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Effect of Different Microstructure on Corrosion Behavior of Magnesium Alloy Sheets

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AZ31 magnesium alloy sheets with different grain sizes produced by continuous variable cross-section direct extrusion (CVCDE) were rolled at different temperatures. The results show that the combination of CVCDE and hot rolling results in the combination of compressive stress and tensile stress, thus the grain size is greatly refined. When the grains are in a certain size, the magnesium alloy sheet will obtain a better corrosion resistance. Except for this size, too large or too small will make the corrosion resistance decrease. The residual stress inside the magnesium alloy sheet rolled at 350 °C is relatively large, and it is easy to cause stress corrosion cracking in corrosive medium. Stress corrosion greatly reduces the mechanical properties of magnesium alloys.

Keywords: AZ31 magnesium alloy sheet, CVCDE, Rolling, Corrosion resistance

1. INTRODUCTION

Magnesium has attracted the attention of various industries with its light density ρ=1.738 g/cm^3 [1-3]. The lighter weight makes it a good advantage in weight reduction and pollution reduction [4-6]. The wrought magnesium alloy treated by rolling has better mechanical properties and diversified structures. However, due to the negative difference effect (NDE) in anode dissolution of magnesium compared with other metals [7], the corrosion resistance of magnesium is poor [8-11]. Wang [12] studied the corrosion resistance of rolled AZ31 magnesium alloy in simulated body fluid (SBF) by electrochemical impedance spectroscopy and potentiodynamic polarization at room temperature. The results showed that the corrosion rate of AZ31 magnesium alloy in SBF could be changed by small uniaxial compression. Turen [13] studied the effect of Sn on the corrosion resistance of as-cast and hot-rolled AZ31 magnesium alloys. With the addition of Sn, the corrosion resistance of AZ31 magnesium alloy had a tendency to decrease. Under the condition of homogenization and hot rolling, the decrease was more obvious, but there were some fluctuations in the as-cast state. Cui [14] studied the corrosion process of AZ91D magnesium alloy in simulated haze aqueous solution by electrochemical measurement, immersion test and morphological characterization. The results showed that AZ91D was severely corroded in simulated solution because the surface product film was loose and easily broken, and there was almost no corrosion barrier. However, the passivation film protecting the metal substrate is more likely to form due to the presence of NO_3^-. However NH_4^+ consumed OH^-, resulting in a deficiency of $Mg(OH)_2$ and severe corrosion. Meanwhile, SO_4^{2-} and Cl^- had influence on pitting corrosion. Chen [15] studied the corrosion properties of magnesium alloy prepared by high strain rate rolling (HSRR) and conventional rolling (CR). The HSRR alloy had better biological corrosion resistance than CR alloy. The main reason for the improvement of biological corrosion resistance by HSRR was the decrease of grain size, the relative abundance of DRX and the absence of twins. Meanwhile, the residual second phase particles of the HSRR alloy were coarser, and the nano precipitates were finer and denser. Slightly stronger (0001) texture also helped to enhance corrosion resistance. Jiang [16] studied the effect of crystal texture and grain size on the corrosion behavior of extruded magnesium alloy AZ31 sheet. The increase of base strength and the decrease of grain size in crystallographic structure could reduce the corrosion rate. Delgado [17] studied the effect of increasing the Al concentration between 0.5 and 0.8 wt% in a 10 μm thick surface layer on the corrosion behavior of a commercial AZ31 alloy sheet by double casting rolling. Under long term exposure, the corrosion resistance of AZ31 specimen was significantly increased due to the uniformity of the double layer Mg-Al hydroxide (LDH) formed in the inner layer of the corrosion product on the aluminium-rich surface, and the formation of a significant amount of aluminum hydroxide precipitation.

In summary, magnesium alloy sheets have been widely used in various fields due to their advantages in good performance characteristics. Through the processing of plastic forming technology, the microstructure and properties of magnesium alloy sheets have been significantly improved. However, the poor corrosion resistance of magnesium alloy is still an inevitable problem. In this paper, AZ31 magnesium alloy sheet was prepared by CVCDE [18] and hot rolling process [19]. The effects of rolling at different temperatures on the grain size of magnesium alloy sheets, and the influence of corrosion properties were explored. The suitable temperature range and grain size were obtained based on the comparison results.

2. EXPERIMENT

The composition of the AZ31 alloys can be seen in Table 1. CVCDE and rolling are mainly used as the forming process of magnesium alloy sheets in this experiment, as shown in Fig. 1-a).

Table 1 AZ31 magnesium alloy composition

Al	Zn	Mn	Fe	Si	Cu	Ni	Mg
3.20%	0.86%	0.36%	0.0018%	0.021%	0.0022%	0.00056%	Bal.

AZ31 magnesium alloy billet with diameter of 40 mm was extruded by CVCDE at 350 °C, and the magnesium alloy sheet with thickness of 4 mm and width of 14 mm was obtained, as shown in Fig. 1-b). After that, the extruded sheet was cut and divided into three groups for hot rolling at 250 ℃, 300 ℃ and 350 ℃ respectively. The 4 mm thick sheet was rolled in three passes, as shown in Fig. 1-c). The deformation of the first pass was 25%, that of the second pass was 20% and that of the third pass was 16.67%. Finally, the magnesium alloy sheet with thickness of 2 mm and width of 15.6 mm was rolled.

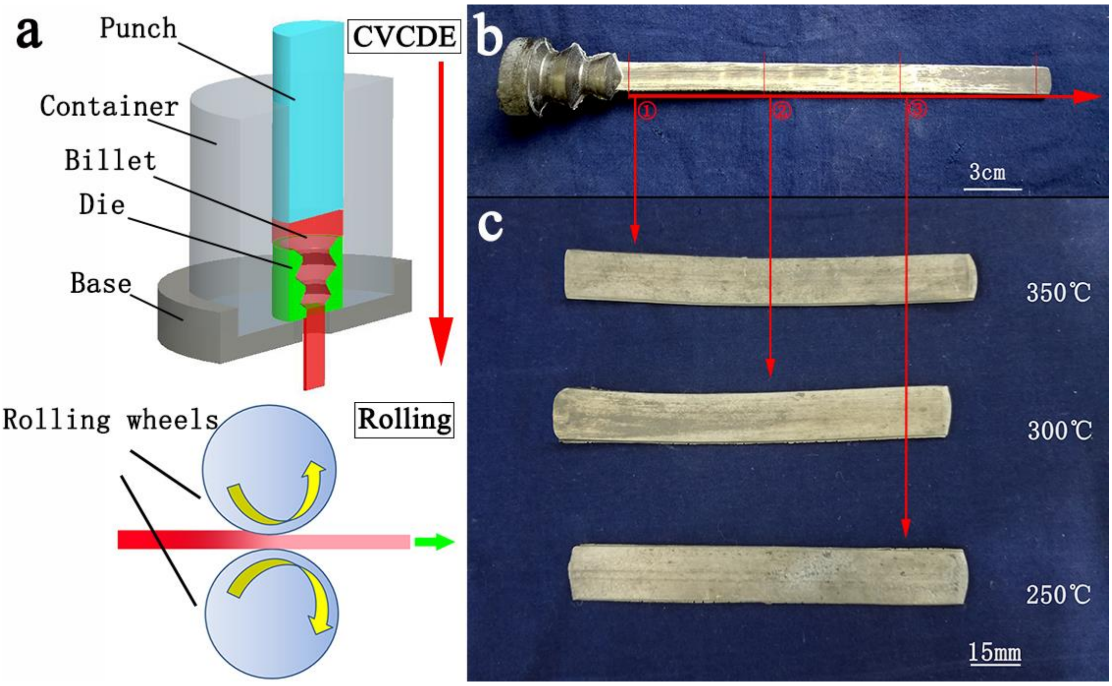

Figure 1. Magnesium alloy sheet and its forming process; (a) CVCDE and rolling; (b) CVCDEed sheet (350 °C extrusion temperature); (c) Rolled sheets at 250 °C, 300 °C and 350 °C

The corrosive solution used in the experiment was 3.5 wt% NaCl solution (simulated seawater). The metallographic structure of magnesium alloy sheets rolled at different temperatures was observed, and the size and distribution of the grains after rolling at different temperatures were observed. The parameters of polarization curve measured by potentiodynamic scanning were set as follows: the scanning rate was 0.05 mV/s, and the sampling interval was 0.001 s. The frequency range of electrochemical impedance measurement was 1 mHz～100 KHz, and the excitation signal was 5-10 mV sinusoidal wave. The time of immersion experiment is 6 h, 12 h, 24 h, 48 h and 72 h, respectively. The difference of stress corrosion among three rolled sheets at different temperatures was studied by slow strain rate tensile test (SSRT). The strain rate was 1.0×10^{-4} s^{-1}.

3. RESULTS

3.1 Microstructure

Fig. 2 is the metallographic and TEM images of AZ31 sheets after CVCDE and rolling at different temperatures. Fig. 2-a), Fig. 2-b) and Fig. 2-c) are the micro-grain morphology and the twin morphology after rolling at 250 °C, 300°C and 350 °C respectively.

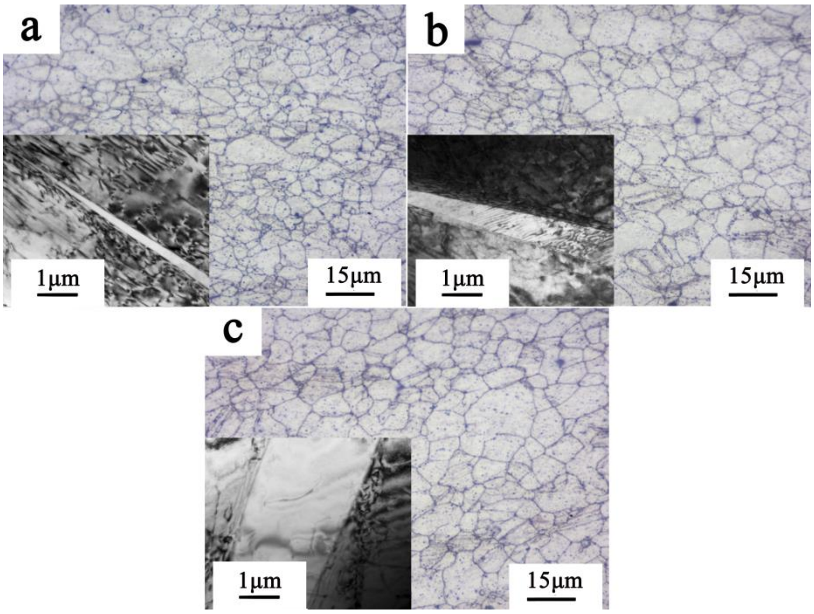

Figure 2. Microstructure comparison (metallography and TEM); (a) 250 °C rolled sheet; (b) 300 °C rolled sheet; (c) 350 °C rolled sheet

It can be seen that the grain size of the magnesium alloy sheet increases with the increase of rolling temperature. The grain size is 4 μm after rolling at 250 °C, 5 μm after rolling at 300 °C, and 7 μm after rolling at 350 °C. The deformed structure of magnesium alloys is sensitive to the change of temperature, and different temperatures have certain effects on the grain size and morphology. Therefore, the rolling temperature has a significant effect on the grain size of the rolled magnesium alloy sheet. Miao showed that the AZ31 magnesium alloy sheet with the thickness of 2 mm was prepared by 6 passes rolling, and the average grain size was 5 μm [20]. However, the average grain size of magnesium alloy after CVCDE can reach 5 μm only after three passes of rolling. The grain size of each sheet has been greatly refined, which is due to the combination of CVCDE and hot rolling, as well as the combination of compressive stress and tensile stress, resulting in the breakage of larger grains and continuous dynamic recrystallization. After rolling at 250 °C, the grains are very fine, but the homogeneity is poor. There are many twins in the grains and they are relatively small. A lot of dislocations are accumulated near the twins. This is due to the low temperature so that the interfacial energy within the grain can not support a large number of lattice slip. Therefore, there are sub-structures in the grains, and the twinning mechanism can effectively increase the deformation direction and reduce the deformation resistance, thus completing the plastic deformation. The grain size after rolling at 300 °C and 350 °C is slightly larger due to the higher rolling temperature, but the homogeneity is good. The number of twins decreases and the size of twins increases obviously.

3.2 Polarization curve

The polarization curves of magnesium alloy sheets rolled at different temperatures are shown in Fig. 3. The difference of the three polarization curves in the figure is mainly caused by the different rolling temperature after CVCDE. Due to the different rolling temperatures, the grain sizes of magnesium alloy sheets after rolling are different, so the parameters such as self-corrosion potentials and corrosion currents of polarization curves are different.

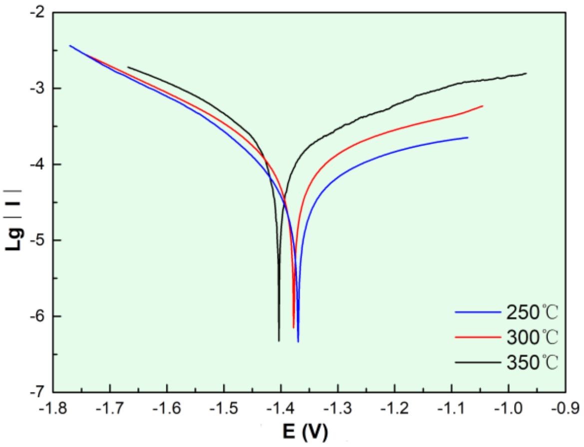

Figure 3. Polarization curves of magnesium alloy rolled at 250 °C, 300 °C and 350 °C (3.5 wt% NaCl solution, 0.05 mV/s scanning rate, 0.001 s sampling interval)

Some parameters calculated from polarization curves are shown in Table 2. It can be seen that the self-corrosion potential Ecorr of the magnesium alloy sheet rolled at 300 °C is -1.37 V. The absolute value of the Ecorr of magnesium alloy sheets rolled at 300 °C compared to the other two temperatures is relatively small. However, the potential difference at different temperatures is not large. The Ecorr at 350 °C is -1.40 V, which is the most negative Ecorr among three temperatures, and the difference between the absolute values of Ecorr of 300 °C and 350 °C is only 0.03 V. That means the temperature has little effect on the self-corrosion potential Ecorr of rolled magnesium alloy sheets in the temperature range of 250 °C and 350 °C. In the table, bc and ba respectively represent the cathode Tafel slope and the anode Tafel slope, and i represents the corrosion current density. It can be seen that the corrosion current of magnesium alloy sheets rolled at 350 °C is larger. The corrosion current of magnesium alloy sheets rolled at 350 °C is one order of magnitude larger than that of magnesium alloy sheets rolled at 250 °C and 300 °C. That means that the corrosion rate of magnesium alloy sheets rolled at 350 °C is faster. The d in the table is the annual corrosion rate calculated from the polarization curve, so it can be seen that d from the largest to the smallest is 2.32E00 > 1.19E00 >

6.51E-01, respectively, the corresponding rolling temperature is 350 °C, 250 °C, 300 °C. So the corrosion resistance of the magnesium alloy sheet rolled at 300 °C is the best. It can be seen from Fig. 2 that the grain size of magnesium alloy sheets rolled at three different temperatures is 350 °C > 300 °C > 250 °C in descending order. Therefore, it is also indicated that the grain size does not correspond to the corrosion resistance [21-26]. When the grain size is a certain size, the magnesium alloy sheet will obtain a better corrosion resistance. Except for this size, too large or too small both will cause a decrease in corrosion resistance, and an excessively large grain size will have a more significant effect on corrosion resistance than an undersized one. Ahmadkhaniha also showed that the effect of grain size on corrosion resistance of magnesium alloy should be discussed according to different processing technology [27].

Table 2. Fitting parameters of polarization curves (3.5 wt% NaCl solution, 0.05 mV/s scanning rate, 0.001 s sampling interval)

	250 ℃	300 ℃	350 ℃
Ecorr (V)	-1.38	-1.37	-1.40
bc (V/dec)	0.142	0.127	0.166
ba (V/dec)	0.189	0.190	0.223
i (A/cm^2)	5.25E-05	2.86E-05	1.02E-04
d (mm/a)	1.19E00	6.51E-01	2.32E00

3.3 Corrosion rate

Fig. 4 shows the average corrosion rate curves of three magnesium alloy sheets rolled at different temperatures by the immersion method. It can be clearly seen that the rolling temperature of corrosion rate from large to small is 350 °C > 250 °C > 300 °C in turn. The corrosion rate of the magnesium alloy sheet rolled at 350 °C is the fastest among three rolling temperatures in three days of immersion and the corrosion resistance of the magnesium alloy sheet rolled at 300 °C is the best among three rolling temperatures. The magnesium alloy sheet rolled at 350 °C and 250 °C has a distinct peak when immersed for 12 hours, and the subsequent corrosion rate gradually decreases.

After immersion for one day, the corrosion rate of magnesium alloy sheet rolled at 350 °C and 250 °C began to keep constant, which means that the corrosion films formed by the corrosion products produced by electrochemical corrosion of magnesium alloys have basically adhered to corrosion surfaces of magnesium alloy sheets.

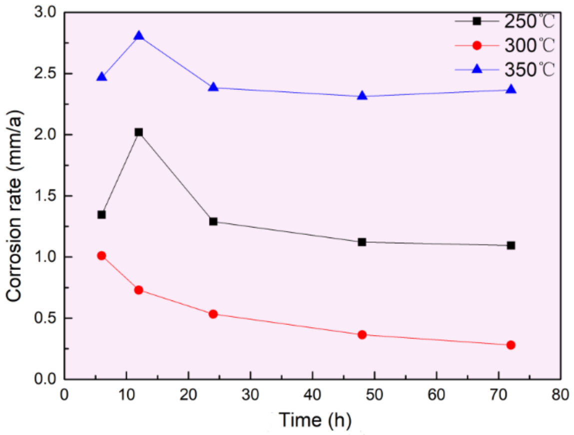

Figure 4. Corrosion rate curves of magnesium alloy rolled at 250 °C, 300 °C and 350 °C (3.5 wt% NaCl solution, soaking time: 6 h, 12 h, 24 h, 48 h and 72 h)

The corrosion film deposited on the corrosion surface forms a barrier which prevents the corrosion surface from sufficiently contacting with the corrosive solution, thereby slowing down the corrosion rate to a certain extent. The corrosion rate curve of the magnesium alloy sheet rolled at 300 °C has no obvious peak value, and the corrosion rate curve shows a downward trend. It shows that the corrosion surface of the magnesium alloy sheet rolled at 300 ℃ has been covered with a layer of corrosion film before 12 hours, and the formation rate of corrosion film is faster than that of the magnesium alloy sheet rolled at 350 °C and 250 °C.

It can be seen from Table 2 that the magnesium alloy sheet rolled at 300 °C has a lower corrosion rate and better corrosion resistance, and the magnesium alloy sheet rolled at 350 °C has a faster corrosion rate and a poor corrosion resistance. This is consistent with the results obtained by the immersion method, which further confirms that the relationship between grain size and magnesium alloy sheet is not linear, but similar to normal distribution. There is a most appropriate grain size, which is too large or too small will lead to the decline of corrosion resistance. This should be due to the finer grain size and higher grain boundary strength of the magnesium alloy sheet rolled at 250 °C, but the number of small twins in the grain is larger. Huang [28] showed that the electrochemical activity of AZ31 magnesium alloy increased with the increase of volume fraction of twins. He believed that twins, as a crystallographic defect, made atoms near twin boundaries have higher storage energy by twin deformation, thus improving the electrochemical activity of magnesium alloy. The grain size of magnesium alloy sheet rolled at 350 ℃ is slightly larger. Aung [29] showed that the effect of grain size was more obvious in corrosion, and the corrosion rate increased significantly with the increase of average grain size. Therefore, it can be seen that the grain size is the main factor affecting the corrosion resistance of magnesium alloys, and the twin is the secondary factor. Based on the above data and analysis, the magnesium alloy sheet rolled at 300 ℃ has better corrosion resistance. In addition, the instantaneous corrosion rate calculated by the polarization curve is similar to the average corrosion rate calculated by the immersion method, and it is slightly higher or slightly lower than the average corrosion rate. Thus, the accuracy of the results of corrosion resistance of three magnesium alloy sheets rolled at different temperatures is further confirmed.

3.4 Electrochemical impedance spectroscopy (EIS)

Fig. 5 shows the Nyquist plot of magnesium alloy sheets rolled at different temperatures and immersed in corrosive solution for different times. Among them, the impedance spectroscopy of magnesium alloy sheet rolled at 250 °C in Fig. 5-a) shows the presence of a capacitive loop and a distinct inductive loop in the low frequency region, while a capacitive loop exists in the high frequency region. Baril showed that high frequency (HF) loops appear to be the result of charge transfer and film effect [30]. With the prolongation of soaking time, it can be seen that the capacitive loop diameter in the high frequency region has no obvious change, and the response points of each frequency substantially overlap. This indicates that the corrosion film has little influence on the charge transfer process during the formation of corrosion film, which means that the corrosion film is thin, and electrons can pass through the film by means of "tunnel effect". Fig. 5-b) is the impedance spectroscopy of the time-varying magnesium alloy sheet rolled at 300 °C. It can be seen that the capacitive loop diameter at low frequency is obviously larger, and there is an obvious inductive loop at high frequency and low frequency at 0 h. The inductive loop at high frequency is mainly caused by the instability of the circuit system or the fact that the metal surface is not completely immersed in the corrosive solution and the inductance inside the conductor. With the prolongation of soaking time, the capacitive loop diameter at the low frequency decreases slightly.

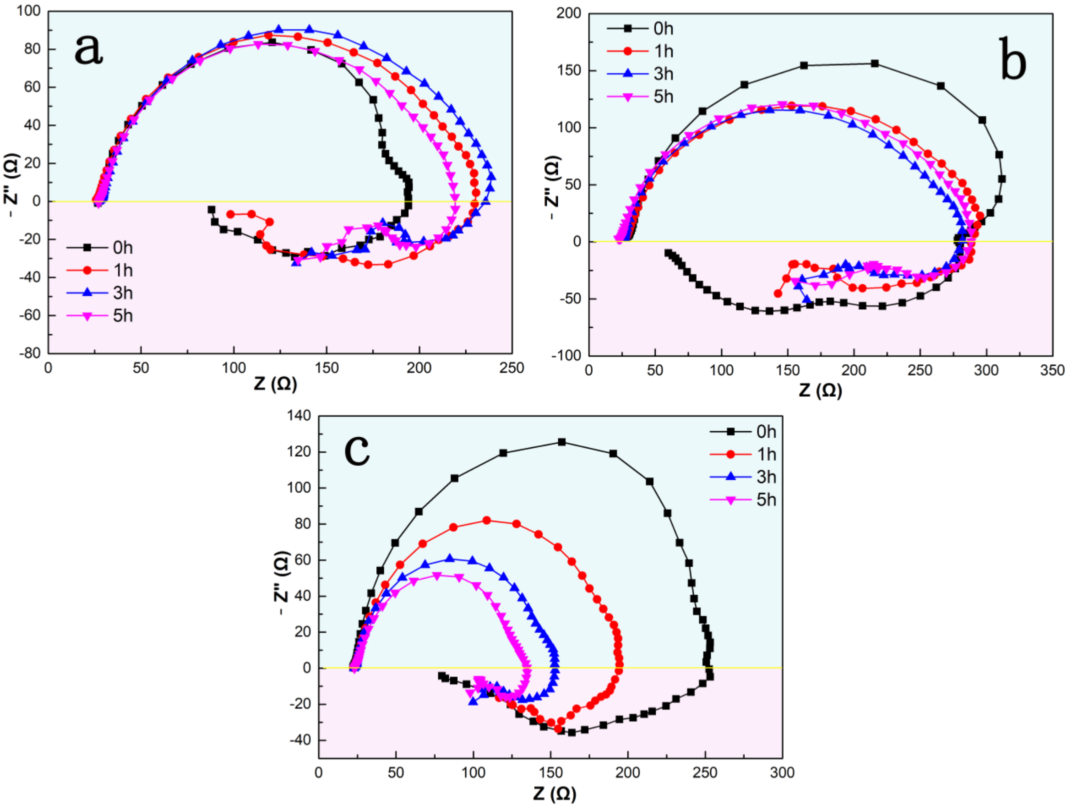

Figure 5. Nyquist plots; (a) 250 °C rolled sheet; (b) 300 °C rolled sheet; (c) 350 °C rolled sheet (3.5 wt% NaCl solution, 1 mHz～100 KHz frequency range, 5-10 mV sinusoidal wave)

In Nyquist plots, the capacitive loop diameters soaked for 1 h, 3 h, and 5 h are basically the same whether at high or low frequencies, and there is no obvious difference, indicating that the corrosion film of magnesium alloy sheet rolled at 300 °C is relatively stable. Fig. 5-c) shows that the impedance spectroscopy of magnesium alloy sheet rolled at 350 °C varies with time. It can be seen that the capacitive loop resistance varies greatly at both high and low frequencies with the prolongation of soaking time. The longer the soaking time, the smaller the capacitive loop diameter, the smaller the charge transfer resistance, and the faster the metal anode dissolves into metal cations.

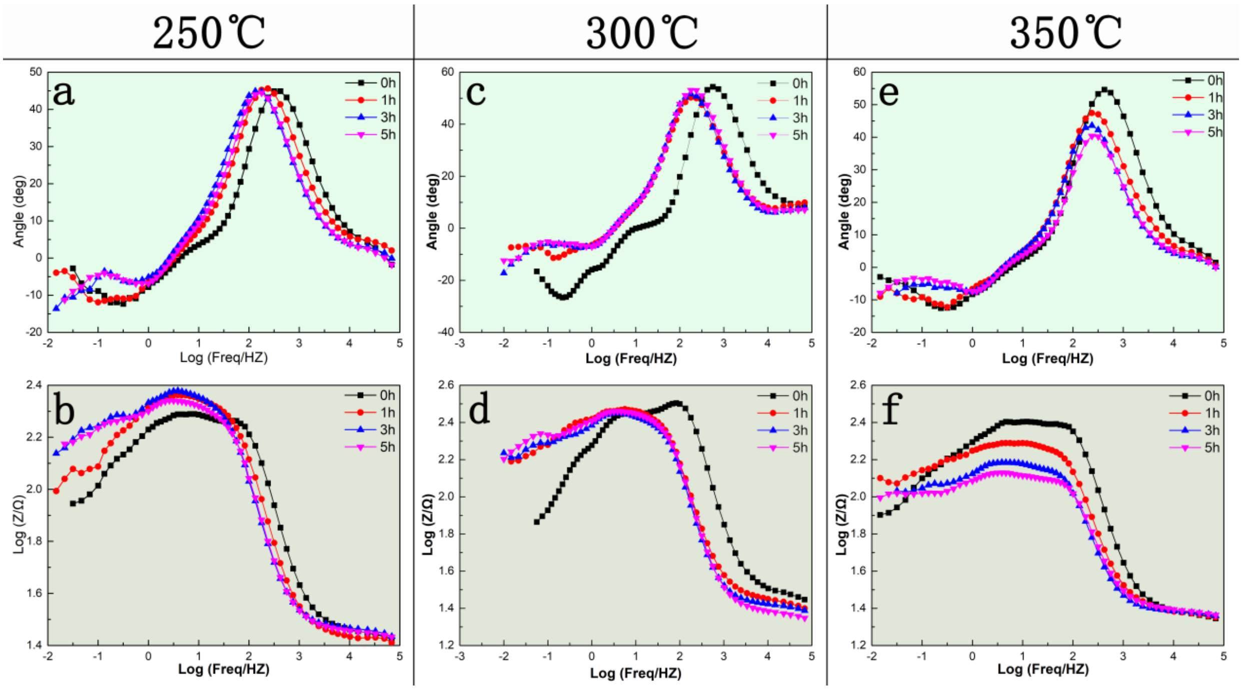

Figure 5. Bode plots; (a-b) 250 °C rolled sheet; (c-d) 300 °C rolled sheet; (e-f) 350 °C rolled sheet (3.5 wt% NaCl solution, 1 mHz～100 KHz frequency range, 5-10 mV sinusoidal wave)

The corrosion resistance of three magnesium alloy sheets rolled at different temperatures is quite different. Oliveira showed that the diameter of the Nyquist curve along the real axis was related to the charge transfer resistance (R_{ct}) of the electrode, and the minimum diameter of the capacitor loop indicated that its protection performance was poor [31]. The magnesium alloy sheet rolled at 300 °C has the largest capacitive loop diameter, and the stability of the corrosion film is the best, that is, the corrosion rate is relatively stable and the corrosion resistance is good. The capacitive loop diameter of the magnesium alloy sheet rolled at 250 °C is slightly smaller than that of the magnesium alloy sheet rolled at 300 °C. The stability of the corrosion film of the magnesium alloy sheet rolled at 250 °C is slightly poor, and the reaction rate of the electrode is not very stable, which result in the non-uniform diffusion of reactants or products. The corrosion resistance of magnesium alloy sheet rolled at 350 °C is the worst, and the corrosion film is extremely unstable, which leads to the decrease of Faraday impedance Z_f and the increase of active ions. The extra electrons transfer to the interface between the corrosion film and the solution, which destroys the charge balance in the film and accelerates the electrochemical corrosion rate [32]. However, three magnesium alloy sheets rolled at different temperatures have a certain similarity during the formation of corrosion film, that is, the inductive loop diameter at low frequency decreases gradually with the prolongation of soaking time. This is because the corrosion film gradually tends to be a dynamic equilibrium in the process of continuous formation and dissolution, and correspondingly, the change of the electric field strength φ due to the change in the thickness of the film layer is gradually reduced, and thus the inductive loop diameter is also gradually reduced. Fig. 6 shows Bode plots of magnesium alloy sheets rolled at different temperatures soaked in corrosive solution for different hours. From Bode plots, we can see that the impedance and phase angle change with the increase of frequency.

When the rolling temperature is 250 °C, there are two time constants corresponding to the two capacitive loops in the Nyquist plots, and the impedance of different soaking time is similar, indicating that the formation of corrosion film doesn't have a great impact on the corrosion rate. When the rolling temperature is 300 °C, except for the soaking time of 0 h, the other soaking times also have two time constants. When the rolling temperature is 350 °C, it appears two time constants, and as the soaking time increases, the impedance also decreases. It indicates that corrosion resistance of the magnesium alloy sheet rolled at 350 °C is declining, but it can be seen from the magnitude of the decline that the corrosion of magnesium alloys is tending to a steady state.

Under steady state conditions, the formation rate of the corrosion film is equal to the dissolution rate of the film layer, so the thickness of the film layer remains unchanged. At this time, all the anode current flowing through the metal electrode is used to form a new film layer, which confirms that the corrosion film does have a certain protective effect on the metal substrate [33].

Table 3. Fitting parameters of impedance (3.5 wt% NaCl solution, 1 mHz ~ 100 KHz frequency range, 5-10 mV sinusoidal wave)

	R_s (Ω)	R_{ct} (Ω)	R_L (Ω)
250 ℃	8.89	57.61	114.1
300 ℃	7.46	81.62	169.3
350 ℃	7.68	33.83	86.71

Table 3 shows the fitting parameters of impedance. It can be seen from the table that the solution resistance R_s values [34] of the three magnesium alloy sheets have little difference, because of the same corrosive solution and the same three electrode system. For the three magnesium alloys, R_{ct} and R_L are quite different. It is obvious that the values of R_{ct} and R_L of the magnesium alloy rolled in 300 ℃ are the highest among the three magnesium alloy sheets, while the values of R_{ct} and R_L of the magnesium alloy rolled in 350 ℃ are the lowest. There is a difference of more than two times in the values of R_{ct} and R_L between the 300 ℃ rolled magnesium alloy and 350 ℃ rolled magnesium alloy. As a result, the charge transfer of the 300 ℃ rolled magnesium alloy is inhibited during the corrosion process, so that the corrosion resistance of the 300 ℃ rolled magnesium alloy is improved. After soaking 5 h, the order of corrosion resistance is 300℃ rolled magnesium alloy > 250 ℃ rolled magnesium alloy > 350 ℃ rolled magnesium alloy.

3.5 Corrosion morphology

As shown in Fig. 7, the figure shows the micro-morphology of magnesium alloy sheets rolled at different temperatures for different hours. It can be seen that after immersion for 1 hour, the magnesium alloy sheets rolled at different temperatures are mainly crevice corrosion. Fig. 7-a) shows that besides the large area of crevice corrosion, filiform corrosion occurs locally in the magnesium alloy sheet rolled at 250 °C, while only crevice corrosion occurs in the magnesium alloy sheet rolled at 300 °C in Fig. 7-b). In Fig. 7-c), the obvious stress corrosion can be seen in magnesium alloy sheet rolled at 350 °C. This is because the residual tensile stress during the rolling process interacts with the corrosive solution. The stress corrosion cracking can be seen as the result of the mutual promotion of electrochemical corrosion and stress mechanical damage. Cl^- is an active anion. Under the combined action of tensile stress and chloride ion, it is possible to produce plastic deformations and slip planes of step shape [35-36]. If slip planes of step shape are sufficiently large to break the surface film, the potential of the metal surface relative to the passivation surface becomes more negative, forming an area with a particularly small anode. It will be rapidly dissolved and form a pit due to a large corrosion current density and electrons flow out to the pit which means they flow to the cathode and $2H^+ + 2e \rightarrow H_2$ occurs on the cathode. When the soaking time is extended to 5 hours, as shown in Fig. 7-d)~Fig. 7-f), the magnesium alloy sheet rolled at 250 °C has developed from crevice corrosion to some large corrosion pits, and is continually corroded to the interior along the path of crevice corrosion.

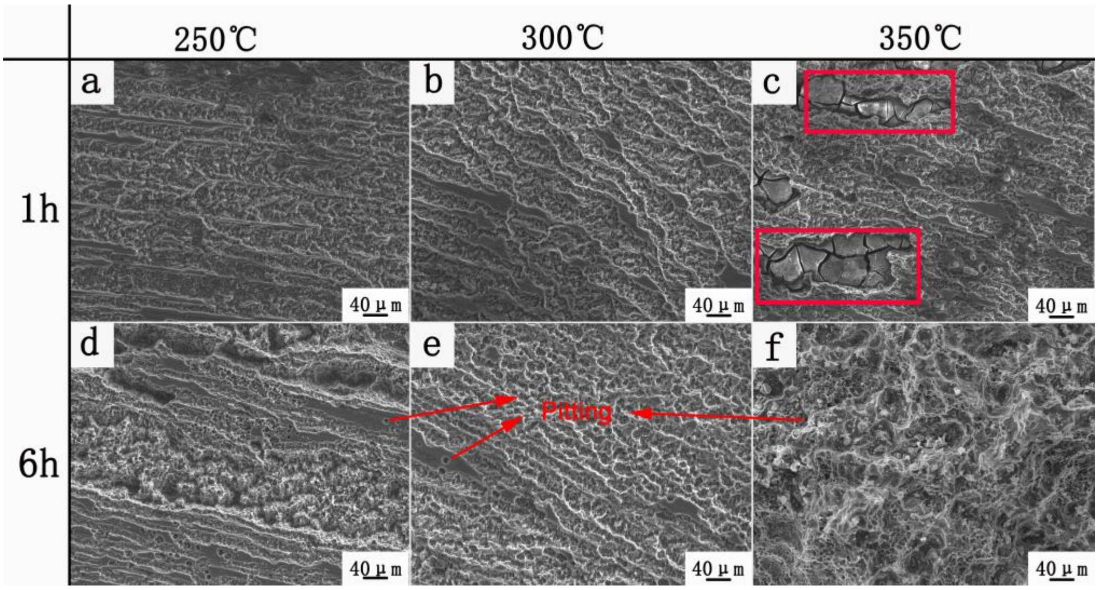

Figure 6. Corrosion morphologies of magnesium alloy sheet rolled at 250 °C, 300 °C and 350 °C; (a, b, c) Soaking for 1 h; (d, e, f) Soaking for 6 h (3.5 wt% NaCl solution)

The magnesium alloy sheet rolled at 300 °C began to appear pitting corrosion on the basis of crevice corrosion, but the pitting corrosion was not serious, and did not cause the morphology of large corrosion pits. It only destroyed the morphology of the previous crevice corrosion. It can be seen that even if the soaking time is extended from 1 h to 5 h, the corrosion degree is not significantly enhanced, which means that the corrosion resistance of magnesium alloy sheets rolled at 300 ℃ is better. The corrosion degree of the magnesium alloy sheet rolled at 350 °C is the most serious. The surface of the magnesium alloy sheet has been corroded very seriously, and the morphology of crevice corrosion has completely disappeared. The size of the corrosion pit is larger than that of the magnesium alloy sheet rolled at 250 °C. It can be seen that when the temperature of hot rolling is set at 350 ℃ after CVCDE, the residual stress inside the rolled magnesium alloy sheet is large. Therefore, stress corrosion cracking is more likely to occur when placed in a corrosion environment, which affects its corrosion resistance [37]. It can be seen that the corrosion degree of magnesium alloy sheets is increasing with the prolongation of time. Under the same conditions of soaking time, the rolling temperature in turn is 300 °C < 250 °C < 350 °C according to the corrosion degree from light to heavy.

3.6 Slow strain rate tensile test

From Fig. 8, it can be seen that the ultimate tensile strength of magnesium alloy sheets decreases gradually with the increase of rolling temperature when the strain is less than 8%. The magnesium alloy sheet rolled at 250 ℃ exhibits strong tensile strength due to the highest degree of grain refinement. However, the strain of the magnesium alloy sheet rolled at 250 ℃ and 350 ℃ is much less than that of the magnesium alloy sheet rolled at 300 ℃, which is due to the interaction of stress and corrosion environment. Because the corrosion resistance of the magnesium alloy rolled at 300 ℃ is better, the corrosive environment has relatively little effect on it, so it can bear a large strain.

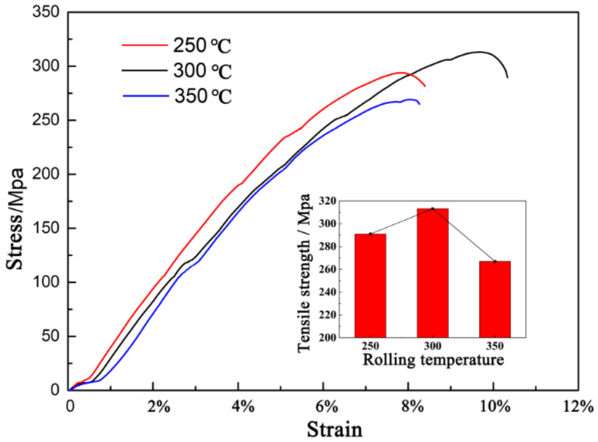

Figure 7. Stress-strain curves and tensile strength of magnesium alloy sheet rolled at 250 °C, 300 °C and 350 °C (Strain rate 1.0×10^{-4} s^{-1})

Therefore, though the magnesium alloy rolled at 250℃ has better grain refinement, its tensile strength is still lower than that of the magnesium alloy rolled at 300 ℃. Therefore, it can be seen that stress corrosion has a great impact on magnesium alloys, which can directly lead to the decline of mechanical properties and damage the service effect [38].

3.7 Tensile fracture

Fig. 9 shows the fracture morphology after stress corrosion. There are many dimples in the magnesium alloy sheet rolled at 250 ℃, but the dimple size varies greatly, the fracture surface fluctuates greatly, and there are very obvious thin tearing edges around dimples.

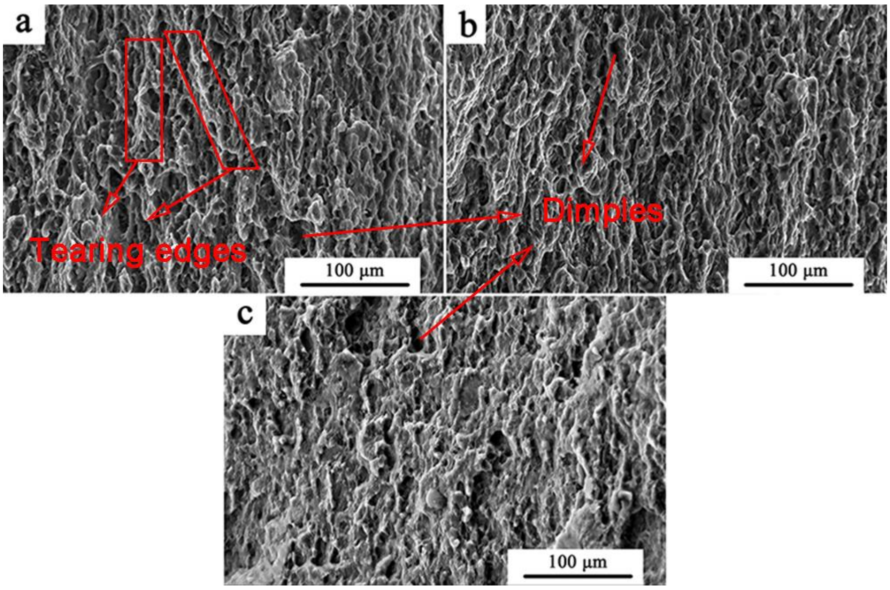

Figure 8. Fracture morphologies of magnesium alloy sheet rolled at 250 °C, 300 °C and 350 °C; (a) 250 ℃ rolled sheet; (b) 300 ℃ rolled sheet; (c) 350 ℃ rolled sheet

It can be seen that the grain size and grain boundary strength of magnesium alloy sheet rolled at 250 ℃ are fine, but the number of twins is large so that the stress corrosion sensitivity increases. Therefore, the dimple size is different and the homogeneity is poor. After rolling at 300 ℃, the magnesium alloy sheet shows the characteristics of ductile fracture. There are a lot of dimples on the fracture surface, that the dimples slightly deepen, and the dimples are relatively uniform in size. Oskooie showed that the dimple size was related to the grain structure, and the dimple size varied with the grain size [39]. The number of dimples and the size of dimples in the magnesium alloy sheet rolled at 350 ℃ are small, showing a weak plastic deformation ability.

4. CONCLUSIONS

1. Because of the combination of CVCDE and hot rolling, the compressive stress and tensile stress are combined, so that dynamic recrystallization occurs continuously and grain size is refined greatly. With the increase of rolling temperature, the grain size of the rolled magnesium alloy sheet increases, and the number of twins decreases.
2. The comprehensive analysis of electrochemical method and immersion method shows that there is no corresponding relationship between grain sizes and corrosion resistance. The magnesium alloy sheet will obtain a better corrosion resistance at a certain grain size. Except for this

size, too large or too small will make the corrosion resistance decrease. The effect of too large grain size on corrosion resistance is more significant than that of too small grain size.

3. For rolled magnesium alloy sheets, grain sizes are the main factor affecting their corrosion resistance, and twins are the secondary factor. Meanwhile, the increase of the number of twins will correspondingly reduce the corrosion resistance of magnesium alloy sheets.
4. Corrosion environment has a great influence on the mechanical properties of rolled magnesium alloy sheets, which greatly reduces their tensile strength and elongation, thus reducing their plastic deformation ability and service effect.
5. The residual tensile stress inside the magnesium alloy sheet rolled at 350 °C is relatively large, so it is easy to cause stress corrosion cracking in corrosive solution. With the extension of time, the corrosion degree of magnesium alloy sheet becomes more and more serious, and under the condition of the same soaking time, the rolling temperature in turn is 300 °C < 250 °C < 350 °C according to the degree of corrosion from the light to heavy.

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References

1. R.j. Sun, Y.C. Guan and Y. Zhu, *Surf. Rev. Lett.,* 23 (2016) 17.
2. M. Nishida, K. Ishida, F. Kodama, K. Hayashi, Y. Akahoshi, K. Hokamoto and Y. Kawamura, *Procedia Eng.,* 173 (2017) 65.
3. S. Samuha, E. Kahana, O. Sadot and R.Z. Shneck, *Materials,* 11 (2018) 329.
4. Z.M. Wang, H.Y. Zhao, X.D. Hu, Y.Q. Lu and D.Y. Ju, *Key Eng. Mater.,* 725 (2016) 636.
5. L. Ruan, S. Ezaki, F. Masahiro, S. Shen and Y. Kawamura, *J. Magnesium Alloys,* 4 (2016) 27.
6. S. Suttner and M. Merklein, *Mater. Sci. Forum,* 854 (2016) 112.
7. S. Bender, J. Goellner, A. Heyn and S. Schmigalla, *Mater. Corros.,* 63 (2012) 707.
8. M. Esmaily, J.E. Svensson, S. Fajardo, N. Birbilis, G.S. Frankel, S. Virtanen, R. Arrabal, S.Thomasand and L.G. Johansson, *Prog. Mater Sci.,* 89 (2017) 92.
9. E. Ghali, W. Dietzel and K.U. Kainer, *J. Mater. Eng. Perform.,* 13 (2004) 7.
10. D.F. Zhang, Z.B. Qi, B.B. Wei, H. Shen and Z.C.Wang, *Ceram. Int.,* 44 (2018) 9958.
11. S.A. Salman, K. Kuroda, N. Saito and M. Okido, *Magnesium Technol.,* 39 (2016) 203.
12. C. Wang, H. Ding, B.S. Wang, K. Wang, J.J. Shi and J.F. Chen, *Acta Metall. Sinica,* 10 (2017) 3.
13. Y. Turen, D. Güzel, H. Zengin, Y. Sun and H. Ahlatci, *Key Eng. Mater.*, 750 (2017) 124.
14. L.Y. Cui, Z.Y. Liu, P. Hu, J.M. Shao, X.G. Li, C.W., Du and B. Jiang, *Materials,* 11 (2018) 970.
15. J.H. Chen, G.Q. Chen, H.G. Yan, B. Su, X.L. Gong and B. Zhou, *J. Mater. Eng. Perform.,* 26 (2017) 4748.
16. B. Jiang, Q. Xiang, A. Atrens, J. Song and F. Pan, *Corros. Sci.,* 126 (2017) 374.
17. M.C. Delgado, F.R. García-Galvan, I. Llorente, P. Pérez and S.F. Jr., *Corros. Sci.,* 123 (2017) 182.
18. Y. Wang, F. Li, X.W. Li and W.B. Fang, *J. Mater. Process. Technol.,* 275 (2020) 116360.
19. Y. Chen, L. Hu, L.X. Shi, T. Zhou, J. Tu, Q. Chen and M.B. Yang, *Mater. Sci. Eng. A,* 769 (2020) 138497.
20. Q. Miao, L.X. Hu, E. Wang, S.J. Liang and H.Y. Chao, *Int. J. Mod. Phys. B,*23 (2009) 984.

21. N. Birbilis, K.D. Ralston, S. Virtanen, H.L. Fraser and C.H.J. Davies, *Corros. Eng. Sci. Technol.,* 45 (2010) 224.
22. D. Song, A.B. Ma, J.H. Jiang, P.H. Lin, D.H. Yang and J.F. Fan, *Corros. Sci.,* 52 (2010) 481.
23. M.K. Chung, Y.S. Choi, J.G. Kim, Y.M. Kim and J.C. Lee, *Mater. Sci. Eng. A,* 366 (2004) 282.
24. M.A. Lopez, M.D. Pereda, J.A. Valle, M.F. Lorenzo, M.C.G. Alonso, O.A. Ruano and M.L. Escudero, *Acta Biomater.,* 6 (2010) 1763.
25. Y. Li, T. Zhang and F. Wang, *Electrochim. Acta,* 51 (2006) 2845.
26. D. Song, A.B. Ma, J.H. Jiang, P.H. Lin, D.H. Yang and J.F. Fan, *Corros. Sci.,* 53 (2011) 362.
27. D. Ahmadkhaniha, M. Fedel, M. Heydarzadeh Sohi and F. Deflorian, *Surf. Eng. Appl. Electrochem.,* 53 (2017) 439.
28. G.S. Huang, Y.C. Zhao, Y.X. Wang, H. Zhang and F.S. Pan, *Mater. Lett.,* 113 (2013) 46.
29. N.N. Aung and W. Zhou, *Corros. Sci.,* 52 (2010) 589.
30. G. Baril and N. Pébère,. *Corros. Sci.,* 43 (2001) 471.
31. M.C.L.D. Oliveira, V.S.M. Pereira, O.V. Correa and R.A. Antunes, *J. Mater. Eng. Perform.,* 23 (2013) 593.
32. J. Chen, J. Wang, E. Han, J. Dong and W. Ke, *Corros. Sci.,* 50 (2008) 1292.
33. C.D. Lee, C.S Kang and K.S. Shin, *Met. Mater. Int.,* 6 (2000) 441.
34. U.C. Nwaogu, C. Blawert, N. Scharnagl, W. Dietzel and K.U. Kainer, *Corros. Sci.,* 52 (2010) 2143.
35. R.C. Newman and C. Healey, *Corros. Sci.,* 49 (2007) 4040.
36. R. M. Rieck, A. Atrens and I.O. Smith, *Mater. Sci. Technol.,* 2 (1986), 1066.
37. A. Mazur and B. Paweowski, *Corros. Sci.,* 26 (1986) 7.
38. N. Winzer, A. Atrens, W. Dietzel, G. Song and K.U. Kainer, *JOM,* 59 (2007) 49.
39. M.S. Oskooie, H. Asgharzadeh and H.S. Kim, *J. Alloys Compd.,* 632 (2015) 540.