Effect of Heat Treatment on Stress Corrosion Cracking of AZ91 Magnesium Alloy

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Abstract. The effects of different heat treatment conditions (T4 solid solution, T6 solid solution + artificial aging) on the stress corrosion cracking behavior of cast AZ91 magnesium alloy were investigated. The results show that the heat treatment can significantly improve the stress corrosion cracking resistance, which will be attributed to the change of microstructure and composition distribution after heat treatment, improve the corrosion resistance of the alloy, and hinder the hydrogen evolution process of the cathode, thus weakening the hydrogen embrittlement effect. The heat treatment stress corrosion fracture is still cleavage fracture, but the plasticity characteristics are significantly increased compared with the as-cast fracture.

1. Introduction
Magnesium alloys are widely used in 3C, automotive, aerospace and other fields due to their low density, high specific strength and good casting performance. They enjoy the reputation of “green metal structural materials in the 21st century” [1-4]. However, due to its low electrode potential, magnesium alloys are prone to corrosion in corrosive media such as humid atmosphere, distilled water, seawater, and corrosion resistance is poor [5-6]. At the same time, the H generated in the corrosion process easily enters the interior of the magnesium alloy and induces hydrogen embrittlement of the magnesium alloy [7]. The synergistic effect of the two causes the magnesium alloy to fail under relatively low stress and brittle fracture. Therefore, it is particularly important to improve the stress corrosion resistance of magnesium alloys [8].

2. Experiment
The AZ91D magnesium alloy was placed in a graphite crucible resistance furnace, and a protective gas mixture of CO₂ (98%) and SF₆ (2%) was introduced, heated to 680 °C, and kept for 10 min, and cast in a metal mold. The composition thereof is shown in Table 1. The castings are solution treated in a vacuum resistance furnace (420 °C + 24 h), then hot-quenched in 80 °C hot water, and then partially solid solution castings are aged (200 °C + 24 h).

| Alloy | Al  | Zn  | Mn  | Fe   | Si   | Mg   |
|-------|-----|-----|-----|------|------|------|
| AZ91  | 8.56| 0.61| 0.28| 0.0008| 0.02 | Bal  |

The stress corrosion cracking sensitivity was measured by a slow strain rate stretching machine at a tensile rate of 10⁻⁶ s⁻¹. The working area of the stretched sheet was 20mm×3mm×3 mm. Wrap the work area in lens paper and wrap it around the cotton rope to simulate a humid atmosphere. The stress
corrosion test environment includes: air (inert medium), Cl\textsuperscript{−}\textsuperscript{−}\textsuperscript{−}free humid atmosphere (corrosive medium, thin liquid membrane component is deionized water) and Cl\textsuperscript{−}\textsuperscript{−}\textsuperscript{−}moist atmosphere (corrosive medium, thin liquid membrane component is 3.5 wt. % NaCl saturated Mg(OH)\textsubscript{2} solution). The stress corrosion cracking sensitivity index I\textsubscript{UTS} is derived from equation (1):

\[
I_{\text{UTS}} = \frac{\text{UTS}_{\text{air}} - \text{UTS}_{\text{SCC}}}{\text{UTS}_{\text{air}}} \times 100\% \tag{1}
\]

UTS\textsubscript{air} and UTS\textsubscript{SCC} represent the ultimate tensile strength during stress corrosion cracking in air (inert medium) and corrosive medium in the public test;

3. Results and discussion

3.1. Microstructure analysis

Figure 1 is a scanning electron micrograph of the as-cast, solid solution and aging magnesium alloy microstructure. It can be clearly seen from Figure. 1(a) that the as-cast AZ91 magnesium alloy is mainly composed of primary α-Mg, eutectic α-Mg, and eutectic β-Mg\textsubscript{17}Al\textsubscript{12}. After solution treatment, the coarse skeletal eutectic β-Mg\textsubscript{17}Al\textsubscript{12} is mostly dissolved in the matrix Mg, and only a small amount, discontinuous and small size β-Mg\textsubscript{17}Al\textsubscript{12} phase remains on the grain boundary as shown in Figure. 1(b). Figure 1(c) is the microstructure and partial enlargement after aging treatment. It can be seen from the figure that the secondary phase β is mainly re-precipitated from two forms, one is the discontinuous precipitation at the grain boundary. The β phase precipitated at this point has a certain orientation, and is distributed in the lamellar form at the grain boundary; the other is continuous precipitation in the crystal, mainly distributed in the form of particles, and the number is large and the distribution is uniform.

![Figure 1](image1.png)

Figure1. Corrosion morphology of different magnesium alloy samples:(a)As-cast;(b)T4;(c)T6

3.2. Stress corrosion performance test

Figure 2 shows the stress-strain curves and specific mechanical properties of the as-cast and T4, T6 treated AZ91 magnesium alloys, respectively. It can be seen from Figure. 2 that the ultimate tensile strength (UTS) and elongation at break (ε\textsubscript{f}) of the as-cast AZ91 magnesium alloy are 163 MPa and 9.3%, respectively, in the air medium. The UTS and ε\textsubscript{f} of the T4 treated AZ91 magnesium alloy were 183 MPa and 10.82%, respectively. After T6 treatment, the UTS and ε\textsubscript{f} of AZ91 magnesium alloy were 198 MPa and 8.8%, respectively. In the absence of Cl\textsuperscript{−}\textsuperscript{−}\textsuperscript{−}moist atmosphere, the AZ91 magnesium alloys in three treatment states have different degrees of stress corrosion cracking, and the mechanical properties of the alloys are significantly reduced. The UTS and ε\textsubscript{f} of the as-cast AZ91 magnesium alloy were 110 MPa and 5.1%, respectively. After T4 treatment, the strength and elongation at break of the alloy increased, and the UTS and ε\textsubscript{f} of the alloy reached 140 MPa and 7.3%, respectively. After T6 treatment, the ultimate tensile strength of the alloy was further increased to 161 MPa, but the elongation at break decreased, only 6.5%. When the slow strain rate stretching was carried out in a humid atmosphere containing Cl\textsuperscript{−}\textsuperscript{−}\textsuperscript{−}, the mechanical properties of the AZ91 magnesium alloys in the three treatment states were more pronounced, and the stress corrosion performance was seriously
deteriorated. The UTS and εf of the as-cast AZ91 magnesium alloy are only 88 MPa and 3.5%. After T4 treatment, the UTS and εf of the AZ91 magnesium alloy were improved to 121 MPa and 4.8%, respectively. After T6 treatment, the UTS of the alloy was further improved to 142 MPa, and the elongation at break was lower than that of the T4 treatment, but still higher than that of the as-cast AZ91 magnesium alloy, and the εf was 4.1%.

Figure 2. The stress-strain curves of as-cast and different heat treated AZ91 magnesium alloys in different environments: (a) AZ91; (b) T4; (c) T6

Figure 3 shows the stress corrosion sensitivity index of as-cast and T4, T6 treated AZ91 magnesium alloys. It can be seen from the figure that the stress corrosion sensitivity index of the magnesium alloy in any of the treated conditions is greater than the stress corrosion sensitivity index of the humid atmosphere without Cl⁻. This is mainly due to the strong erosion of Cl⁻.

After T4 treatment, regardless of whether or not Cl⁻ is contained in the humid atmosphere, the stress corrosion sensitivity of the alloy is reduced and the stress corrosion resistance is improved. The IUTS of as-cast AZ91 magnesium alloy was 46% and 32.5% in two humid atmospheres, respectively, while the IUTS of T4 treated AZ91 magnesium alloy was 34% and 23.5%, respectively, with a decrease of 26.1% and 27.7%, respectively. Compared with T4 treatment, the stress corrosion sensitivity index of T6 treated AZ91 magnesium alloy in two humid atmospheres is further reduced, indicating that the stress corrosion resistance of AZ91 magnesium alloy is better than T4 treatment after T6 treatment.

In general, in the as-cast AZ91 magnesium alloy, the coarsely skeletal β-Mg₁₇Al₁₂ phase accelerates the corrosion of the Mg matrix by the galvanic effect. After T4 treatment, the β-Mg₁₇Al₁₂ phase in AZ91 magnesium alloy dissolves and disappears substantially, which makes the micro-galvanic corrosion effect weakened, the corrosion rate of the alloy decreases, and the stress corrosion sensitivity decreases. After T6 treatment, a large amount of fine β-Mg₁₇Al₁₂ phase is re-precipitated on the grain boundary, which can form a corrosion barrier and block the development of corrosion. On the other hand, after the β-Mg₁₇Al₁₂ phase is refined, the hydrogen segregation is alleviated and the local hydrogen concentration is lowered. Therefore, the T4 and T6 treatments improve the corrosion resistance of the alloy by improving the microstructure and composition distribution of the AZ91 magnesium alloy, and reduce the segregation of hydrogen, thereby improving the stress corrosion resistance of the AZ91 magnesium alloy.
3.3. Fracture morphology

The fracture morphology of the as-cast, T4 and T6 treated AZ91 magnesium alloy in air is shown in Figure 4. It can be seen from the figure that there are cleavage steps and secondary cracks on the as-cast fracture, but there are many tearing ridges due to large plastic deformation. In addition, there are a small number of dimples on the fracture surface. The fracture of T4 treated AZ91 magnesium alloy is mainly composed of tearing ribs, dimples and a small number of cleavage small steps. Among them, the dimples have different depths, and the tearing edges due to plastic deformation are prominent and petal-like. The fracture mode of the alloy is close to ductile fracture. This is because after the T4 treatment, the brittle β-Mg17Al12 phase in the AZ91 magnesium alloy dissolves, which reduces the cracking of the matrix during the deformation process, inhibits the initiation and expansion of the crack, and improves the plasticity of the alloy. After T6 treatment, the fracture morphology of the alloy exhibits typical quasi-cleavage fracture characteristics. Compared with the T4 treatment, the number of dimples on the fracture surface is reduced, the number of cleavage steps is increased, and the cleavage plane is plastically deformed and connected in a tearing manner. This is because after T6 treatment, a large amount of β-Mg17Al12 phase is re-precipitated inside the grain boundary and the grain, which can play the role of pinning, which improves the bonding force between the grains to some extent, resulting in quasi-cleavage fracture of the alloy fracture.

Figure 4. Fracture morphologies of As-cast(a), T4 (b) and T6 (c) treated AZ91 magnesium alloys in air

Figure 5 shows the fracture morphology of as-cast, T4 and T6 treated AZ91 magnesium alloys in a Cl⁻free atmosphere. Because the hydrogen generated by the cathode reaction of magnesium alloy diffuses into the magnesium matrix without Cl⁻moist atmosphere, hydrogen embrittlement is induced and the alloy is subjected to low stress brittle fracture. Therefore, the fracture of as-cast AZ91 magnesium alloy exhibits brittle cleavage fracture characteristics. The pattern is obvious and there are a large number of secondary cracks on the fracture surface Figure 5 (a). After T4 and T6 treatment, the fracture mode of the alloy is still dominated by brittle cleavage fracture, but the number of plastic deformation zones on the fracture surface increases, a small number of dimples exist locally, and some micropores gather even form a dimple zone Figure5(c). This is because after the heat treatment, the cathode hydrogen evolution reaction process of AZ91 magnesium alloy is retarded, which weakens the influence of hydrogen embrittlement on the stress corrosion process of the alloy.
Figure 5 Fracture morphologies of as-cast (a), T4(b) and T6 (c) treated AZ91 magnesium alloys in humid atmosphere without Cl\textsuperscript{-}\textsubscript{1}.

Figure 6 shows the fracture morphology of as-cast, T4 and T6 treated AZ91 magnesium alloys in a Cl\textsuperscript{-}\textsubscript{1}containing humid atmosphere. The figure shows that the fracture mode of as-cast AZ91 magnesium alloy is still brittle cleavage fracture, and there are a large number of cleavage steps on the fracture surface. There are still a large number of cleavage steps in the fracture of T4 treated AZ91 magnesium alloy, but the size of the cleavage step is reduced and the number of dimples is obviously increased. After T6 treatment, the alloy is still mainly brittle fracture. Compared with the as-cast AZ91 magnesium alloy, the size of the cleavage step on the fracture surface is reduced, and the number of tearing ribs is increased.

Figure 6 Fracture morphologies of as-cast (a), T4 (b) and T6 (c) treated AZ91 magnesium alloys in humid atmosphere with Cl\textsuperscript{-}\textsubscript{1}

4. Conclusions

1. After the solution treatment, the coarse skeletal β of AZ91 magnesium alloy is mostly dissolved into the matrix, and after aging treatment, the β phase re-sinters in the grain boundary and the crystal as discontinuous lamellar and continuous particles.

2. The T4 and T6 treatments improved the corrosion resistance of the alloy by changing the microstructure and composition distribution of the AZ91 magnesium alloy, thereby weakening the hydrogen embrittlement and significantly improving the stress corrosion resistance of the AZ91 magnesium alloy.

3. The stress corrosion fracture of as-cast AZ91 magnesium alloy is characterized by brittle cleavage fracture. The SCC fractures treated by T4 and T6 are still dominated by brittle cleavage fractures, but the number of plastic deformation zones on the fracture surface increases and the size of the cleavage step decreases.
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