

## Article

# Developing Improved Mechanical Property and Corrosion Resistance of Mg-9Li Alloy via Solid-Solution Treatment

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**Abstract:** Cast Mg-9Li alloy was successfully solid-solution (SS) treated via heating at 575 °C for 4.5 h and rapidly quenched with ice-water mixture. The mechanical property and corrosion resistance of the SS alloy were simultaneously improved. Rapid bcc/hcp phase transition of the alloy occurred during the quenching process, creating the newly precipitated needle-like fine  $\alpha$ -Mg phase, uniformly distributed in the  $\beta$ -Li phase matrix. Dramatic grain refinement and uniform distribution of the  $\alpha$ -Mg phase, as well as the massively increased  $\alpha/\beta$  phase interfaces, are factors leading to the improved mechanical property of the SS alloy. Meanwhile, due to the modified duplex-phase structure, the SS alloy has a uniform corrosion-resistant surface film on the  $\beta$ -Li phase, which completely covers the entire alloy surface and efficiently protects the substrate. In addition, the SS alloy has fewer difference in the elements concentration and corrosion activity of the duplex phases, which reduces the pitting sensitivity and improves the corrosion resistance of the alloy matrix. The findings in this binary Mg-Li alloy can also serve as a benchmark for other more practical and complicated Mg-Li alloys.

**Keywords:** Mg-9Li alloy; solid-solution treatment; modified duplex phase; mechanical property; corrosion resistance

## 1. Introduction

Magnesium-lithium (Mg-Li) alloys are the lightest structural metallic materials with a density of about 1.35–1.65 g·cm<sup>-3</sup> and are usually regarded as ultra-light alloys [1]. Due to the obvious advantages, including extremely low density, high specific strength, and stiffness, Mg-Li alloys have broad application prospects in the industrial fields, such as aerospace, automobile, and transportation [2,3]. Li does not only reduce the density of Mg alloys, but also changes the phase structure and the mechanical properties of alloys with a different Li content [4,5]. A small amount of Li reduces the activation barrier for the prismatic slip, leading to the synchronization of this slip with the basal slip at room temperature, which improves the room-temperature ductility and deformation ability of hexagonal close-packed (hcp) Mg matrix [6]. When the Li content increases by 5.7 wt.%, the hcp-structured Mg matrix will be partially transformed into a Li-rich phase with a body-centered cubic (bcc) structure, creating the duplex phase structure of Mg-Li alloy with a hcp Mg-enriched  $\alpha$  phase (can be usually named as  $\alpha$ -Mg phase briefly) and bcc Li-enriched  $\beta$  phase (can be usually named as  $\beta$ -Li phase briefly). At this point, the ductility of the Mg-Li duplex alloys will be greatly enhanced due to the various slip systems of the

bcc  $\beta$ -Li phase [7]. However, the alloys' strength will be negatively influenced by the formation of soft  $\beta$ -Li phase. As the Li content further increases by 11 wt.%, the Mg-Li alloy will transfer into the single  $\beta$ -Li phase with better ductility but less strength.

Duplex-phase Mg-Li alloys have been studied extensively among all the Mg-Li alloy series due to their outstanding comprehensive mechanical properties. However, their insufficient absolute strength still needs to be further improved [8,9]. Recent researches of Mg-Li alloys propose that alloying is a good choice to improve the mechanical property, such as alloying with Al, Zn, Y, RE, etc. [10–13]. Via proper alloying, the Mg-Li-x alloys can be further strengthened by grain-boundary strengthening with fine grains [14], dispersion strengthening with composited hard particles [15], and solid solution and aging strengthening via heat treatment [16,17]. However, alloying of the Mg-Li alloys will inevitably sacrifice the advantage of low density. Therefore, it is of great importance to improve the mechanical properties of binary Mg-Li alloys and achieve high service performance without any increase in density. Solid-solution (SS) treatment may be the potential way to improve the mechanical property of the binary Mg-Li alloys. According to the Mg-Li binary phase diagram (see Figure 1), only the duplex-phase binary Mg-Li alloys have the opportunity to drastically change the microstructure of both  $\alpha$ -Mg phase and  $\beta$ -Li phase via the phase transition during the solid solution and quenching process [18]. Furthermore, the potential types of duplex-phase binary Mg-Li alloys are limited, only the alloys with a Li content from about 15 at.% to 17.8 at.%, and 24.5 at.% to 30 at.%, have the opportunity. In addition, the temperature range available for SS treatment of the duplex-phase Mg-Li alloy is also very limited, especially for the lower-density Mg-Li binary alloys with sufficient Li content, such as Mg-9 wt.% Li alloy (with a Li content of 25.7 at.%, usually named the Mg-9Li alloy). To those alloys, the SS treatment can only be conducted at a high temperature nearing melting-point temperature, which brings the potential risk of high-temperature oxidation and burnout due to the high chemical activity of Mg and Li atoms. Therefore, it will be a meaningful attempt to efficiently change the microstructure and improve the mechanical property of the binary Mg-Li alloys via SS treatment. As reported by M.V. Kral [19], the finer  $\alpha$ -Mg phase will be newly precipitated via the phase transition during the quenching process, presenting the composited phase structure with the needle-like finer  $\alpha$ -Mg phase, residual coarse  $\alpha$ -Mg phase, and  $\beta$ -Li phase matrix of the Mg-8 wt.% Li alloy after SS treatment. With the greatly refined  $\alpha$ -Mg phase, the SS-treated Mg-8 wt.% Li alloy may have an improved mechanical property due to the grain-boundary strengthening with a finer  $\alpha$ -Mg phase grains and the increased  $\alpha$ -Mg/ $\beta$ -Li phase interface.

Low corrosion resistance and excessively fast corrosion rate is another factor restricting the wide application of Mg alloys. Generally believed, Mg and Mg alloys present a low corrosion resistance in the environment due to the low electrode potential and strong corrosion activity. Meanwhile, the low protective efficiency of the surface film, cathodic hydrogen evolution, and negative difference effect are other key factors to the low corrosion resistance of the Mg alloys [20–22]. Li is a more active metallic element than Mg, it is supposed to weaken the corrosion resistance of Mg matrix via adding Li element [23–26]. However, recent studies reported that the Li-enriched  $\beta$  phase will benefit the formation of a protective surface film and improve the corrosion resistance of the alloy [27,28]. Thus, one can infer that the microstructure characteristic of the duplex phases can greatly influence the corrosion behavior and corrosion resistance of Mg-Li alloys. As mentioned above, the SS treatment has the opportunity to change the duplex-phase structure properly. Therefore, the improved corrosion resistance of the duplex-phase Mg-Li alloy after SS treatment can be expected.

In this study, the cast Mg-9Li duplex-phase alloy was SS treated via an optimized processing parameter, creating the greatly modified duplex-phase structure of the alloy. The SS-treatment simultaneously improves the mechanical property and corrosion resistance of the Mg-9Li alloy. The strengthening mechanism and corrosion-resistance enhancement mechanism of the SS-treated Mg-9Li alloy were systematically investigated.

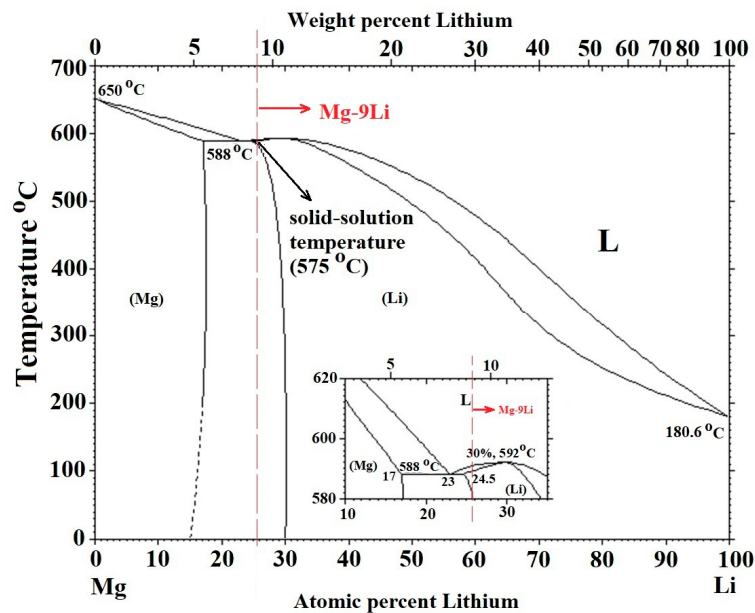


Figure 1. Binary phase diagram of the Mg-Li alloy [18].

## 2. Experimental

### 2.1. Solid-Solution Treatment

A commercial cast Mg-9Li alloy was selected as the target raw material. The chemical composition of the cast alloy was examined by an optical emission spectrometer (GNR S3, Milan, Italy), as listed in Table 1. Figure 1 is the binary phase diagram of the Mg-Li alloy [18]. As marked by the dash line, the Mg-9Li alloy has the duplex phase in most temperature ranges below its melting point (589 °C). Theoretically, the alloy can be SS treated into a single  $\beta$ -Li phase in a very narrow temperature range (from a minimum temperature of 580 °C to a maximum temperature of 589 °C). In fact, due to the influence of inclusion elements, the actual melting point temperature and SS temperature of the Mg-9Li alloy may be lower than the corresponding theoretical temperatures. In order to avoid high-temperature burnout and ensure sufficient SS efficiency, the heating temperatures of the preliminary SS treatment of the alloy were set to 570 °C, 575 °C, and 580 °C, and the heating time were set from 3 to 6 h with an interval of 0.5 h. A total of 6 bulk alloy samples with an individual size of 20 × 20 × 40 mm were simultaneously heated via a KSL-1000 electric furnace (MTI, Hefei, China) with a heating accuracy of  $\pm 1$  °C. In view of the intensive chemical activity of Li and Mg elements, the samples were closely covered by graphite powder and continuously protected by argon gas during the whole heating process. After the heating process, the alloy samples were quenched quickly. In order to achieve a sufficient cooling rate, the ice-water mixture was used as the quenching medium and the samples were mechanically stirred during the quenching process. Based on the preliminary experiments, the optimized SS treatment of the Mg-9Li alloy was conducted via the heating at 575 °C for 4.5 h. Under those process parameters, the satisfactory SS-treated Mg-9Li alloy sample can be achieved with a minimum surface burnout and most uniform microstructure. It is noteworthy that the SS-treated alloys presented a certain ratio of residual coarse  $\alpha$ -Mg phase after heating at a low temperature (570 °C) and less time due to the lower SS efficiency. Meanwhile, the alloys bore the high risk of burnout via a higher heating temperature (580 °C) and longer heating time under current equipment. After SS treatment, the alloy samples were mechanically grinded to remove the partially oxidized surface, showing the metallic luster. Herein, the SS-treated Mg-9Li alloy was named as a SS alloy briefly, and the original cast Mg-9Li alloy was named as a cast alloy.

**Table 1.** Chemical composition of Mg-9Li alloy (mass fraction %).

| Mg      | Li    | Zn    | Si    | Ce    | Fe    | Mn    |
|---------|-------|-------|-------|-------|-------|-------|
| Balance | 8.809 | 0.014 | 0.012 | 0.011 | 0.010 | 0.024 |

## 2.2. Microstructure Characterization

Scanning electron microscopy (SEM, FEI Quanta 3D FEG, Hillsboro, OR, USA) was conducted to observe the microstructure of both cast and SS alloys. Before SEM observation, samples were gradually grinded by the abrasive papers and mechanically polished using alumina powder (with 0.05  $\mu\text{m}$  particle size) contained suspension. The polished samples were etched with a solution mixture of 4.3 mL of picric acid, 95 mL of ethanol, and 0.7 mL of phosphoric acid. Phase analysis was conducted by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K1 radiation. The  $\theta$ -2 $\theta$  diffraction patterns were scanned from 10° to 90° with a scanning rate of 5°·min<sup>-1</sup>.

## 2.3. Mechanical Test

The mechanical property of the alloys was evaluated using the uniaxial tensile test at room temperature via a UTM4204X electronic tensile machine (Suns, Shenzhen, China) with a strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$ . The bone-shaped samples with a gauge dimension of 6 × 2 × 2 mm were used and five parallel samples were tested to obtain the average values of the mechanical property. After the tensile test, the fracture morphologies were observed by SEM (FEI Quanta 3D FEG, Hillsboro, OH, USA).

## 2.4. Corrosion Test

Electrochemical tests were conducted via a CHI660E (Huacheng, Shanghai, China) electrochemical workstation with a three-electrode cell, including the saturated calomel potassium chloride reference electrode, Pt auxiliary electrode, and working electrode with an exposure of 1 cm<sup>2</sup> of the tested sample. Samples were connected with a copper wire, mounted by an epoxy resin and mechanically polished before the electrochemical tests. The open circuit potential (OCP) test, potentio-dynamic polarization (PDP) test, and electrochemical impedance spectroscopy (EIS) test were systematically conducted in 0.1 mol/L NaCl aqueous solution. The OCP test was executed immediately after the sample was immersed into the electrolyte. The PDP test was performed at a scan rate of 1 mV·s<sup>-1</sup>. The frequency range of the EIS test was from 10 kHz to 10 mHz, and the applied amplitude of sinusoidal potential was 5 mV. At least five parallel samples for each kind of testing method were tested to get the average values of the electrochemical parameters. Hydrogen evolution test is the most intuitive method for evaluating the corrosion rate and corrosion resistance of Mg alloys [29]. The hydrogen evolution immersion test of both Cast and SS alloys were conducted in 0.1 mol/L NaCl aqueous solution at room temperature. Samples were prepared according to the same standard to that of the electrochemical test, but copper wires were not used here. A home-made device was used to collect the hydrogen. Cast and SS alloy samples were tested individually, and three parallel samples of each kind of alloy were simultaneously placed in one device for testing. The top-view corrosion morphologies of the hydrogen-evolution tested samples were observed via a digital microscope (Hirox, KH-7700, Hackensack, NJ, USA), and the cross-sectional view corrosion morphologies were observed via SEM (Coxem, EM-30 plus, Daejeon, Korea).

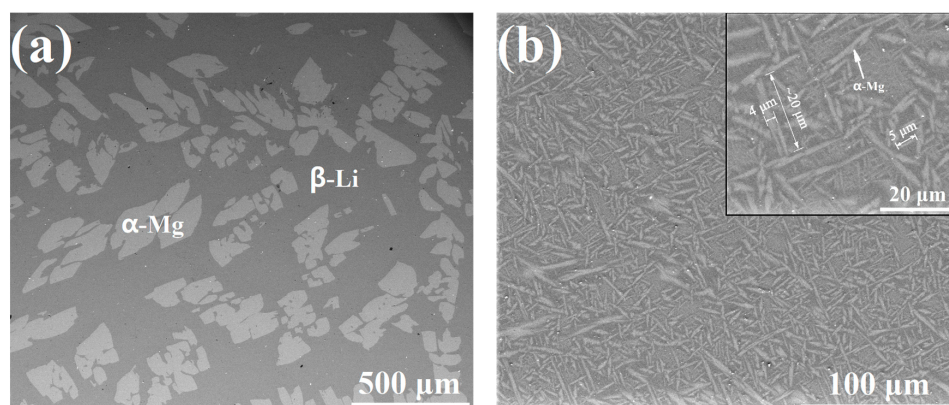
# 3. Result and Discussion

## 3.1. Microstructure Characteristic

Figure 2 is the SEM microstructure of the Mg-9Li alloy before and after SS treatment. As seen in Figure 2a, the cast alloy presents the typical duplex-phase structure, including the bright lath phase and dark matrix phase. As has been widely reported [30,31], the lath phase in the Mg-Li

duplex alloy is the Mg-enriched  $\alpha$  phase (Mg-Li solid-solution phase) with a hcp structure, which is usually named as  $\alpha$ -Mg phase briefly. The matrix phase of the Mg-Li duplex alloy is the Li-enriched  $\beta$  phase (Li-Mg solid-solution phase) with a bcc structure and is usually named as  $\beta$ -Li phase briefly. As reported by M.V. Kral and his collaborators [19], due to the intensive chemical activity of Li and Mg elements, the rapid bcc/hcp phase transition will occur to the single Li-Mg solid-solution phase (the high-temperature achieved phase during the heating process) during the quenching process, creating the newly precipitated needle-like  $\alpha$ -Mg phase. In our study, the ice-water mixture was used as the quenching medium to improve the cooling rate. However, the decomposition of supersaturated solid solution and the phase-transition induced precipitation of new  $\alpha$ -Mg phase was not stopped during the quenching. Figure 2b is the SEM microstructure of the as-quenched Mg-9Li alloy after SS treatment. Clearly, the phase morphologies were greatly modified, especially the  $\alpha$ -Mg phase. The original coarse lath  $\alpha$ -Mg phase has been completely changed into needle-like, fine  $\alpha$ -Mg phase, no original coarse  $\alpha$ -Mg phase was retained in the SS alloy. This phenomenon is obvious different to the SS-treated Mg-8Li alloy reported by M.V. Kral [19], which still contained a certain ration of residual coarse  $\alpha$ -Mg phase. A great difference can be properly explained by the binary phase diagram of Mg-Li alloy, and the difference also indicates the satisfactory SS treatment efficiency of the Mg-9Li alloy. The magnified image in the right-up corner of the Figure 2b shows that the  $\alpha$ -Mg phase has the crisscross feature and varying sizes. The large ones have sizes of 10~20  $\mu\text{m}$  in length and 3~5  $\mu\text{m}$  in width, while the smaller ones have sizes of about 5  $\mu\text{m}$  in length and 1  $\mu\text{m}$  in width.

Decomposition of supersaturated solid solutions is a very important process occurring upon SS-treated materials, which greatly changes the microstructure and properties of the alloy. Generally believed, precipitation at grain boundaries is easier than in the bulk due to the reduction of grain-boundary area, and thus grain-boundary energy favors nucleation [32]. Recent researches reported that the phase transition of SS-treated alloy can be greatly influenced by the so-called complete and incomplete wetting of grain boundaries by the second solid phase [33], and the wetting of grain boundaries can be apparently complete in case of a high amount of wetting phase [34]. Thus, the morphology and distribution of the secondary phase at the grain boundary (GB) of the matrix phase will be greatly influenced by the grain boundary wetting [35,36]. Differently in the SS Mg-9Li alloy of this study, the newly obtained fine  $\alpha$ -Mg phase uniformly distributes in the  $\beta$ -Li phase matrix. Note that, as seen in Figure 2b, most of the new fine  $\alpha$ -Mg phase was precipitated in side of the of  $\beta$ -Li phase grains. This phenomenon may be explained by the combined effect of the two factors, including the rapid precipitation due to the intensive activity of Li atoms, and the limitation to the long-rang diffusion of the atoms due to the fast cooling rate of quenching.



**Figure 2.** SEM microstructure of the Mg-9Li alloys. (a) Cast alloy; (b) solid-solution (SS) alloy.

Figure 3 is the XRD patterns of the cast and SS Mg-9Li alloys. As marked in the patterns, the typical Mg peaks and Li peaks were detected in both the cast and SS alloys. Compared to the standard peaks, all the diffraction peaks of both  $\alpha$ -Mg phase and  $\beta$ -Li phase occur slightly shifted due to

their solid solution atoms. Another phenomenon to be emphasized is that the  $\alpha$ -Mg phase peaks were strengthened while the  $\beta$ -Li phase peaks are weakened after SS treatment. Clearly, the (0002) basal plane,  $(10\bar{1}0)$  prismatic plane,  $10\bar{1}2$  and  $(11\bar{2}2)$  pyramidal planes of the  $\alpha$ -Mg phase were all strengthened. Meanwhile,  $\beta$ -Li phase peaks were significantly weakened and their (211) and (220) planes even disappear. As revealed in the SEM microstructure of Figure 2, the  $\beta$ -Li phase matrix of the SS alloy was been uniformly covered by the small needle-like  $\alpha$ -Mg phase. One can deduce that the strengthening in  $\alpha$ -Mg phase peak intensity and weakening in  $\beta$ -Li phase peak intensity may be induced by the improved coverage of the  $\alpha$ -Mg phase on the  $\beta$ -Li phase matrix after SS treatment, which weakened the signal from the  $\beta$ -Li phase matrix. Another feature of the XRD pattern of the SS alloy that needs to be noted is the small protrusion on the left side of the  $(0002)_\alpha$  plane peak (as marked by the blue arrow). Hsu et al. considered this phenomenon was caused by the formation of a spin structure during the quenching process, which is believed to have a certain positive influence in improving the strength and hardness of the material [37,38].

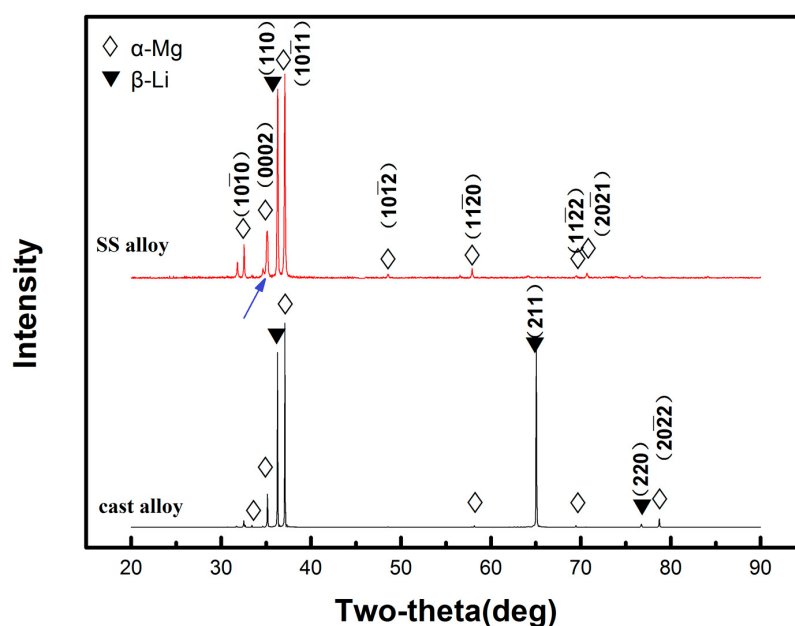


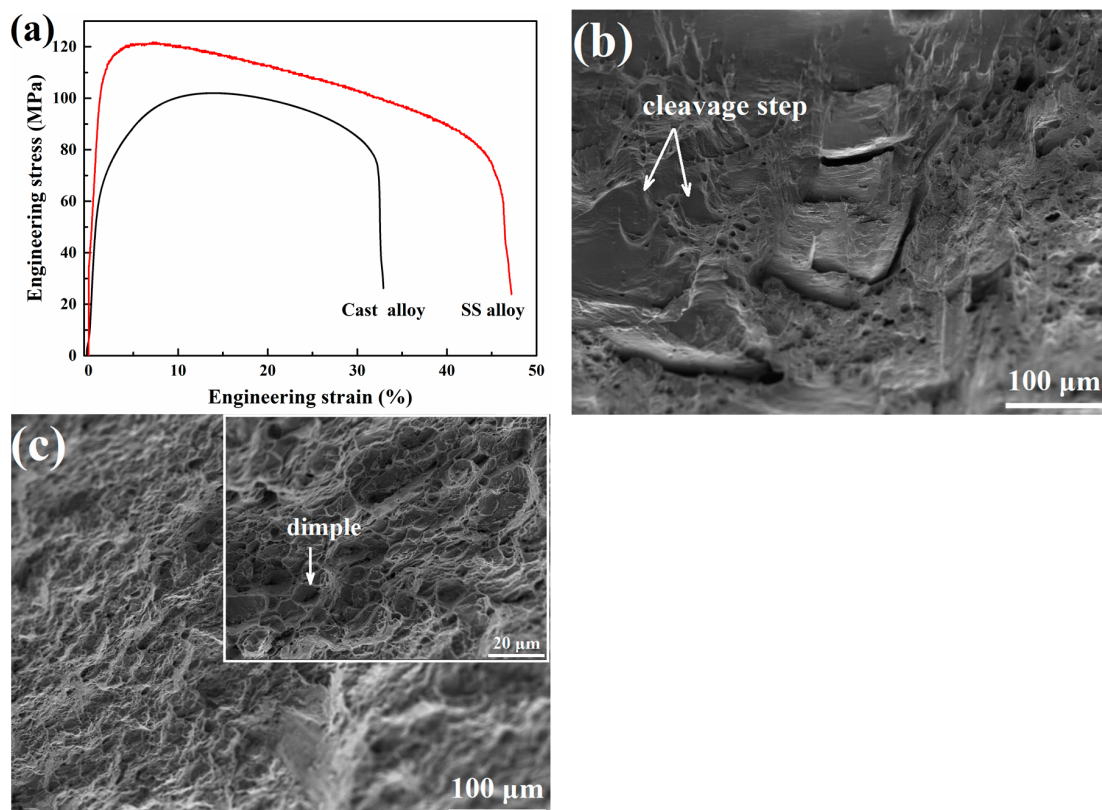
Figure 3. XRD patterns of the cast and SS Mg-9Li alloys.

### 3.2. Mechanical Property and Strengthening Mechanism

The mechanical property of the Mg-9Li alloy before and after SS treatment was evaluated by uniaxial tensile test at room temperature. Figure 4a presents the engineering tensile strain-stress curves of the cast and SS alloys, and the related tensile mechanical parameters are summarized in Table 2. Clearly, an obvious improvement was achieved in both the strength and ductility of the Mg-9Li alloy after SS treatment. The yield tensile strength (YTS) was elevated from about 62 MPa to 110 MPa, and about 45% improvement in YTS was achieved. Meanwhile, the ultimate tensile strength (UTS) was also improved from about 100 MPa to 120 MPa. The evolution of elongation seems to be complicated. The elongation to failure ( $E_f$ ) was greatly increased from about 32% of the cast alloy to 45% of the SS alloy. However, the uniform elongation ( $E_u$ ) of the alloy was decreased from about 14% to 6% after SS treatment. The improved mechanical property of the alloy was dominated by the dramatic alternation of the microstructure, especially the size, morphologies, and distribution of the  $\alpha$ -Mg phase. Generally believed, grain refinement is an important approach to improve both the strength and ductility of a metallic material. As validated by the SEM microstructure, the  $\alpha$ -Mg phase has been dramatically refined after SS treatment. Hence, grain boundary strengthening is obvious in the  $\alpha$ -Mg phase of the SS alloy, and its contribution can be expressed based on the well-known Hall–Petch equation [39,40]:  $\sigma_y = \sigma_0 + kd^{-1/2}$ . The improved strength of the SS alloy may also have benefited from

the solid-solution strengthening in the  $\beta$ -Li phase. Although the  $\alpha$ -Mg phase immediately precipitated during the quenching process, an increased content of Mg atoms were dissolved and kept in the  $\beta$ -Li phase matrix due to the rapid cooling process and insufficient atomic diffusion, leading to the higher lattice distortion and increased strength of  $\beta$ -Li phase matrix. Recent studies reported that phase interface plays a positive influence on the strength and ductility of the metallic materials [41–45]. In this study, a massively increased  $\alpha/\beta$  phase interface was created due to the dramatic refinement of  $\alpha$ -Mg phase, which is believed to have a positive influence on the enhanced strength and ductility of the SS Mg-9Li alloy.

Grain refinement can greatly enhance the ductility of Mg alloys by reducing the plastic anisotropy. Plasticity of HCP-structured metals like Mg is limited due to insufficient slip systems to accommodate the global strain [46,47]. Such anisotropy can be alleviated in fine grains by narrowing the gap of critical resolved shear stress for enhanced coordinated deformation [48]. High elongation to failure has been evidenced in other fine/ultra-fine grained Mg alloys [49,50]. In the SS Mg-9Li alloy, the needle-like fine  $\alpha$ -Mg phase with fine grains has been achieved. The width of the  $\alpha$ -Mg phase is even finer, which has been refined into 1–5  $\mu\text{m}$ . Based on the above analysis, one can believe that the enhanced  $E_f$  value of the SS alloy should be directly benefited from the dramatic refinement in the  $\alpha$ -Mg phase. Different to the elongation to failure, the uniform elongation of the SS alloy was reduced compared to that of the cast alloy. As reported by the reference [51], the dislocation storage capability of the fine grains was obviously less than that of the coarse grains, leading to the reduced work-hardening efficiency and more obvious necking effect during the tensile deformation. Thus, the SS alloy presented a less uniform elongation compared to the cast alloy.



**Figure 4.** Engineering tensile strain-stress curves of Mg-9Li alloys (a) and SEM fracture morphologies of the cast alloy (b) and SS alloy (c).

**Table 2.** Tensile data before and after solution treatment of Mg-9Li alloys.

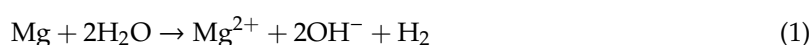
| Samples    | YTS (MPa)       | UTS (MPa)       | $E_u$ (%)      | $E_f$ (%)      |
|------------|-----------------|-----------------|----------------|----------------|
| Cast alloy | $62.0 \pm 5.1$  | $100.2 \pm 5.0$ | $14.3 \pm 1.0$ | $32.0 \pm 4.2$ |
| SS alloy   | $110.2 \pm 5.2$ | $120.3 \pm 5.5$ | $6.2 \pm 0.5$  | $45.5 \pm 5.0$ |

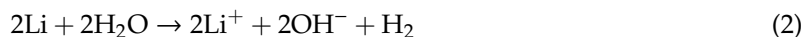
Figure 4b,c are the SEM fracture morphologies of the cast and SS alloys. A significant difference can be easily identified between those two alloys. The fracture of the cast alloy is dominated by the typical cleavage steps. Meanwhile, some of the holes and dimples can also be found in this alloy. Comparatively, the fracture of the SS alloy is mainly composed of small dimples with a size of about 5  $\mu\text{m}$ , which indicates the better ductility of the SS alloy. Generally believed, in the duplex structure of the Mg-9Li alloy, the bcc  $\beta$ -Li phase has a better plastic-deformation ability due to the sufficient slip systems, while the hcp  $\alpha$ -Mg phase has a limited plastic-deformation ability due to its insufficient slip systems [52]. In the tensile plastic deformation process, once the micro-cracks have initiated in the  $\alpha$ -Mg phase, they can only expand along the specific crystal planes under tensile stress due to the limited slip systems. In addition, the non-uniformly distributed coarse  $\alpha$ -Mg phase could also increase the resistance to micro-crack propagation [53]. In combination with the above two factors, a large number of cleavage planes formed in the  $\alpha$ -Mg phase of the cast alloy. During the formation process of cleavage plane, the cleavage plane also encountered the screw dislocations and edge dislocations, leading to the occurrence of cleavage offset. In this situation, a Burgers-vector step formed at the head of the crack, so that the crack returned and further expanded along the original cleavage plane. Repeating the above process produced a cleavage step as shown in Figure 4b. Based on the above analysis, it can be deduced that the typical cleavage steps of the cast alloy should be located at the coarse  $\alpha$ -Mg phase.

Besides the cleavage, micro-holes were also a typical fracture feature of the cast Mg-9Li alloy. According to reference [54,55], the dislocations preferentially accumulate on the  $\alpha$ -Mg grain boundaries. With the increase in tensile stress, the dislocation-induced internal stress was greater than the grain-boundary strength, creating the micro-holes at the place where dislocations accumulated. Due to the existence of the bcc structure of the  $\beta$ -Li phase, the work hardening rate of the Mg-9Li alloy was insufficient, resulting in the extremely limited dislocation density of the matrix around the micro-hole. With the continuation of the tensile stress, the micro-hole expanded and connected, leading to the initiation and propagation of the micro cracks, finally promoting the plastic deformation until necking and fracture occurred. Different to the cast alloy, the coarse  $\alpha$ -Mg phase was modified into the needle-like fine  $\alpha$ -Mg phase in the SS alloy, which was uniformly distributed in the  $\beta$ -Li phase matrix. The great refinement of the  $\alpha$ -Mg phase dramatically benefited the nucleation of the small and uniform dimples and finally reduced the possibility of fractures in a cleavage manner. Thus, one can judge that the great change in the fracture feature of the Mg-9Li alloy after SS treatment was dominated by the newly precipitated fine  $\alpha$ -Mg phase.

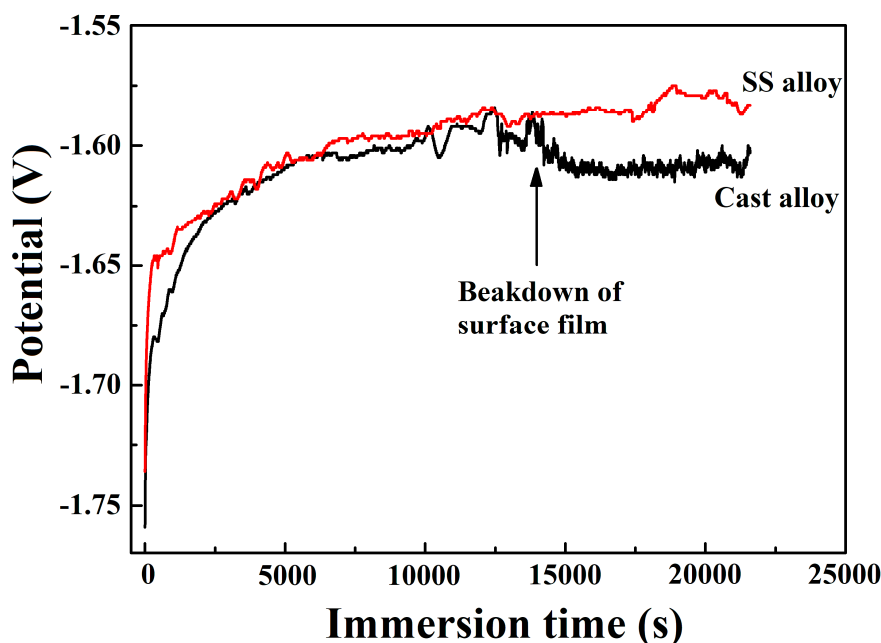
### 3.3. Corrosion Behavior and Corrosion-Resistance Enhancement Mechanism

The OCP test was continuously conducted to investigate the formation and breakdown of the surface film of the Mg-9Li alloy during the initial constant immersion in the NaCl solution. Figure 5 is the OCP curves of the cast and SS Mg-9Li alloys obtained via immersion in the 0.1 mol/L NaCl solution for about 6 h. Both samples presented two stages in the OCP curves, including the rapid increasing stage and the following slow increasing stage. Generally believed, the increase of the OCP value of the Mg alloys during the initial immersion period in the water solution was induced by the formation of magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) surface film according to the chemical-reaction in Equation (1). For the Mg-Li alloys, the Li element reacted with water according to the chemical reaction Equation (2), and their surface film was mainly composed of both the  $\text{Mg}(\text{OH})_2$  and LiOH [25].





The obvious difference is that there was a sudden decrease in OCP value of the cast alloy after immersion for about 4 h, which should be induced by the localized breakdown of the surface film due to the aggression of chloride ions [56,57]. Meanwhile, the SS alloy kept a continuous slow increase in OCP value during the whole tested immersion period, indicating the superior stability of the surface film.

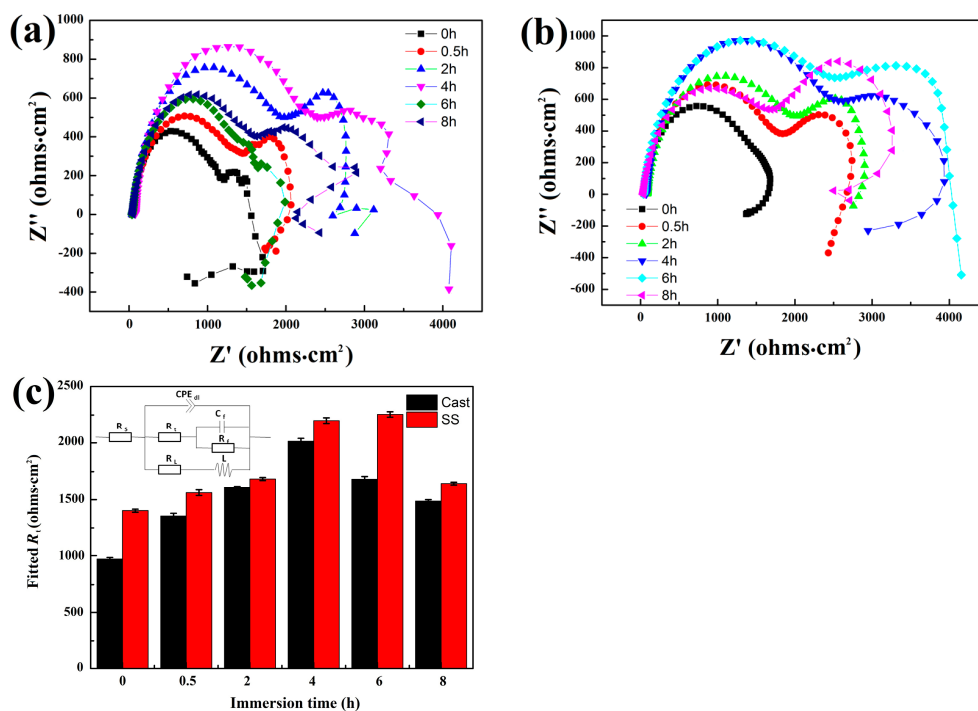


**Figure 5.** Open circuit potential (OCP) curves of the Mg-9Li alloys during the initial immersion in 0.1 mol/L NaCl solution.

EIS is widely used in the investigation of electrochemical corrosion behavior of metallic materials, which has a great advantage in continuously monitoring the evolution of corrosion characteristic [58–60]. Figure 6a,b are the EIS Nyquist plots of the tested alloys obtained from the different immersion periods in the 0.1 mol/L NaCl solution. As seen in Figure 6, both alloys presented two capacitive arcs in the high and middle frequency and one inductive arc in the low frequency. The capacitive arc in the high frequency is the EIS signal from the substrate metal while the capacitive arc in the middle frequency reflects the signal from the interface of the surface film and the electrolyte [61]. Meanwhile, the appearance of the inductive arc usually indicates the initiation and propagation of pitting corrosion. The high-frequency capacitive arc of both alloys experienced an initial increase and then a further decrease with this phenomenon dominated by the competition between the thickening and the breakdown of the surface film. The transition period of the cast alloy was 4–6 h, which coincided with the evolution of OCP. For SS alloy, the transition period was prolonged to 6–8 h, which also evidenced the better stability of its surface film. Thirdly, during the whole tested immersion periods, the SS alloys always presented the larger capacitive arcs compared to the cast alloy, indicating its superior corrosion resistance of the surface film [62].

Equivalent circuits are widely used to simulate the electrochemical characteristic parameters of the tested corrosion system. Herein, in view of the characteristic of this test, the equivalent circuit  $R_s(CPE_{dl}(R_t(R_fC_f)(R_L)))$  was used to simulate the tested EIS plots. In this equivalent circuit, the  $R_t$  and  $CPE_{dl}$  present the charge transfer resistance and double-layer capacitance of the high-frequency containing arc.  $CPE_{dl}$  is often used in a non-equilibrium system, which is expressed as  $Y_0$  and  $n$  [63]. For the corrosion system of Mg alloys,  $n$  is generally between 0.5–1.  $R_f$  and  $C_f$  are used to present the middle-frequency containing arc. As reported by Y.X. Qiao [64], the medium-frequency capacitive arc is caused by the diffusion of medium in porous solid film on metal surface. The middle-frequency

capacitive arc of both cast and SS Mg-9Li alloys prove the appearance of surface films on both samples. Herein, the  $R_f$  and  $C_f$  present the resistance and capacitance of the surface film, respectively.  $R_L$  and  $L$  are used to represent the resistance and inductance of low frequency inductive arc, respectively. The low frequency inductive arc resistance is generally related to the nucleation of localized corrosion [65]. The  $R_t$  and  $CPE_{dl}$  are the most important EIS parameters, which can be used to directly evaluate the corrosion resistance of the tested metallic material. Table 3 summarizes the fitted  $R_t$  and  $CPE_{dl}$  values of both alloys in a different exposure time. Meanwhile, the histogram of the  $R_t$  values, as well as the used equivalent circuit, are presented in the Figure 6c. The  $R_t$  and  $CPE_{dl}$  values are consistent with the results of OCP, indicating the better corrosion resistance of the SS alloy for the whole exposure period compared to the cast alloy.



**Figure 6.** Electrochemical impedance spectroscopy (EIS) Nyquist plots of the cast alloy (a) and SS alloy (b) and the histogram of  $R_t$  values (c).

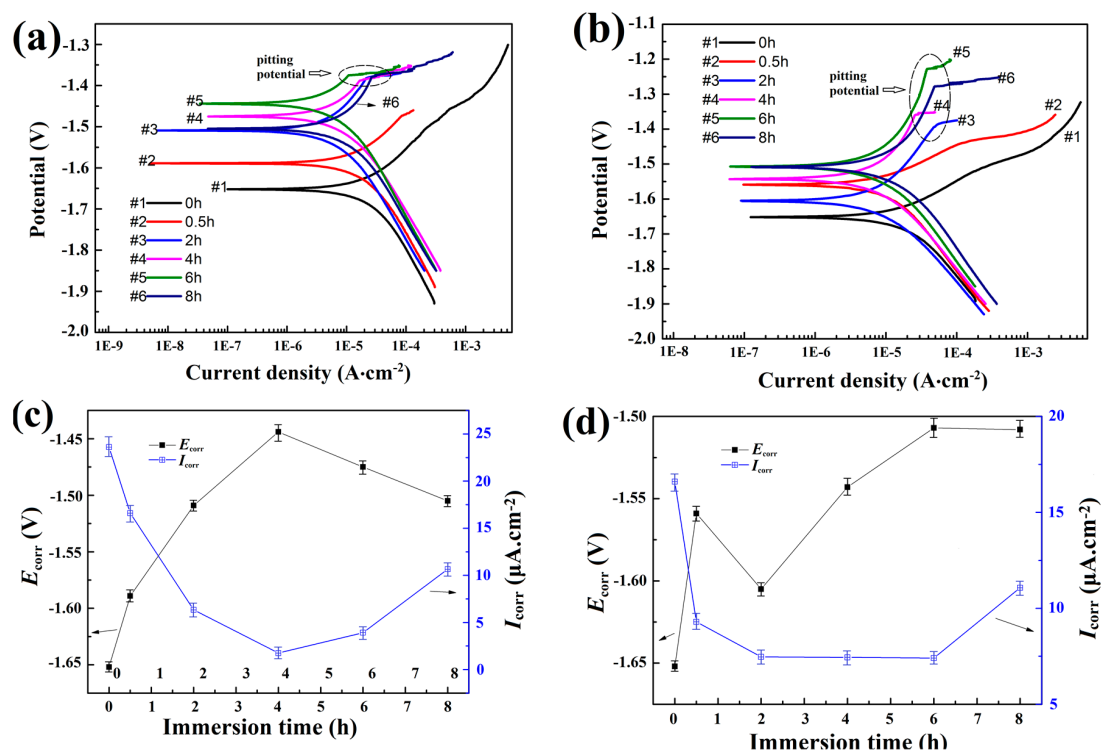
**Table 3.** Fitted EIS parameters of Mg-9Li alloys with a different exposure time.

| Samples and Immersion Time (h) |     | $R_S$ ( $\Omega\text{-cm}^2$ ) | $R_t$ ( $\Omega\text{-cm}^2$ ) | $Y_0$ ( $\Omega^{-1}\text{-cm}^{-2}\text{-s}^{-n} \times 10^{-6}$ ) | $n$ ( $\times 10^{-2}$ ) |
|--------------------------------|-----|--------------------------------|--------------------------------|---------------------------------------------------------------------|--------------------------|
| Cast alloy                     | 0   | $39.2 \pm 3.3$                 | $9.7 \pm 0.5 \times 10^2$      | $12.2 \pm 0.2$                                                      | $89.8 \pm 0.2$           |
|                                | 0.5 | $49.1 \pm 3.0$                 | $13.5 \pm 0.8 \times 10^2$     | $22.7 \pm 0.2$                                                      | $84.6 \pm 0.2$           |
|                                | 2   | $42.0 \pm 3.2$                 | $16.1 \pm 1.0 \times 10^2$     | $19.3 \pm 0.2$                                                      | $87.7 \pm 0.3$           |
|                                | 4   | $80.3 \pm 5.1$                 | $20.1 \pm 1.2 \times 10^2$     | $21.1 \pm 0.2$                                                      | $87.5 \pm 0.2$           |
|                                | 6   | $39.3 \pm 3.2$                 | $16.9 \pm 1.0 \times 10^2$     | $27.4 \pm 0.3$                                                      | $82.1 \pm 0.3$           |
|                                | 8   | $48.3 \pm 4.0$                 | $14.9 \pm 0.8 \times 10^2$     | $22.1 \pm 0.2$                                                      | $87.1 \pm 0.2$           |
| SS alloy                       | 0   | $42.2 \pm 3.1$                 | $14.0 \pm 0.8 \times 10^2$     | $11.9 \pm 0.2$                                                      | $87.0 \pm 0.3$           |
|                                | 0.5 | $63.0 \pm 4.2$                 | $15.6 \pm 0.8 \times 10^2$     | $19.8 \pm 0.2$                                                      | $88.1 \pm 0.2$           |
|                                | 2   | $76.2 \pm 5.3$                 | $16.8 \pm 0.9 \times 10^2$     | $20.8 \pm 0.2$                                                      | $88.9 \pm 0.4$           |
|                                | 4   | $42.1 \pm 3.1$                 | $22.0 \pm 1.5 \times 10^2$     | $21.4 \pm 0.2$                                                      | $88.9 \pm 0.2$           |
|                                | 6   | $86.3 \pm 5.2$                 | $22.6 \pm 1.5 \times 10^2$     | $22.8 \pm 0.2$                                                      | $88.1 \pm 0.3$           |
|                                | 8   | $38.0 \pm 4.0$                 | $16.6 \pm 0.9 \times 10^2$     | $26.2 \pm 0.3$                                                      | $86.2 \pm 0.2$           |

A PDP test was conducted to investigate the electrochemical behavior of the Mg-9Li alloy. Figure 7 presents the PDP curves, corrosion potential ( $E_{\text{corr}}$ ), and corrosion current density ( $I_{\text{corr}}$ ) after immersion in 0.1 mol/L of NaCl, various times. As seen from Figure 7c,d,  $E_{\text{corr}}$  values of both cast and SS alloys

increased firstly and decreased later. The transition period of the cast alloy is 4–6 h while the time of the SS alloy is 6–8 h, which is consistent with the findings of the OCP and EIS tests. It is clear for both alloys that the  $I_{\text{corr}}$  decreased at the initial immersion period and increased after a transition period. The  $I_{\text{corr}}$  value of the alloy was determined by both the thickening/breakdown of the surface film and corrosion damage in the matrix. Herein, one can deduce that the film thickening process dominates the decreased  $I_{\text{corr}}$  before the transition period, while the film breakdown and corrosion damage in the matrix dominates the increased  $I_{\text{corr}}$  after the transition period. Besides the  $E_{\text{corr}}$  and  $I_{\text{corr}}$ , pitting potential ( $E_{\text{pit}}$ ) is another parameter, which is usually used to evaluate the resistive ability of the materials against pitting corrosion. For the Mg-9Li alloy, the  $E_{\text{pit}}$  can be used to evaluate the stability of the surface film against the  $\text{Cl}^-$  aggression. The more noble  $E_{\text{pit}}$ , the better stability of the surface film formed on the tested alloy. Clearly, as marked in Figure 7a, the  $E_{\text{pit}}$  values kept nearly constant for cast alloy at around  $-1.4 \text{ V}_{\text{SCE}}$  during immersion periods of up to 2 h. However, the SS alloy  $E_{\text{pit}}$  values gradually increased during immersion periods up to 6 h.

Figure 8 is the hydrogen evolution test of the cast and SS Mg-9Li alloys during the 10-day immersion in 0.1 mol/L of NaCl solution. As seen from Figure 8, the cast alloy had nearly double hydrogen evolution values compared with the SS alloy at the first day. With the increase of constant exposure time, both alloys presented a gradually increased hydrogen evolution rate. However, the SS alloy always had the obviously less hydrogen evolution rate than that of the cast alloy during each exposure period. As marked by the blue dotted line on the cast alloy and the green straight line on the SS alloy, both alloys had two stages of hydrogen evolution rates (i.e., the slopes of the dotted line and straight line), that both alloys experience a rapid hydrogen evolution rate after a transition period. The transition periods for the cast and SS alloys are six days and seven days, respectively. This is consistent with the results of the electrochemical test.



**Figure 7.** Potentio-dynamic polarization (PDP) curves and related parameters of the Mg-9Li alloys tested at different exposure time. (a,c) are the pdp curves and the evolution of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  values of the cast alloy. (b,d) are the pdp curves and the evolution of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  values of the SS alloy.

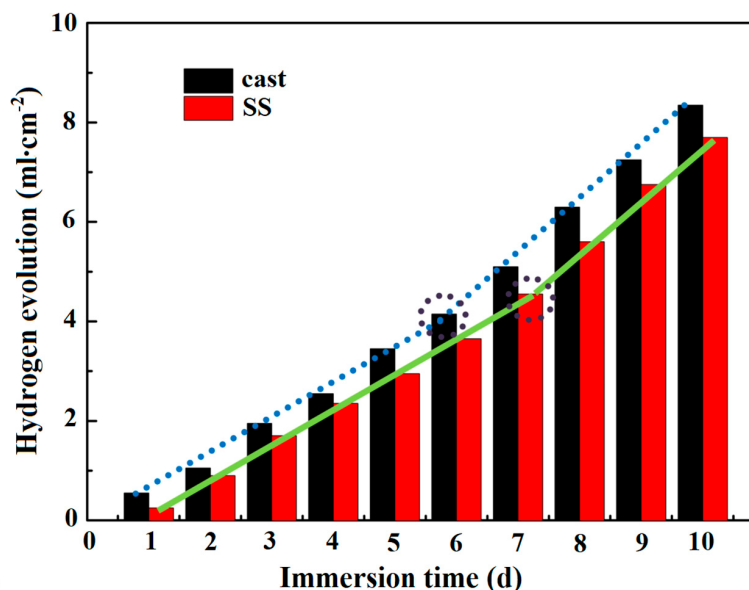
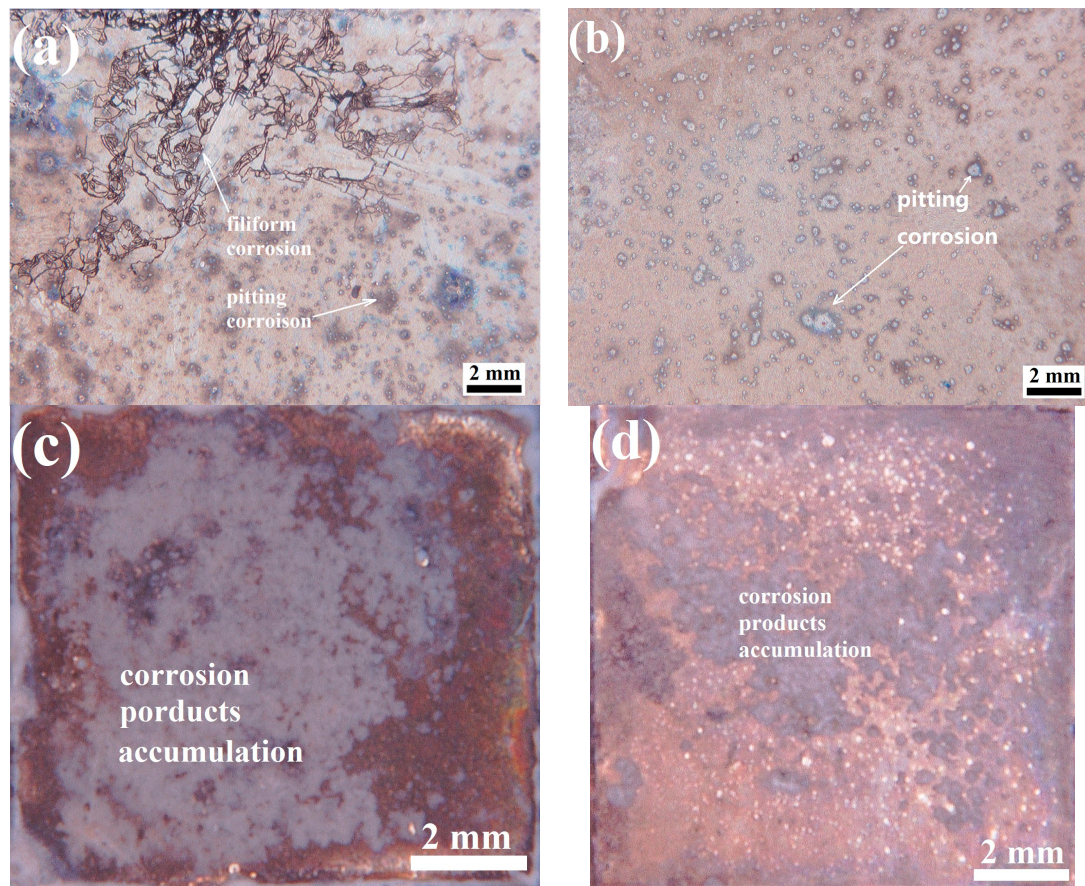


Figure 8. Hydrogen evolution of the cast and SS Mg-9Li alloys.

Figure 9 presents the top-view optical corrosion morphologies of the alloys after different corrosion time. As marked in Figure 9a,b, the SS alloy suffered relatively lighter pitting corrosion after hydrogen evolution corrosion for 4 h while the cast alloy suffered serious both pitting corrosion and the typical filiform corrosion. As seen in Figure 9c,d, both samples suffered serious corrosion damage when the exposure time extended to 10 days, but the difference in corrosion damage between the two alloy was still obvious. Most of the sample surface of the cast alloy was covered by corrosion products, indicating the serious corrosion damage of this alloy. Relatively, the SS alloy still retained a large area of non-severely corroded surface, presenting the less corrosion damage of this alloy. Figure 10 presents the cross-sectional view SEM corrosion morphologies of the alloys after different corrosion time. Figure 10a is the corrosion morphologies of the cast alloy obtained from exposure for 4 h. As marked by the white arrows, corrosion pits with different width and depth had occurred, which were covered by the corrosion product. Note that, this image was obtained from the place of the cast alloy where the most serious corrosion damage located. Since the pitting corrosion of the SS alloy after 4 h of corrosion was obviously more alleviated than the cast alloy, no typical corrosion pits was found from the cross-sectional view of the SS alloy at this corrosion period.

Figure 10b was the typical corrosion morphology of the cast alloy after constant exposure for 5 days, which shows the significantly more severe corrosion damage than the situation after 4-h exposure. Wider and deeper corrosion pits can be clearly found. One detailed corrosion characteristic needs to be emphasized, that the deep corrosion pits and most of the suspected corrosion product was located on the  $\alpha$ -Mg phase, while the  $\beta$ -Li phase suffered less corrosion damage and less loss in depth. Energy Dispersive Spectrometer (EDS) was conducted to analyze the chemical composition of the suspected corrosion product. From Figure 10c, one can clearly find that the suspected corrosion product (marked as spectrum 1 in both Figure 10b,c) has the typical composition of Mg and high content of O, which can be related to the typical corrosion product of  $\text{Mg}(\text{OH})_2$  and/or  $\text{MgO}$ . Meanwhile, the environmental elements, such as Cl and Na, were also found. Based on the above analysis, the suspected corrosion product can be completely validated. Besides, the EDS result of the spectrum 2 reflects the major composition of Mg and limited content of O, which can be used as the evidence of the  $\alpha$ -Mg phase. Noteworthy, the Li elements is too light to be detected by EDS, and the C element of both detected spectrums may originate from both the surface contamination and the corrosion product of the Li element (i.e.,  $\text{LiCO}_3$ ). As seen in Figure 10d, the SS alloy suffered much lighter corrosion damage compared to the cast alloy after constant exposure for 5 days, presenting less corrosion propagation in width and depth, as well as the less accumulated corrosion product. Furthermore, the corrosion pit

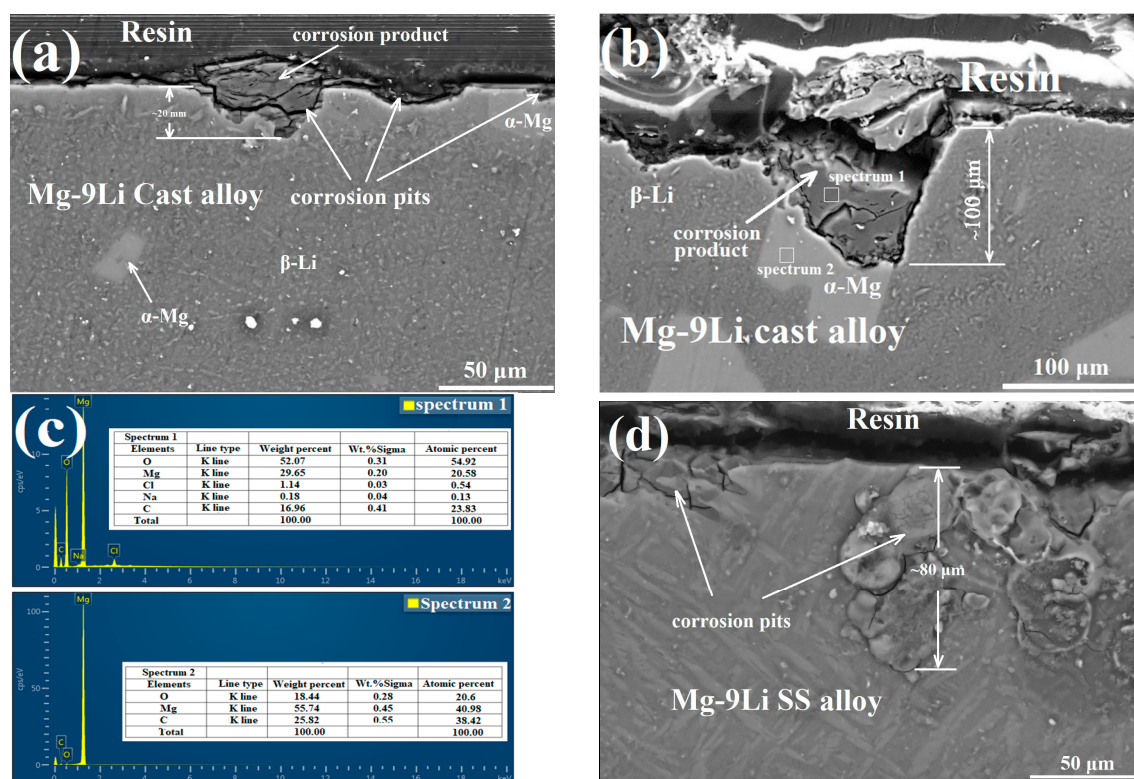
morphology of the SS alloy was quite different to that of the cast alloy, that no obvious difference in corrosion damage of the  $\alpha$ -Mg phase and  $\beta$ -Li phase could be found. The above phenomenon may be closely related to the great modification of the  $\alpha$ -Mg phase.



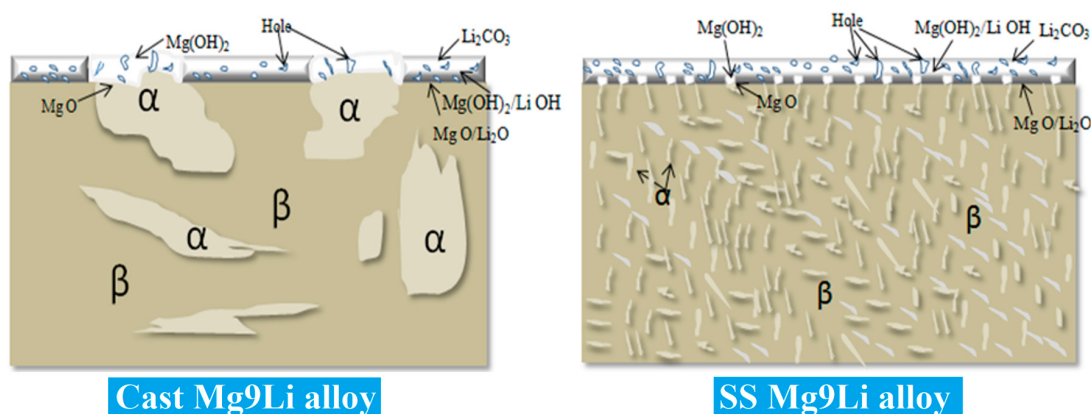
**Figure 9.** Optical surface corrosion morphologies of the Mg-9Li alloys after hydrogen evolution corrosion for different times. (a) Cast alloy after 4h corrosion; (b) SS alloy after 4 h corrosion; (c) cast alloy after 10-day corrosion; and (d) SS alloy after 10-day corrosion.

From both the electrochemical tests and hydrogen evolution test, one can get a clear conclusion that the corrosion resistance of the Mg-9Li alloy was significantly improved by the SS treatment. To better understand the mechanism for revealed improvement in corrosion resistance, the schematics of surface film of both cast and SS alloy have been presented in Figure 11 for comparative investigations. For ordinary magnesium alloys, a surface film mainly composed of magnesium hydroxide can be formed on the surface in an aqueous solution. This surface film is not stable under a chloride ion attack, and its protection of the substrate is extremely limited. Moreover, the breakdown of the surface film is accelerated by the hydrogen evolution, which led to an accelerated corrosion process of the Mg alloys. The surface film formation, corrosion initiation, and propagation of the Mg-Li alloys are more complicated. As illustrated in Figure 9a, due to the limited solid-solubility of Li element in the  $\alpha$ -Mg phase of the cast Mg-9Li alloy, the surface film formed in air and in water of the  $\alpha$ -Mg phase are mainly composed of MgO and Mg(OH)<sub>2</sub>, respectively. Meanwhile, the solid-solubility of Mg in the  $\beta$ -Li phase is greater than 11%. LiO with an amount of MgO will simultaneously form in air on the  $\beta$ -Li phase, and the LiOH and Mg(OH)<sub>2</sub> will form in water. In addition, as reported by Wanquan XU [27], LiOH will react with the dissolved CO<sub>2</sub> in the solution to form a more stable Li<sub>2</sub>CO<sub>3</sub>, which is adsorbed on the outmost surface of the  $\beta$ -Li phase. Thus, surface film formed on a  $\beta$ -Li phase is mainly composed of the LiOH, Mg(OH)<sub>2</sub>, and Li<sub>2</sub>CO<sub>3</sub>. It is worthy to note that the protective ability of

the  $\text{Li}_2\text{CO}_3$  was higher than that of the loose hydrated oxide films (including  $\text{Mg}(\text{OH})_2$  and  $\text{LiOH}$ ). Due to the coarse  $\alpha$ -Mg phase in the as-cast alloy, the chemical composition of the surface film formed on the  $\alpha$ -Mg phase is different from that on the  $\beta$ -Li phase. Those places are easy to breakthrough, leading to the initiation of the localized corrosion. For the SS alloy, due to the uniform distribution of the fine  $\alpha$ -Mg phase, the surface film formed on the  $\beta$ -Li phase will completely cover the entire surface of the alloy, and the substrate will be protected. This is the key factor to the superior corrosion resistance of the SS alloy, especially in the short-term exposure in the tested medium.



**Figure 10.** SEM cross-sectional view corrosion morphologies of the alloys obtained in different exposure time. (a,b) are the cast alloy obtained after 4-h and 5-days exposure, respectively; (c) EDS analysis of the cast alloy; and (d) SS alloy after 5-days exposure.



**Figure 11.** Illustration of surface film of the cast and SS Mg-9Li alloys.

Under the continuous attack of  $\text{Cl}^-$ , the surface film dissolved in some weak areas. In this situation, the corrosive medium diffused directly through the partially damaged film layer, leading to the pitting initiation of the substrate. In turn, the corrosion-induced hydrogen evolution also accelerated the

destruction of the surface film, which led to the accelerated corrosion degradation of the alloy substrate. Thus, the microstructure characteristic of the alloy had a great influence on the corrosion properties of the alloy. Pitting corrosion was easy to occur at the interface between two adjacent phases due to the different potential and corrosion activity of the adjacent phases [66]. In the studied Mg-9Li alloy, the difference of hydrogen overpotential of the  $\alpha$ -Mg and  $\beta$ -Li phases induced the instability of the  $\alpha/\beta$  phase interface, resulting in the preferred pitting nucleation at these sites. For the cast alloy, there was a long interface due to the coarse  $\alpha$ -Mg phase. Once the pitting nucleates somewhere in the interface, it propagated due to the oxygen concentration cell driving from the difference in the oxygen concentration inside and outside the pit. Since the interface is the corrosion sensitive place, the pit preferentially propagated along the long interface, leading the typical filiform corrosion of the cast Mg-9Li alloy [25]. For the SS alloy, the  $\alpha$ -Mg phase modified into the uniformly distributed small  $\alpha$ -Mg phase, leading to the massive independent short interface. Thus, it was more difficult for the propagation of the pits without long interface, which led to the typical light pitting morphologies of the SS alloy in the initial exposure. The corrosion behavior and resistance of the SS alloy may also have been influenced by the elements concentration and corrosion activity of the modified duplex-phase structure. Since the needle-like fine  $\alpha$ -Mg phase rapidly precipitated during the quenching process, it can be inferred that the atomic diffusion was insufficient. Thus, there is a great possibility that the  $\alpha$ -Mg phase and  $\beta$ -Li phase of the SS alloy kept a lesser difference in element concentration and corrosion activity, which reduced the pitting sensitivity of the interface and improved the corrosion resistance of the alloy matrix. In the long-term exposure, the difference in the corrosion damage of the cast and SS alloys included not only the amount of corrosion, but also the different corrosion propagation progress in the  $\alpha$ -Mg phase and  $\beta$ -Li phase. Since the  $\alpha$ -Mg phase had less protection from the unstable surface film, the corrosion propagation would have priority in the  $\alpha$ -Mg phase. While the  $\beta$ -Li phase had better protection from its  $\text{LiCO}_3$ -contained surface film, it suffered less corrosion damage. This difference is more obvious in the cast alloy, which had been validated by the cross-sectional view corrosion morphology presented in Figure 10b,d.

#### 4. Conclusions

The cast Mg-9Li alloy was successfully solid-solution treated via heating at 575 °C for 4.5 h and quickly quenched in ice-water mixture. The typical coarse  $\alpha$ -Mg phase and  $\beta$ -Li phase duplex structure of the cast alloy had been completely modified after SS treatment. Due to the extremely high chemical activity of Li and Mg elements, the decomposition of supersaturated solid solution induced the rapid bcc/hcp phase transition during the quenching process, creating the newly precipitated needle-like fine  $\alpha$ -Mg phase in the  $\beta$ -Li phase matrix.

The SS treatment significantly improved both the strength and ductility of the Mg-9Li alloy. The YTS of the alloy was improved from about 62 MPa to 110 MPa, and an estimated 45% of improvement was achieved. The UTS was improved from about 100 MPa to 120 MPa, and the  $E_f$  was improved from 32% to 45%. Dramatic grain refinement and uniform distribution of the  $\alpha$ -Mg phase were major factors to improved mechanical property. In addition, the massively increased  $\alpha/\beta$ -phase interface also played a positive role in improving the mechanical property.

SS treatment also remarkably improved the corrosion resistance of the Mg-9Li alloy. Due to the uniform distribution of the finer  $\alpha$ -Mg phase, the uniform corrosion-resistant surface film formed on the  $\beta$ -Li phase completely covered the entire alloy surface, which efficiently protected the substrate of the SS alloy. In addition, the SS alloy had a lower difference in element concentration and corrosion activity of the duplex phases, which reduced the pitting sensitivity of the  $\alpha/\beta$ -phase interface and improved the corrosion resistance of the alloy matrix.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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