy are \( \beta\)-Mg\(_{12}\)Al\(_{17}\) phase. Since the atomic radius of Mg and Al are closer. Therefore, Mg and Al preferentially form \( \beta\)-Mg\(_{12}\)Al\(_{17}\) phase, and the content of Mn is small, even if Al-Mn is formed. Therefore, a small amount of Al\(_6\)Mn phase can be observed in Fig.3, and the rest are \( \alpha\)-Mg equiaxed crystals. The \( \beta\)-Mg\(_{12}\)Al\(_{17}\) phase and Al\(_6\)Mn phase in the alloy are brittle phase. After being deformed twice by extrusion and forging, the \( \beta\)-Mg\(_{12}\)Al\(_{17}\) phase Al\(_6\)Mn in the alloy are crushed and dispersed in the matrix or dissolved in the matrix under the action of three-dimensional compressive stress. Due to the low stacking fault energy of magnesium alloy, certain dynamic recrystallization occurs during the solution aging heat treatment of magnesium alloy. The alloy microstructure is uniform equiaxed grains, but the average grain size does not change significantly.
3.2. Microstructure after corrosion

It can be seen from Fig.4(a)–(e) that the corrosion degree of as-forged AZ81 magnesium alloy in different concentrations of NaCl solution has increased significantly, pitting corrosion first appears in 1% and 2% NaCl solution, and then gradually develops into filamentous corrosion feature; after 30 min corrosion in 3% and 4% NaCl solution, the filamentous corrosion paths on the alloy surface merge with each other and cover most of the alloy surface; however, in 5% NaCl solution, the corrosion of the alloy surface extends to the whole surface, and the corrosion of the sample surface is relatively uniform, which indicates that the concentration of NaCl solution has great influence on the as-forged AZ81 magnesium alloy. In addition, it can be seen from Fig.5 that during the etching process of forged magnesium alloy in NaCl solution of different concentrations, it basically starts from the position of grain boundary, and spreads along the grain boundary, and gradually connects to form a network structure. With the increase of concentration, the grain boundary becomes coarser, and the pitting characteristics appear inside the grain boundary, which becomes the path of pitting corrosion. The propagation characteristics of filamentous corrosion can also be clearly seen on the macrosurface.
When the as-forged AZ81 magnesium alloy is allowed to stand for 24h in NaCl solutions of different concentrations, a large amount of filiform corrosion can be observed covering on the whole alloy surface, forming corrosion "ditch" or corrosion pit with different depth along the deformation direction of the sample, and obvious cracks along the grain boundary can also be seen in the severe parts, as show in Fig.6. The reason is that β-Mg₁₂Al₁₇ is the main component in the forged AZ81 magnesium alloy, among them, Zn has little tendency to stress corrosion cracking, and Al is corrosion cracking has a greater impact, which causing stress corrosion cracking to spread along the intergranularity\(^{[12]}\), as shown in the fig.7, the arrow in the figure refers to the cracks formed on the surface of as forged alloy after being etched in 3% NaCl solution for 24h. In addition, a large area of spalling can be observed on the surface of the alloy.

Fig. 5 Optical micrographs of as-forged AZ81 Mg alloy in different concentrations of NaCl solution at high magnification, immersion for 30min

Fig.6 optical micrographs of AZ81 magnesium alloy surface soaked in different concentrations of NaCl solution for 24h
3.3. Corrosion rate curve

It can be seen from the corrosion rate curve (as shown in Fig.8) that in the initial stage, with the increase of corrosion time, the corrosion rate of alloys in different concentrations of NaCl solution decreases rapidly, and then increases in a fluctuating manner. When the corrosion time is 24h, the corrosion rate reaches the peak value. With the continuous increase of corrosion time, the corrosion rate decreases rapidly. When the corrosion time exceeds 72h, the corrosion rate tends to be constant, as shown in Fig.8; However, when the corrosion time is fixed, the corrosion rate of the alloy in the range of 1%~2% and 4%~5% is relatively fast, while the corrosion rate of the alloy in the concentration range of 2%~4% is relatively slow, as shown in Fig.9.

The corrosion rate of as-forged AZ81 magnesium alloy in different concentrations of NaCl solution is obviously different. It is mainly due to the formation of micro galvanic corrosion of magnesium alloy in different concentrations of NaCl solution:

Magnesium alloy has the following reactions[13]:

\[
\text{Anode: } \quad \text{Mg} \rightarrow \text{Mg}^{2+} + 2e \quad (2)
\]
\[
\text{Cathode: } \quad 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \quad (3)
\]

With the continuous precipitation of OH\(^-\), the passivation film of Mg(OH)\(_2\) is formed, and the reaction is as follows:

\[
\text{Mg} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (4)
\]

The corrosion of NaCl solution to as-forging AZ81 magnesium alloy is mainly characterized by the formation and thickening of surface film, and the pitting corrosion of Cl\(^-\)[14]. The Mg(OH)\(_2\) film is porous, hard and brittle, and easy to be corroded[14], but the Cl\(^-\) radius is very small. In the process of competitive adsorption, it is easier to penetrate into the film and destroy the Mg(OH)\(_2\) film. Therefore, the formation and thickening of the surface film can only weaken the action of the active anionic Cl\(^-\), but cannot prevent the corrosion of the NaCl Solution on magnesium matrix. So the corrosion rate of the alloy will decrease rapidly at the initial stage of corrosion. However, with the increase of corrosion time, the diffusion and adsorption of active anion Cl\(^-\) destroy the Mg(OH)\(_2\) film, make the magnesium alloy contact with NaCl solution and accelerate the dissolution of magnesium alloy. At this time, the active anion Cl\(^-\) pitting corrosion is the main feature, which makes the metal particles separate from the corrosion resistant parts, the corrosion rate is increased. During the reaction process, Mg and OH\(^-\) are reformed and thickened, and the barrier effect of Cl\(^-\) increases, which lead to the corrosion rate gradually decreases, so reciprocating, so it is found in the corrosion rate curve of as-forged AZ81 magnesium alloy increased fluctuatingly with the increase of corrosion time, and the corrosion rate of Mg(OH)\(_2\) increases after 24h of corrosion, the Mg(OH)\(_2\) passivation film was the thinnest, which makes the magnesium alloy fully exposed to the NaCl solution, and its corrosion rate reaches a certain peak. With the further extension of corrosion time, the thickness of the film formed and increased, and the barrier effect to Cl\(^-\) was the strongest, and the corrosion rate decreased significantly. After 72h, the blocking effect of Cl\(^-\) and the formation of Mg (OH)\(_2\) passivation film reaches a certain equilibrium state, and the corrosion rate tends to be stable.
When the corrosion time is constant, the higher the concentration of Cl\(^{-}\) ions in NaCl solutions of different concentrations, the stronger the pitting effect on the matrix. In the concentration range of 1\%~2\%, the formed Mg(OH)\(_2\) passivation film is thinner, Cl\(^{-}\) ion pitting is the dominant role, and the average corrosion rate increases faster; in the concentration range of 2\%~4\%, the corrosion rate increases relatively slowly, mainly due to the Mg(OH)\(_2\) passivation film is relatively thick in the concentration range, which makes the effect of Cl\(^{-}\) ion relatively weak, and the corrosion rate increases relatively slowly; in the concentration range of 4\%~5\%, the corrosion rate increases faster, mainly because of the enhanced effect of Cl\(^{-}\) ion, which leads to the faster increase of corrosion rate.

![Fig. 8 corrosion rate curve of as-forged AZ81 Mg alloy immersed in different concentrations of NaCl solution](image1)

![Fig. 9 Corrosion rate curve under different NaCl concentrations](image2)

### 3.4. Corrosion mechanism analysis

The grain size of as forged AZ81 magnesium alloy changes little after solution and aging treatment, but a large amount of fine dispersed \(\beta\)-Mg\(_{12}\)Al\(_{17}\) phase and a small amount of Al\(_6\)Mn phase are precipitated. Among them, the electronegativity of Mn and Al is the same. According to the relevant literature\(^{15-16}\), the electrode potential of \(\beta\)-Mg\(_{12}\)Al\(_{17}\) phase and Al\(_6\)Mn phase is higher than that of \(\alpha\)-Mg matrix. The \(\beta\)-Mg\(_{12}\)Al\(_{17}\) phase and Al\(_6\)Mn phase and the nearby \(\alpha\)-Mg matrix form the micro cell, which makes the Mg\(^{2+}\) in the solution adsorbed to the cathode area, while the active anions Cl\(^{-}\) and OH\(^{-}\) in the solution will move to the anode area to form Mg(OH)\(_2\) and cover the surface of the alloy. However, as an acid radical ion, Cl\(^{-}\) easily reacts with Mg(OH)\(_2\) and destroys the film, which will be exposed to the solution again, which provides conditions for further micro-galvanic corrosion. Therefore, the surface of forged AZ81 magnesium alloy is mainly characterized by pitting corrosion. At the same time, due to the distribution of \(\beta\)-Mg\(_{12}\)Al\(_{17}\) and Al\(_6\)Mn phases along the deformation direction, the corrosion path of the alloy in NaCl solution presents a certain path extension, that is, it is
characterized by filamentous growth seen from the macroscopic view, and the corrosion path basically extends along the grain boundary of the alloy. With the increase of NaCl concentration, Cl⁻ in the solution increases to form more micro galvanic couples, that is to say, the increase of Cl⁻ increases the probability of damage to Mg(OH)₂ film, and then the probability of pitting corrosion increases obviously. Therefore, the corrosion rate increases with the increase of NaCl concentration. However, when the Cl⁻ destruction and the formation of Mg(OH)₂ tend to balance, the corrosion rate tends to remain unchanged.

4. Conclusion
1) The crystal gains of the as-forged AZ81 magnesium alloy are homogenized after solution aging heat treatment, but it has little effect on the grain size of the alloy.
   2) The results show that when the corrosion time is constant, the corrosion rate of as-forged AZ81 magnesium alloy increases obviously with the increase of NaCl concentration; with the increase of corrosion time, the corrosion rate of as-forged AZ81 magnesium alloy increases in a fluctuating manner, and then decreases after reaching the peak value, and the corrosion rate of tends to be stable after 72h
   3) The results show that β-Mg₁₂Al₁₇ and Al₆Mn phases distribute along the deformation direction in the as-forged AZ81 magnesium alloy, which results in the formation of obvious filamentous corrosion characteristics in NaCl solution, and these filamentous corrosion characteristics basically extend and distribute along the grain boundary.

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