

Influence of Ca on microstructure and corrosion resistance of Mg-14Li alloy

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Abstract: In order to improve the corrosion resistance of magnesium lithium alloy, Mg-14Li alloy with different content of Ca (0, 3, 5, 10wt.%) was prepared with a induction melting furnace. Electrochemical test and corrosion test were carried out in NaCl solution with different Cl^- concentrations. The results indicate that the microstructure of the Mg-14Li alloy with Ca consists of dendritic β phase and eutectic structure ($\beta+\text{CaMg}_2$). With the increase of Ca addition from 0, to 3, 5, 10wt.%, the corrosion resistance of the Mg-14Li alloy initially increases first and then decreases, and that of alloy with 3% Ca is the best. Therefore, the corrosion resistance of Mg-14Li alloy in NaCl solution can be effectively improved by adding proper amount of Ca. In addition, the concentration of Cl^- was one of important factors affecting the corrosion resistance of the Mg-14Li alloy, and the influence of Ca was slighter than that of Cl^- .

Key words: magnesium lithium alloy; Ca; refine; electrochemistry; corrosion resistance

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As the lightest metal structure material today, Mg-Li alloy has very high specific strength, specific stiffness, vibration resistance property, high-energy particle penetration resistance and other excellent performances^[1], so it shows huge development potential in aerospace, automobile, 3C industry, communications, medical equipment and other fields. But the Mg-Li alloy is hard to melt and cast, its absolute strength is not high and the mechanical properties are not stable, and because of negative electrode potential and high chemical activity, Mg-Li alloy is easy to be corroded in the humid air, sulfur atmosphere and ocean atmosphere^[2], which seriously prevents its application. The researchers at home and abroad have done much work to refine the microstructure of Mg-Li alloy and improve its mechanical properties by adding alloying element or other means^[3-5]. However, the corrosion resistance and strength of Mg-Li alloy usually shows a negative correlation^[6], so it is necessary to study the influence of refining elements on the corrosion resistance of Mg-Li alloy, but there are only few studies at present.

Some studies showed that Ca had significant influence on refinement of grains and increase of

mechanical properties of Mg-Li alloy. The refinement mechanism of Ca on Mg-Li alloy was due to the aggregation of Ca atoms and Mg atoms in the solid-liquid interface of primary β phase at the preliminary stage of solidification, which generated constitutional supercooling layer in the front of solid-liquid interface, and prevented the grain from growing^[7-11]. However, as Ca is an active metal with electrode potential of -2.87 V , the influence of Ca addition on the corrosion resistance of Mg-Li alloy has rarely been reported so far^[12]. In addition, with different content of Li, the microstructure of Mg-Li alloy would be α , $\alpha + \beta$ or β , respectively^[13], and alloys with different microstructures would have different corrosion characteristics. LA141 (commercial standard of America of the United States) is a typical Mg-Li alloy with single β phase. Therefore, in this work, the Mg-14Li alloys with different content of Ca were prepared with an induction melting furnace, and then the influence of Ca content on the corrosion resistance of Mg-14Li alloy was studied. In order to figure out the effect of Ca, the aluminum was not added in this study. Due to the fact that Mg-Li alloy is a material with great development potential, exploring the corrosion resistance of the alloy is important to promote application of it.

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1 Experimental materials and methods

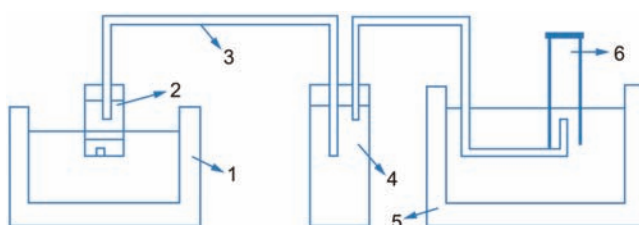
The Mg-14Li-xCa alloys were melted in an induction

melting furnace. The raw materials were pure magnesium ingot ($Mg \geq 99.95$ wt.%), pure lithium of battery grade (in fragmented, $Li \geq 99.9$ wt.%), and pure Ca (in fragmented, $Ca \geq 99.7$ wt.%). The compositions of test alloys were analysed by a high frequency plasma emission spectrometer (PLASMA2000), and the result is shown in Table 1. Since the chemical property of the alloy was very lively and the hardness was very low, the alloy were first polished in turn by sandpapers of #1000, #1500 and #2000, and then polished by velvet with the diamond grinding paste. The microstructure was observed using a Nikon ECLIPSE MA100 optical microscope after corroded for about 5–10 s by alcohol solution with 2% nitrate.

Table 1: Chemical composition of test alloys (wt.%)

Alloys	Mg	Li	Ca
Mg-14Li	85.5	14.5	
Mg-14Li-3Ca	83.3	13.4	3.3
Mg-14Li-5Ca	80.5	14.3	5.2
Mg-14Li-10Ca	76.1	14.1	9.8

Electrochemical samples were burnished by sandpaper to expose a work area of 1 cm^2 , the rest was sealed by an insulation material. The surface oxide layer of corroded samples were removed by sandpaper. The solutions of electrochemical experiments and the corrosion experiments were deionized water and NaCl solution with Cl^- contents of $0.2 \text{ mol} \cdot L^{-1}$ and $0.7 \text{ mol} \cdot L^{-1}$, respectively. Electrochemical experiments were performed on a LK2005A electrochemical workstation, using a three electrode system. The studied electrode was Mg-14Li-xCa alloys, reference electrode was saturated calomel electrode, and auxiliary electrode was platinum electrode. Due to the fact that the corrosion process of magnesium and magnesium alloy was always accompanied by hydrogen evolution, so the method of drainage gas-collecting was adopted to collect hydrogen in this work. The corrosion resistance of the samples were evaluated according to the amount of hydrogen collected, and the more the hydrogen was collected, the worse the corrosion resistance was^[14]. Schematic diagram of experiment is shown in Fig.1. Corrosion experiments were carried out at room temperature. The surface morphology of corroded samples were observed on a scanning electron microscope (SEM, HITACHI-4800), and the constituents of corrosion products was analysed using X-ray



1-constant temperature water bath, 2-reactor, 3-pipe, 4-condensing unit, 5-sink, 6-cylinder (scale accurate to 0.1 ml)

Fig. 1: Schematic diagram of corrosion test device using drainage method

diffractometer (XRD, Bruker D8 focus).

2 Experimental results and analysis

2.1 Microstructure of cast Mg-14Li-xCa alloys

Figure 2 shows the microstructures of cast Mg-14Li-xCa alloys. Figure 2(a) is the microstructure of Ca-free Mg-14Li alloy. According to the binary-phase diagram of Mg-Li alloy, it could be inferred from Fig. 2(a) that the gray irregular block matrix structure is the β phase that is a solid solution of Mg dissolved in Li, and the grain size was coarse. There were much dark punctate particles at the grain boundary, which is α phase (α phase is a solid solution of Li dissolved in Mg), and this was caused by the segregation during solidification. As shown in Fig. 2(b), after adding 3wt.% Ca, the microstructure of Mg-14Li-3Ca consisted of initial dendritic β phase and laminate eutectic structure ($\beta+CaMg_2$) distributing between dendrites β phases. The eutectic structure was bright white and evenly distributed at the boundary of β phases, and β phase was obviously finer than that in Fig. 2(a). With Ca content increasing gradually [Fig. 2(c)], the grain size of β phase decreased slightly, while the size of eutectic structure increased obviously compared with that of Mg-14Li-3Ca alloy. When the content of Ca reached 10wt.% [Fig. 2(d)], the irregular eutectic phase distributed dispersively between β phases, and the size was smaller but the amount was large.

2.2 Electrochemical property of Mg-14Li-xCa alloys

The electrode potential of Mg and Li are very low, which are -2.37 and -3.05 , respectively^[14-15], so the chemical property of Mg-Li alloy is very active, and the alloy is easily corroded in an aqueous solution. Therefore, in order to explore the corrosion performance of the Mg-Li alloys with and without Ca, it is necessary to study the electrochemical corrosion behavior of the alloy.

Figure 3 is E_{corr} of Mg-14Li-xCa alloys in three different electrolytic solutions. It can be seen that the E_{corr} of Mg-14Li-3Ca in three kinds of solutions is higher than that of Ca-free Mg-14Li alloy, which indicates the corrosion resistance of Mg-Li alloy can be improved by adding small amount of Ca. But with further increasing Ca content to 5wt.% and 10wt.%, the E_{corr} of these two alloys in three kinds of solution had a downward trend, this indicated the corrosion resistances of these alloys had been weakened. This is due to the fact that when the Ca content is high, the grains are refined, and the number of eutectic phase at the grain boundary increases, even making eutectic phase dispersively distribute, which causes the quantity of galvanic corrosion formed between second phase at the grain boundary and matrix increase, so the corrosion resistances of Mg-14Li-5Ca and Mg-14Li-10Ca alloy are weakened.

Figure 4 is the polarization curves of Mg-14Li-xCa alloys in three kinds of electrolytic solution. The anodic polarization region of curves in Fig. 4(a) became smooth gradually, which

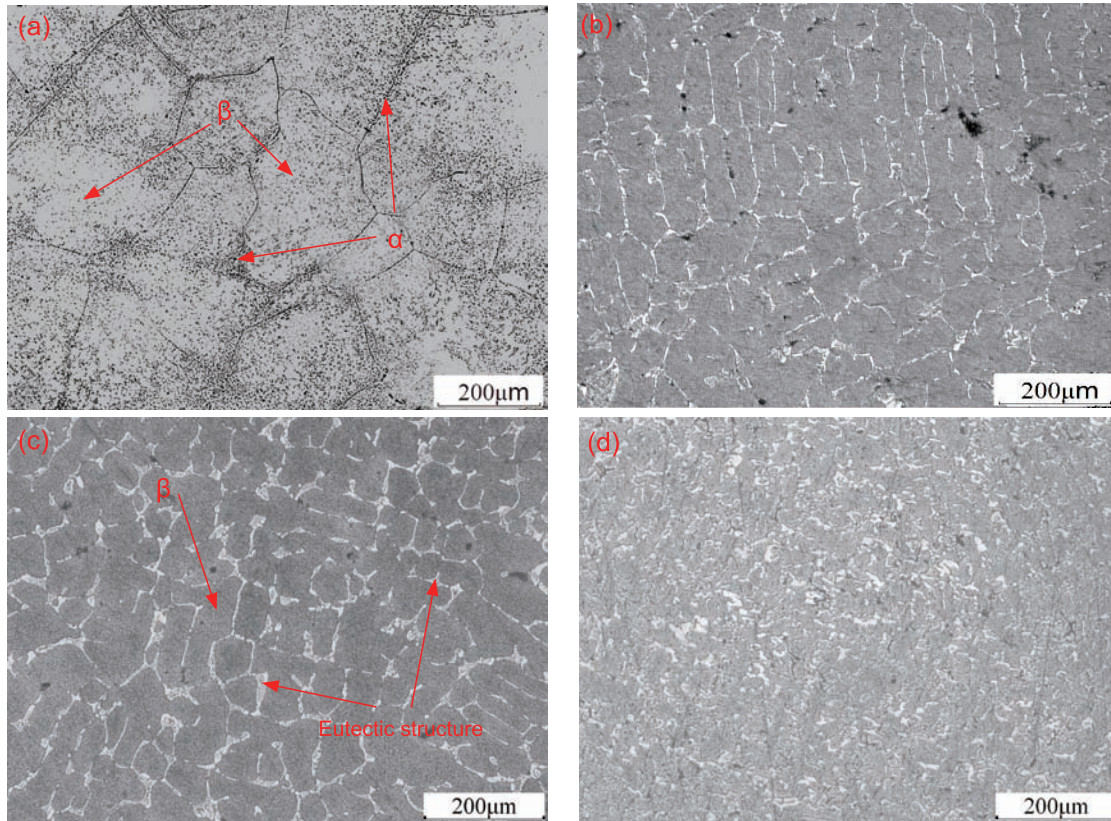


Fig. 2: Microstructure of as-cast Mg-14Li-xCa alloys: (a) $x=0$; (b) $x=3$; (c) $x=5$; (d) $x=10$

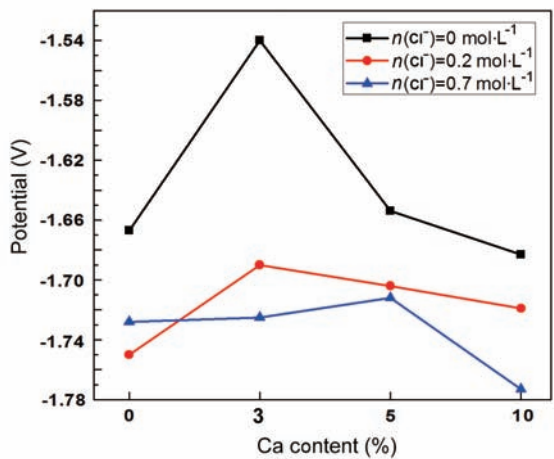


Fig. 3: E_{corr} of Mg-14Li-xCa alloys in three different concentrations of solutions

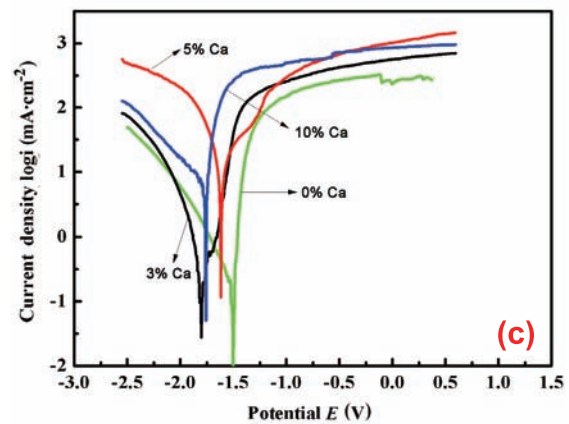
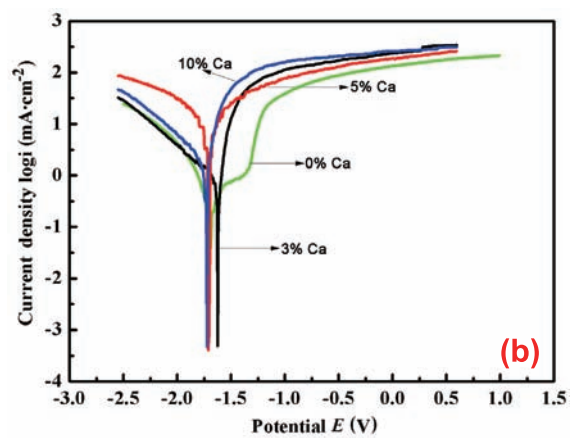
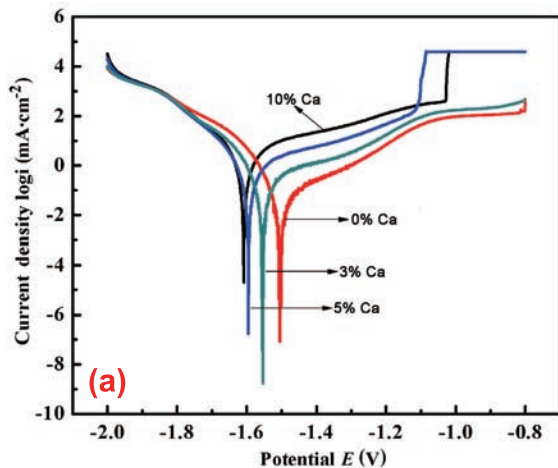


Fig. 4: Polarization curves of Mg-14Li-xCa alloys in three kinds of solutions: (a) $n(Cl^-)=0 \text{ mol}\cdot\text{L}^{-1}$; (b) $n(Cl^-)=0.2 \text{ mol}\cdot\text{L}^{-1}$; (c) $n(Cl^-)=0.7 \text{ mol}\cdot\text{L}^{-1}$

indicated passivation phenomenon occurred in the four alloys. Because electrochemical oxidation product $Mg(OH)_2$ of the electrode was attached to the electrode surface under positive oxide electrode, and as the reaction proceeded, the passive film $Mg(OH)_2$ on the sample surface was accumulated continuously, which prevented electrolyte from entering the alloy to react, so the passivation phenomenon appeared. When Cl^- was added into the solution, strong penetrability and hydration adsorption of Cl^- effectively destroyed the passive film of surface, weakening the passivation and leading to reduction of the corrosion resistance of the Mg-14Li-xCa alloys. So the E_{corr} would fall down and corrosion current density would increase with increasing Ca content and Cl^- concentration.

2.3 Corrosion resistance of Mg-14Li-xCa alloys in NaCl solution

According to the corrosion mechanism of magnesium alloys, the corrosion rate of magnesium alloys were closely related to the rate of hydrogen evolution, this was also a fundamental principle of measuring the corrosion of magnesium alloys by the way of hydrogen evolution^[16]. Figure 5 shows the influence of Ca on maximum hydrogen evolution rate of Mg-14Li-xCa alloys in three kinds of solutions with different Cl^- concentrations. As shown in Fig. 5(a), except the Mg-14Li-10Ca alloy, the reaction rate of the rest samples in the $n(Cl^-) = 0 \text{ mol}\cdot\text{L}^{-1}$ solution decreased in 10 minutes. This was because the water reacted with the element of alloy surface, generating passive film at the surface, so the corrosion rate decreased. But as shown in the Figs. 5(b) and (c), the reaction rate of four samples did not obviously decrease with the increase of Cl^- concentration. This was due to the better absorption ability of Cl^- than that of oxygen in the metal surface, so Cl^- was preferentially absorbed rather than oxygen to the metal surface, preventing the formation of passive film on the surface of alloy. However, the absorption of Cl^- was not stable, it would react with corrosion products of Mg-14Li-xCa alloys, generating soluble substances and leading to part dissolution of passive film on the alloy surface^[17], which made corrosion of Mg-14Li-xCa alloy proceed. The Cl^- concentration had little effect on the reaction rate of Mg-14Li-10Ca alloy. But with the increase of Cl^- concentration, the reaction rate of the samples with low content of Ca accelerated, and they were closed to the rate of Ca-free Mg-14Li alloy, even the reaction rate of Mg-14Li-3Ca alloy was less than that of Mg-14Li alloy in $n(Cl^-)=0.2 \text{ mol}\cdot\text{L}^{-1}$ solution. This indicated that the additional amount of Ca in a certain range would improve corrosion resistance of Mg-14Li alloy, but with the increase of Ca content further, the corrosion resistance of alloy would decrease gradually. When Ca content exceeded 5wt.%, the corrosion rate would exceed that of Ca-free Mg-14Li alloy, so the amount of hydrogen evolution increased at the same time (Fig. 6). The experiment showed that the hydrogen evolution reaction of Mg-14Li-10Ca samples finished after 70 minutes in the solution of $n(Cl^-)=0.2 \text{ mol}\cdot\text{L}^{-1}$ and $n(Cl^-)=0.7 \text{ mol}\cdot\text{L}^{-1}$. However the amount of hydrogen evolution of Mg-14Li-5Ca

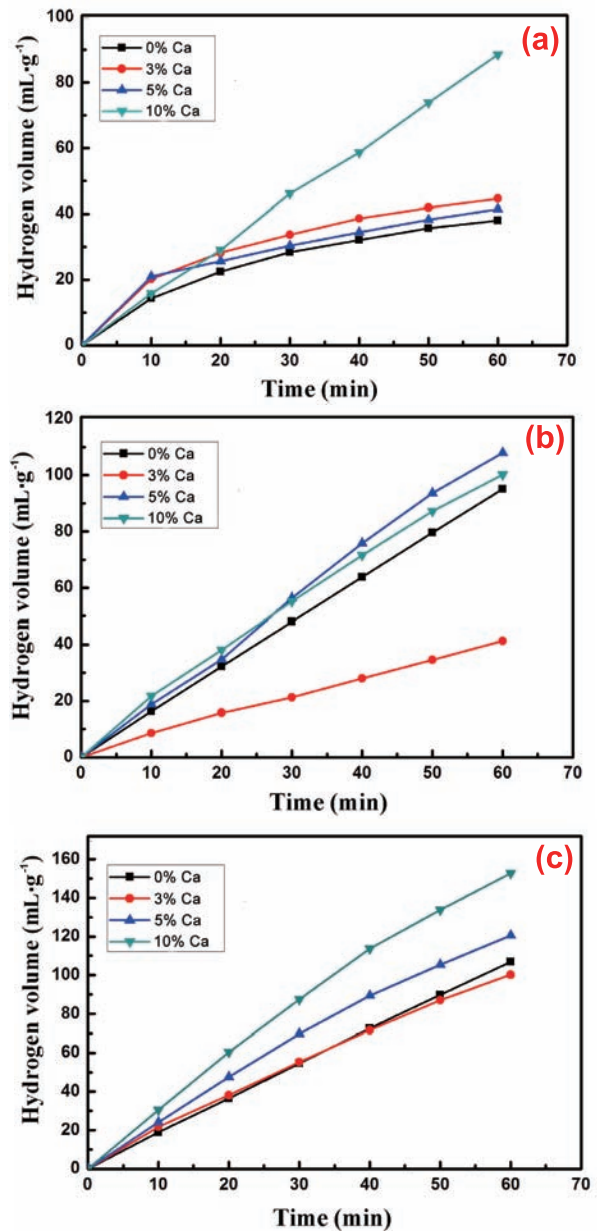


Fig. 5: Effect of different Ca content on hydrolysis hydrogen production rate of Mg-14Li alloy in three kinds of solutions: (a) $n(Cl^-)=0 \text{ mol}\cdot\text{L}^{-1}$; (b) $n(Cl^-)=0.2 \text{ mol}\cdot\text{L}^{-1}$; (c) $n(Cl^-)=0.7 \text{ mol}\cdot\text{L}^{-1}$

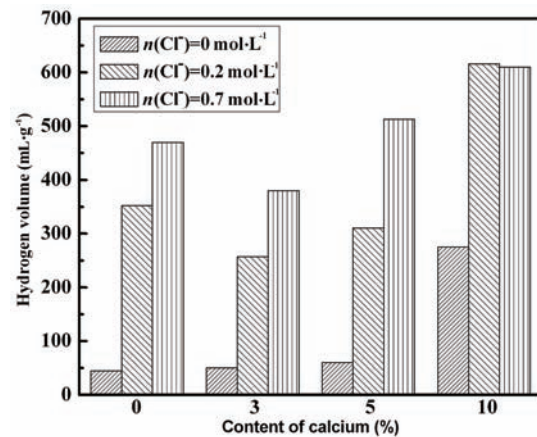


Fig. 6: Total amount of hydrolysis hydrogen production of Mg-14Li-xCa alloys

alloy and Mg-14Li-0Ca alloy in solution of $n(\text{Cl}^-)=0.7 \text{ mol}\cdot\text{L}^{-1}$ were $508 \text{ mL}\cdot\text{g}^{-1}$ and $465 \text{ mL}\cdot\text{g}^{-1}$, respectively, while the amount of hydrogen evolution of Mg-14Li-3Ca alloy was only $374 \text{ mL}\cdot\text{g}^{-1}$, which indicates Mg-14Li-3Ca alloy has the best corrosion resistance.

Figures 7–9 are the surface morphology of Mg-14Li- x Ca alloys which have been corroded in three different solutions.

As proposed in the previous study^[18], the magnesium alloy usually occurred pitting corrosion in the non oxidizing medium with Cl^- , and had a tendency of stress cracking in the solution with Cl^- or even in distilled water. It can be seen from Figs. 7 and 8 that the corrosive pitting and white corrosion products of Mg-14Li-3Ca were less than that of the rest three samples, and the corrosion products of Mg-14Li-10Ca were the most, even

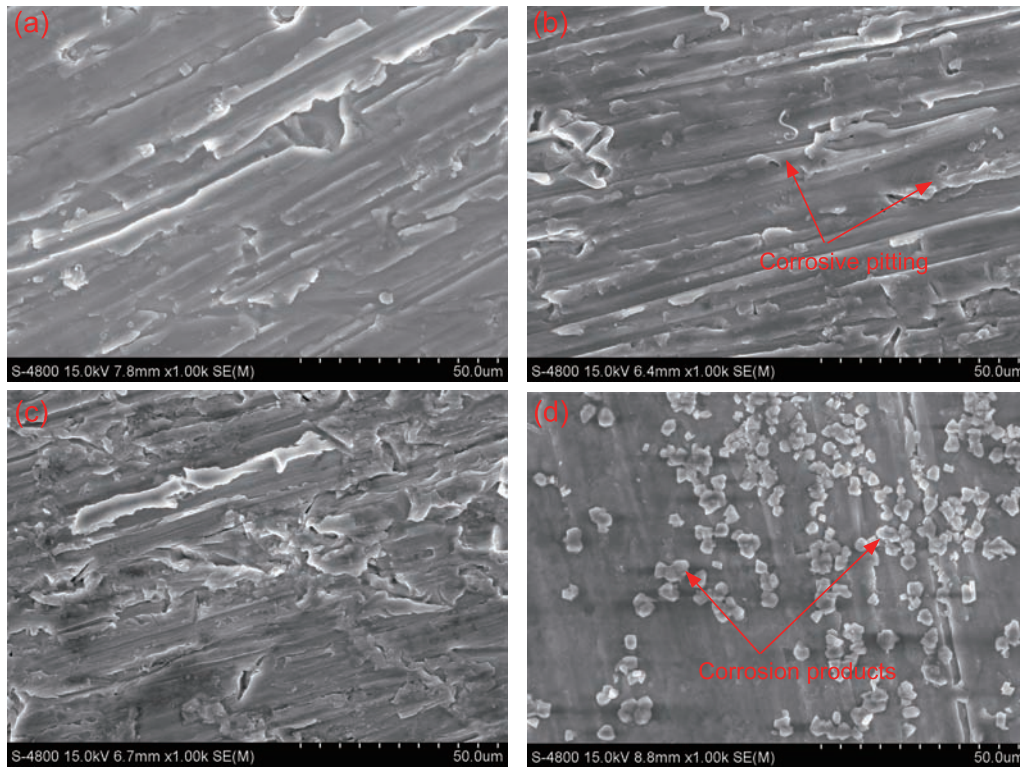


Fig. 7: SEM micrographs of Mg-14Li- x Ca alloys after corrosion in water: (a) $x=0$; (b) $x=3$; (c) $x=5$; (d) $x=10$

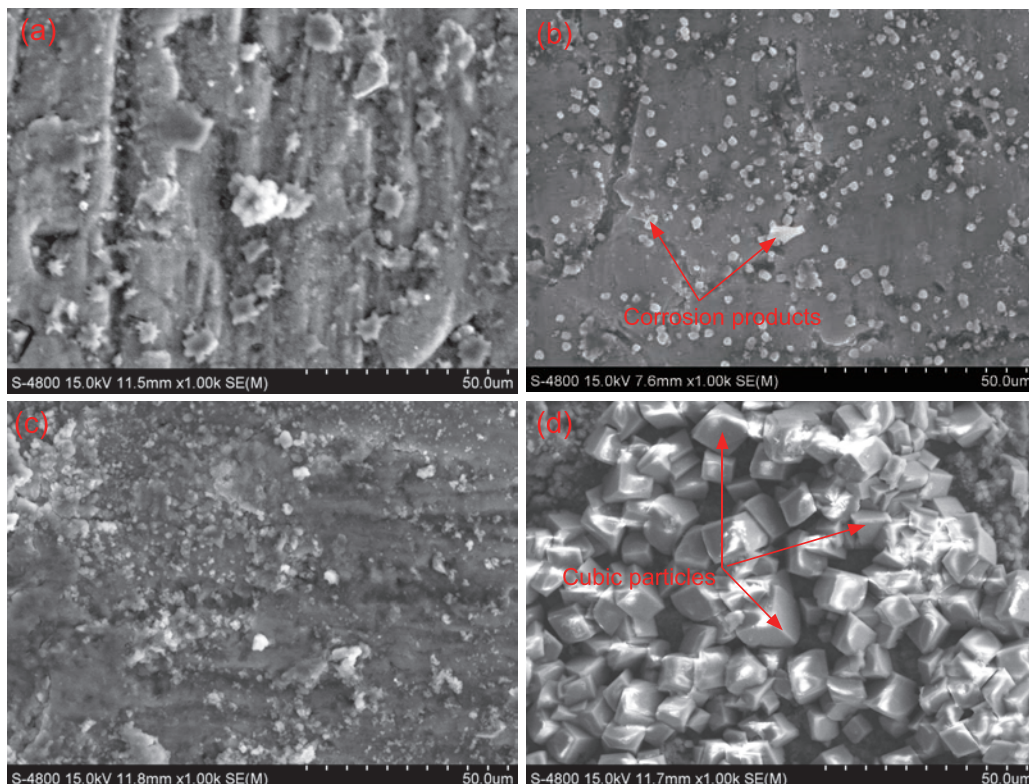


Fig. 8: SEM micrographs of Mg-14Li- x Ca alloys after corrosion in $n(\text{Cl}^-)=0.2 \text{ mol}\cdot\text{L}^{-1}$ solution: (a) $x=0$; (b) $x=3$; (c) $x=5$; (d) $x=10$

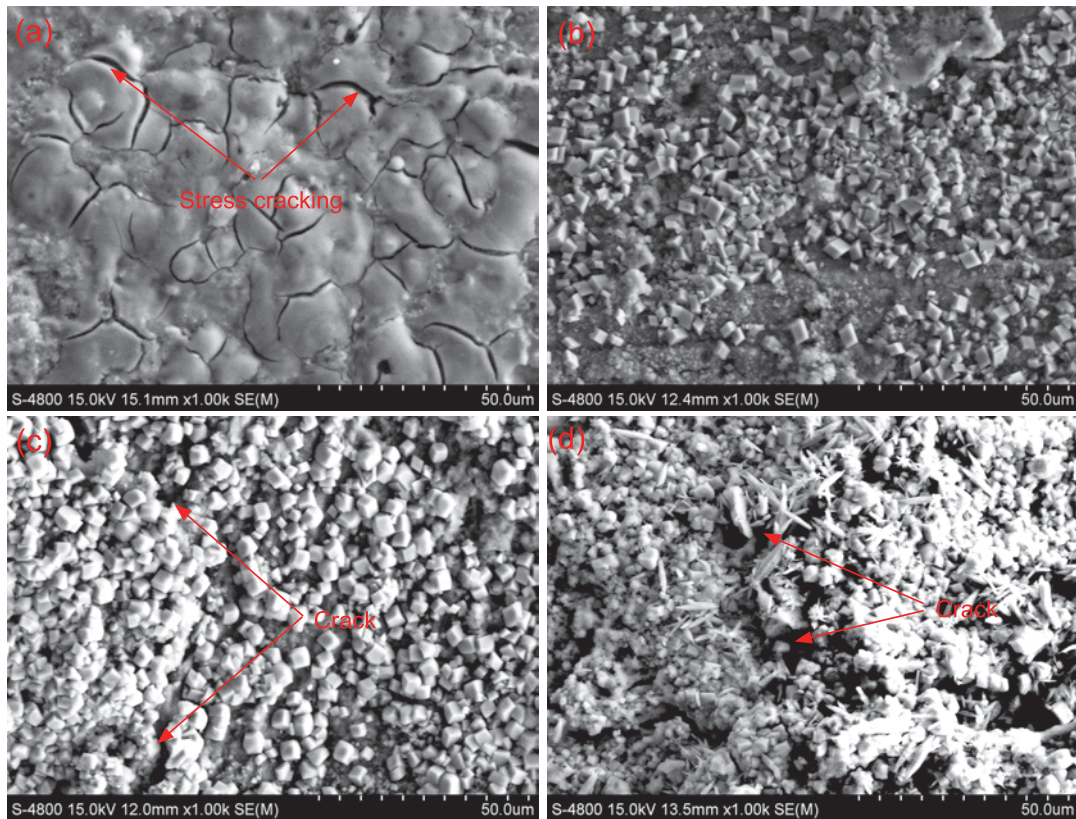
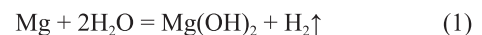


Fig. 9: SEM micrographs of Mg-14Li-xCa alloy after corrosion in $n(\text{Cl}^-)=0.7 \text{ mol}\cdot\text{L}^{-1}$ solution: (a) $x=0$; (b) $x=3$; (c) $x=5$; (d) $x=10$

the alloy was completely covered by white corrosion products in $n(\text{Cl}^-)=0.2 \text{ mol}\cdot\text{L}^{-1}$ solution. Figure 10 is XRD pattern of Mg-14Li-xCa alloy corroded in $n(\text{Cl}^-)=0.7 \text{ mol}\cdot\text{L}^{-1}$ solution. It indicates that white corrosion products were a mixture of CaCO_3 , $\text{Mg}(\text{OH})_2$ and Li_2CO_3 . When the Cl^- concentration reached $0.7 \text{ mol}\cdot\text{L}^{-1}$, the effect of Ca on the corrosion resistance of Mg-14Li alloy was less than the effect of Cl^- on the passive film of Mg-14Li alloy. In this case, with the increase of Ca content, the corrosion products and surface morphology of alloys changed greatly: severe stress cracking happened in the corrosion products which formed on the surface of alloys, causing the reaction to proceed, and there were small regular cubic particles on the surface of Mg-14Li alloy with Ca. As shown in Figs. 9(b), (c), after the metal was corroded, its surface happened serious pit corrosion and fragmentation, and the surface was covered by small regular cubic particles, even the surface morphology of Mg-14Li-5Ca was covered more seriously and there were some cracks on it, which may be caused by combine action of hydrogen evolution and stress cracking. However, as shown in Fig. 9(d), the surface of the Mg-14Li-10Ca alloy was completely covered by small regular cube particles, and its surface structure was very loose and there were more obvious cracks on it. The reason was that under the expansion force of the generation of H_2 , the cubic particles continually peeled from the alloy surface, making the base metal be exposed to the medium, which resulted in reaction to proceed. This also explained why the amount of hydrogen evolution of Mg-14Li-10Ca alloy was the largest, as

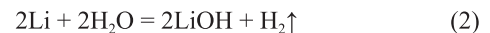
shown in Fig. 6.

Mg element in Mg-14Li-xCa alloys in above solutions would generate $\text{Mg}(\text{OH})_2$ passive film which covered the unreacted metal surface, leading to corrosion kinetics decrease and preventing corrosion reaction from proceeding^[19]. The chemical equation of reaction was as follows:

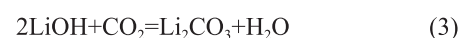


Because the Mg-14Li-xCa alloys were based on β phase, and Mg atoms were dissolved in lithium, so the corrosion product of Mg cannot generate solid passive film, hence it was hard to prevent corrosion reaction.

While, Li element in Mg-14Li-xCa alloys would react in above solution^[20], and the chemical equation of reaction was as follows:



Although LiOH formed on the surface of the alloy could prevent corrosion of alloys, it would react with CO_2 in the water, generating white and loose Li_2CO_3 , which weakened inhibition effect of LiOH on corrosion. The chemical equation of reaction was as follows:



In addition, it can be seen from Fig.10 that the phase constituents of corrosion products of Mg-14Li alloys with Ca were obviously different from that without Ca. After the Ca-containing alloys were corroded, there were new peaks of CaCO_3 phase near 23° , 30° , 40° , 43° , 47° and 49° , and the peak value rose with the increase of Ca content. It demonstrated

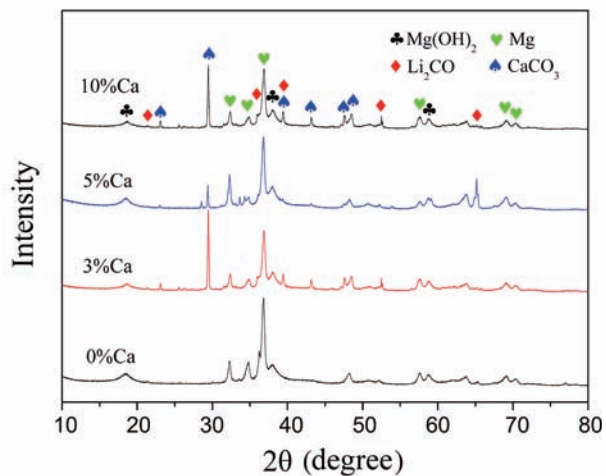


Fig. 10: XRD diagrams of Mg-14Li- x Ca alloy after corrosion: (a) $x=0$; (b) $x=3$; (c) $x=5$; (d) $x=10$

CaCO_3 content in corrosion products increased. Moreover, it can be seen from Fig.10 that the hydrolysis products of Mg-14Li alloy with Ca still contained $\text{Mg}(\text{OH})_2$ phase and Mg phase, and their peak values were similar. This illustrated the adhesion force of corrosion products CaCO_3 on the sample surface was very weak after adding Ca, and the corrosion products easily peeled off, which made the internal metal elements react, the corrosion resistance of alloys deteriorate.

3 Conclusions

(1) The microstructure of Mg-14Li alloy with Ca consisted of dendrite β phase and eutectic structure ($\beta+\text{CaMg}_2$) distributing between the dendrites β phases.

(2) The results of electrochemical tests and corrosion experiments in the NaCl solution with different Cl^- concentrations showed that, with the increase of Ca from 0 to 3wt.%, 5wt.%, 10wt.%, the corrosion resistance of Mg-14Li alloy first enhanced and then weakened; the Mg-14Li alloy containing 3wt.% Ca showed the best corrosion resistance.

(3) The Cl^- concentration was an important factor affecting the corrosion resistance of Mg-14Li alloys. With the increase of Cl^- concentration, the corrosion resistance of the alloys decreased, and the influence of Ca on the corrosion resistance of Mg-14Li alloy was less than that of Cl^- concentration.

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