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Short Communication

Influence of tensile twinning on electrochemical and corrosion behavior of Mg alloy

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The rolled AZ31 alloy sheet was compressed along the rolling direction to obtain Mg alloy sheets with different volume fractions of $\{10\bar{1}2\}$ tensile twins. Subsequently, the electrochemical and corrosion behavior of the deformed alloys after low temperature annealing were studied by hydrogen evolution tests, weight loss tests and electrochemical methods. The results show that the $\{10\bar{1}2\}$ tensile twins can improve the electrochemical activity and corrosion resistance of the AZ31 alloy. In addition, the self-corrosion rate of the alloy gradually slows down with the continuous increase in deformation amount when the deformation amount of the alloy is 0% and 6%, but that is accelerated on the contrary when the deformation amount is further increased to 9%. In other words, when the deformation amount is less than 6% and the volume fraction of $\{10\bar{1}2\}$ tensile twins is low, the corrosion resistance of the alloy increase with the volume fraction of the $\{10\bar{1}2\}$ tensile twin, but too much volume fraction of $\{10\bar{1}2\}$ tensile twins is not conducive to the improvement of the corrosion resistance of Mg alloy.

Keywords: Mg alloys; Tensile twins; Corrosion resistance

1. INTRODUCTION

Mg alloy is the lightest metal structural material, which has the advantages of high specific strength, high specific rigidity, excellent electromagnetic shielding performance, excellent cutting performance, excellent damping and shock absorption performance, and good fatigue resistance [1-3]. It is known as the "green engineering material of the 21st century". Mg alloys have been widely used in automobile manufacturing, 3C industry, national defence and military industry, and aerospace [4-6]. However, the active chemical properties of Mg lead to its rapid corrosion rate in most environments and media, which greatly limits the application and development of Mg alloys.

Microstructures such as twinning, texture and grain size greatly affect the corrosion resistance of Mg alloys [7-11]. Twin crystals are a common crystal defect in Mg alloys and easily generated in Mg alloys with coarse grain structures. However, when the deformation temperature is very low and the deformation rate is extremely fast, twins may also be produced in fine-grained magnesium alloys. Although the influence of twins on the corrosion resistance of Mg alloys has been partially studied, the law of the influence of twins on the corrosion resistance of Mg alloys is not fully understood. There is currently no comprehensive and unified view on the influence of twins on the corrosion resistance of magnesium alloys. Zhou et al. [12] found that intergranular corrosion was the main corrosion method of AZ31-H24 magnesium alloy in 3.5 wt.% NaCl solution. Their point of view is that twins accelerate intergranular corrosion, which reduces the corrosion resistance of magnesium alloys. Zhang et al. [13] increased the number of dislocations, twins and grain boundary density in AZ91 alloy through hot extrusion, and found that the crystals and grain boundaries accelerated the dissolution rate of the alloy.

The most common twinning modes in Mg alloys are $\{10\bar{1}2\}$, $\{10\bar{1}1\}$ and $\{10\bar{1}1\}$-$\{10\bar{1}2\}$ secondary twins, among which $\{10\bar{1}2\}$ tensile twins are the most common. However, the influence of $\{10\bar{1}2\}$ tensile twins on the corrosion resistance of Mg alloys is not clearly understood. Based on this, the effect of $\{10\bar{1}2\}$ tensile twins on the corrosion resistance of Mg alloys was systematically studied in this study. The electrochemical activity greatly affects the corrosion resistance of the metals, so the effect of $\{10\bar{1}2\}$ tensile twins on the electrochemical behaviour of Mg alloys was also studied.

2. EXPERIMENTAL

2.1 Materials

The rolled AZ31 alloy sheet with a thickness of 20 mm is selected as the received experimental material, which has a composition of 2.83 wt.% Al, 0.95 wt.% Zn, 0.25 wt.% Mn and balanced Mg. The alloy sheet is cut into cubes with a size of 20 mm×20 mm×20 mm and compressed along the rolling direction at a rate of 2 mm/s with deformation amounts of 3%, 6%, and 9%. To eliminate crystal defects such as dislocations, the compression-deformed magnesium alloy was annealed at 200℃ for 6 h. Then, the annealed alloy was cut into a disk-shaped sample with a diameter of 18 mm and a thickness of 2 mm along the direction parallel to the rolling surface. The surface of the sample was smoothed with 2000-grit SiC paper, and the grain structure of the alloy sample was observed through an optical metallurgical microscope.

2.2 Hydrogen evolution and weight loss test

The Mg alloy sample is encapsulated with phenolic resin, which leaves a circular test surface with a diameter of 18 mm. A 3.5 wt.% NaCl solution was prepared by distilled water and high-grade pure NaCl reagent. The weight of the sample before and after the hydrogen evolution test was weighed to calculate the weight loss of the sample during the hydrogen evolution test.

2.3 Electrochemical test

The electrochemical test was completed in 3.5 wt.% NaCl electrolyte by a PGSTAT302N electrochemical system at 25±2 °C. The test device includes a working electrode, a reference electrode, and an auxiliary electrode. The reference electrode is a saturated calomel electrode, the auxiliary electrode is a platinum metal sheet with an area of 15 mm×15 mm, and the working electrode is the AZ31 alloy. In the electrochemical impedance spectroscopy (EIS) test, the sweep potential is the open-circuit potential, the sweep frequency is 100 kHz-0.01 Hz, and the AC potential amplitude is 5 mV. In the polarization test, the scan rate is 0.05 mV/s. The sample was soaked in the solution for 30 minutes before the electrochemical test to make the surface of the sample reach a stable state.

3. RESULTS AND DISCUSSION

Fig. 1 shows metallographic photos of AZ31 alloys with different deformation amounts. There are no twins in the received alloy, while twins can be found in the deformed alloy. It is easy to produce $\{10\bar{1}2\}$ tensile twins in rolled Mg alloys when compressing along the direction perpendicular to the c-axis of the Mg alloy grains, so the most twins in the pictures are $\{10\bar{1}2\}$ tensile twins.

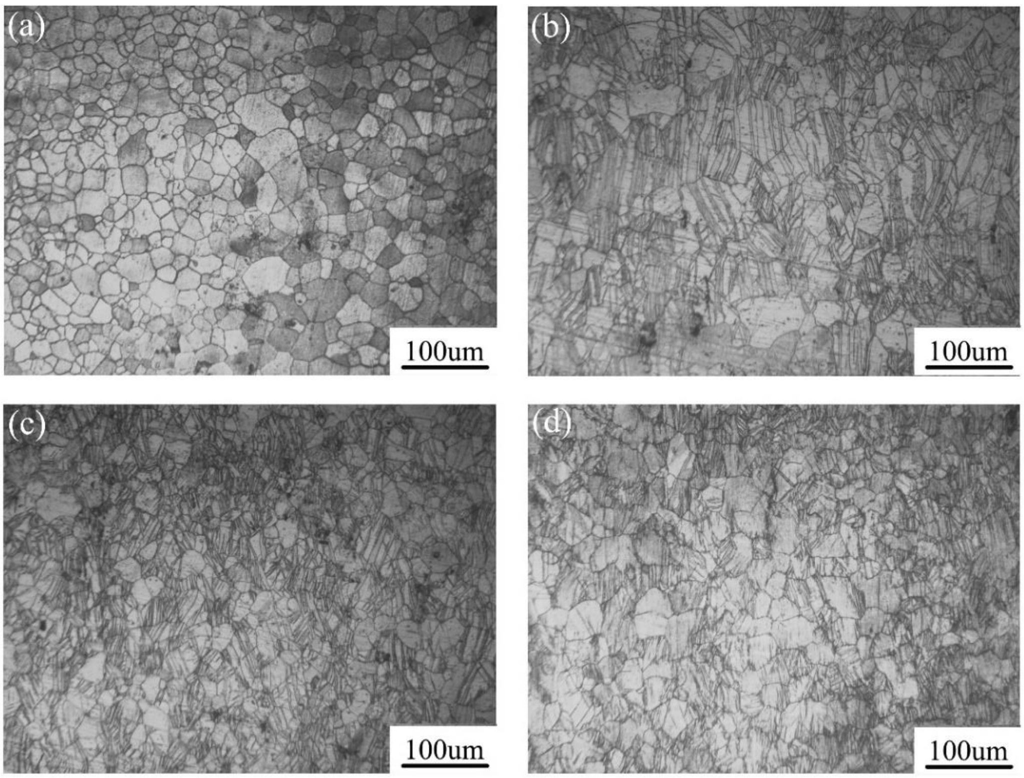

Figure 1. Optical microscopic image of magnesium alloy AZ31 with various deformations: (a) 0%, (b) 3%, (c) 6% and (d) 9%

When the deformation amount of the Mg alloy increases from 0% to 6%, the volume fraction of twins significantly increases. However, when the deformation amount was further increased to 9%, the illusion of a decrease in twins appeared instead. Similar experimental phenomena were reported in extruded AZ31 alloys [14-17]. When the deformation amount was low, both volume fraction of twins and twin boundaries gradually increased with the deformation amount. However, when the amount of deformation increases to a certain extent, the twins will continue to grow with the increase in deformation amount and eventually swallow each other, which decreases the volume fraction of twin boundaries. Moreover, we distinguished the matrix from the twins through the orientation difference between the twins and the matrix in the observation of the microstructure. However, the width of the twins is equivalent to the width of the matrix sandwiched between the twins when the alloy has a large deformation amount, and it is no longer possible to distinguish the matrix from the twins in the observation of the structure. Thus, the volume fraction of twins appears to have decreased but actually has increased.

Fig. 2 shows the polarization curves of AZ31 alloys with different deformation amounts in 3.5 wt% NaCl solution, and the relevant electrochemical data are shown in Table 1. The anode branch and cathode branch of the polarization curves represent the dissolution reaction of the metal and hydrogen evolution reaction, respectively [18, 19]. The corrosion potential of the twinned samples is numerically more negative than that of the received sample. The corrosion potential gradually negatively shifts with increasing deformation amount when the deformation amount is less than 6%, but the corrosion potential moves in the positive direction instead when the deformation amount further increases to 9%. This behaviour indicates that the twinned sample has higher electrochemical activity than the received sample, and the electrochemical activity of the alloy increases with the increase in deformation amount when the deformation amount is less than 6% but deteriorates with further increase in deformation amount to 9%. The possible reason is that the crystal lattice at the twin boundary is destroyed, which increases its atomic energy and results in the higher electrochemical activity of the alloy. Therefore, twins can improve the electrochemical activity of Mg alloys. The volume fraction of twins and twin boundaries gradually increases when the deformation amount increases from 0% to 6%, so the electrochemical activity of the alloy increases. However, when the deformation amount further increases to 9%, although the volume fraction of twins continues to increase, the twin boundaries decreases due to the mutual engulfment between the twin boundaries and contributes to the decreased electrochemical activity of the alloy. In addition, the corrosion current density of the twined sample is lower than that of the received samples, which indicates that the twins improve the corrosion resistance of Mg alloys. The possible reason is that twins act as a physical barrier in the self-corrosion process of magnesium alloys and hinder the spread of corrosion. The corrosion resistance of the alloy increases with increasing deformation amount when the deformation amount is less than 6% (due to the increase in volume fraction of the twin boundaries) but becomes poor when the deformation amount further increases to 9% (due to their mutual swallowing).

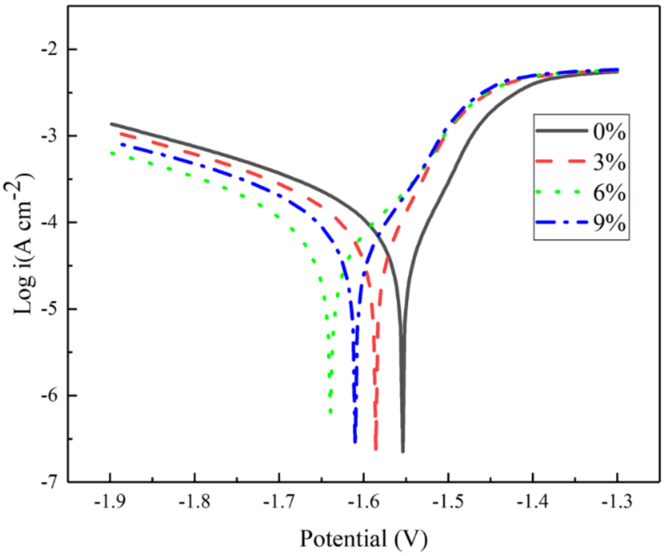

Figure 2. Potentiodynamic polarization curves of magnesium alloy AZ31 with various deformations measured in neutral 3.5 wt% NaCl solution.

Table 1. Corrosion parameters of magnesium alloy AZ31 with various deformations measured in neutral 3.5 wt% NaCl solution.

Deflection	Ecorr (V)	Icorr (μA cm^{-2})
0%	-1.556	166
3%	-1.581	142
6%	-1.642	99
9%	-1.619	123

Fig. 3 shows the hydrogen evolution rate-time curve and hydrogen evolution amount-time curve of the AZ31 alloys with different deformation amounts in 3.5 wt% NaCl solution. The weight loss of the Mg alloy during the hydrogen evolution test is shown in Fig. 5. The deformed sample had significantly lower hydrogen evolution rate and weight loss than the received sample, which indicates that tensile twinning improves the corrosion resistance of the AZ31 alloy. When the deformation amount is less than 6%, a greater deformation amount corresponds to a slower hydrogen evolution rate and a lower weight loss, which indicates corrosion resistance increase with the deformation amount. However, when the deformation is further increased to 9%, the hydrogen evolution rate becomes higher, and the weight loss increases. These results are consistent with the polarization curve results. Meanwhile, in the first 3 h, the hydrogen evolution rate of all samples increases with time and subsequently gradually decreased and stabilized with further increase in time.

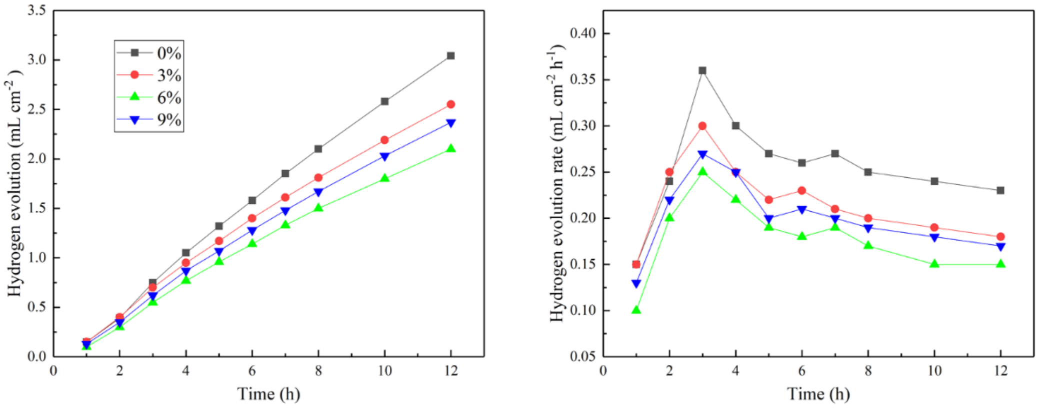

Figure 3. Hydrogen evolution curves of the AZ31 alloys with various deformations measured in neutral 3.5 wt% NaCl solution.

The possible reason is that in the initial stage of the immersion test, the surface of the complete Mg substrate is continuously damaged by corrosion, so the corrosion rate gradually increases; subsequently, the corrosion products accumulate on the surface of the alloy, which will protect the magnesium alloy substrate from corrosion, and the corrosion rate will sharply drop. When the alloy surface is completely covered by corrosion products, the corrosion rate gradually tends to be stable, but the thickness of the corrosion product film will increase with time, and the protective effect on the alloy matrix will gradually become stronger, so the corrosion rate slowly decreases.

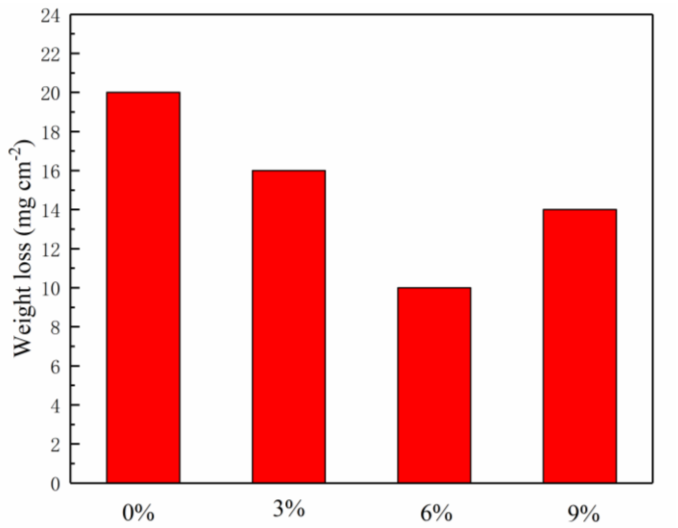

Figure 4. Weight loss of the AZ31 alloys with various deformations during the Hydrogen evolution test

The results of the hydrogen evolution test show that the corrosion rate of the alloys in the early stage of corrosion is very unstable, gradually stabilizes in the later stage and gradually decreases. To further analyse the corrosion resistance of the four alloys in the later stage of the immersion test, the EIS curves of the four alloys after immersion in 3.5 wt.% NaCl solution for 10 h were measured, and the results are shown in Fig. 5. All four EIS curves are composed of two capacitive reactance arcs and one inductive reactance arc. The high-frequency capacitive reactance arc is mainly caused by the charge transfer process in the double-layer capacitor formed by the alloy surface and solution interface, which reflects the corrosion resistance of the sample. The appearance of a capacitive arc in the middle- and low-frequency regions may be caused by the protective corrosion product film on the alloy surface, while the inductive arc in the low-frequency region reflects the incompleteness of the corrosion product film [20, 21].

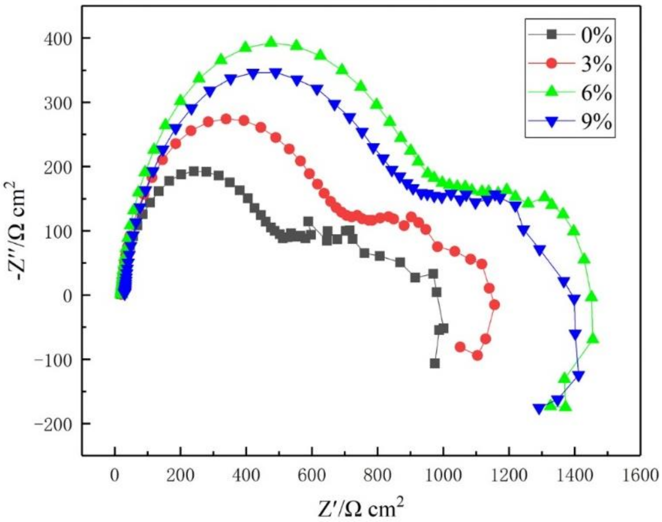

Figure 5. EIS curves of the AZ31 alloy with various deformations measured in neutral 3.5-wt% NaCl solution after 10 h of immersion.

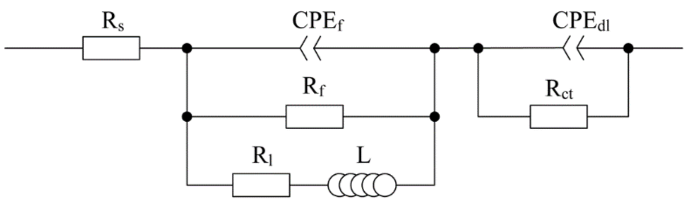

Figure 6. Equivalent circuit of the EIS curves in Figure 5.

After simulating the EIS curves by using ZSimpWin software, the equivalent circuit of the EIS curves is obtained, which is shown in Fig. 6, and the relevant results are listed in Table 2. To compensate for the dispersion effect, the pure capacitance C is replaced by the constant-phase element CPE, which mainly includes two parameters Y and n, where the dimension of Y is ($\Omega^{-1}\times cm^{-2}\times s^{n}$), and n is a dimensionless exponent. In the equivalent circuit model, Rs is the solution resistance, CPE_{dl} is the capacitive reactance of the electric double layer, Rt is the charge transfer impedance, CPE_f is the film capacitance, R_f is the film impedance, R_l is the inductive reactance, and L is the inductance. In general, a larger R_t value corresponds to better corrosion resistance of the alloys. The R_t values of the AZ31 alloy with deformation amounts of 0%, 3%, 6%, and 9% are 466.9 Ω cm^2, 609.5 Ω cm^2, 825.6 Ω cm^2 and 662.7 Ω cm^2, respectively. This result shows that the corrosion resistance of the alloy increases with the deformation amount when the deformation amount is less than 6% but worsens when the deformation is further increased to 9%. This result is consistent with the initial results of the immersion test.

Table 2. Fitting results of the EIS curves in Figure 5.

Deflection	R_s (Ω cm^2)	Y_f ($Ω^{-1}$ cm^{-2} s^n)	n_f	R_f (Ω cm^2)	R_l (Ω cm^2)
0%	20.39	$2.2×10^{-5}$	0.73	435.2	279
3%	19.94	$2.0×10^{-5}$	0.66	503	235
6%	29.95	$1.6×10^{-5}$	0.92	561.9	298
9%	19.74	$2.1×10^{-5}$	0.92	620.7	323
Deflection	L (H cm^2)	Y_{dl} ($Ω^{-1}$ cm^{-2} s^n)	n_{dl}	R_t (Ω cm^2)	
0%	9203	$2.4×10^{-5}$	0.90	466.9	
3%	1690	$1.8×10^{-5}$	0.93	609.5	
6%	2254	$1.8×10^{-5}$	0.60	825.6	
9%	3101	$1.6×10^{-5}$	0.69	662.7	

4. CONCLUSION

In this paper, {10-12} tensile twins are introduced into rolled AZ31 alloy sheets through compression deformation, and the influence of $\{10\bar{1}2\}$ tensile twins on the electrochemical and corrosion behaviour of AZ31 alloys is studied. The main results are shown as follows:

1. The $\{10\bar{1}2\}$ tensile twins can improve the electrochemical activity and corrosion resistance of the AZ31 alloy.

2. The volume fraction of $\{10\bar{1}2\}$ twins and twin boundaries increases with the deformation amount when the deformation amount is less than 6%, which improves the corrosion resistance of the AZ31 alloy.

3. Compression deformation with excessive deformation and excessive $\{10\bar{1}2\}$ tensile twins are not conducive to improving the corrosion resistance of Mg alloys. The AZ31 alloy with a deformation amount of 9% has significantly worse corrosion resistance than the alloy with a deformation amount of 6%. The reason is that when the amount of deformation is too large, the twin boundaries swallow each other and decrease the volume fraction of twin boundaries.

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