Effect of (Pr + Ce) addition and T6 heat treatment on microhardness and corrosion of AlSi5Cu1Mg alloy

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Abstract
The effects of T6 heat treatment and 0.6 wt% (Pr + Ce) addition on microstructure, microhardness, and corrosion of AlSi5Cu1Mg alloy were investigated. Optical microscopy and scanning electron microscopy revealed that the T6 heat treatment and the addition of 0.6 wt% (Pr + Ce) effectively refined the α-Al and eutectic Si phases, which were uniformly distributed with Al2Cu phase in the alloy. Microhardness, weight loss, hydrogen evolution, Tafel polarization, and EIS tests showed that the combination of T6 heat treatment and 0.6 wt% (Pr + Ce) addition resulted in the best corrosion resistance and microhardness of the alloy. The microhardness of the AlSi5Cu1Mg+0.6 wt% (Pr + Ce)/T6 (115 HV) was 27.8% higher than that of the matrix (90 HV). At the same time, the corrosion current density of the alloy also reached the minimum value (38.4 μA cm⁻²). The T6 heat treatment and the addition of (Pr + Ce) can significantly decrease the average grain size, change the redistribution of the precipitated Al2Cu phase, refine the Si phase, and increase the pitting formation position, thus reducing the sensitivity of exfoliation corrosion.

1. Introduction
Aluminum alloys have high commercial value and wide industrial applications due to their excellent properties, especially in the aerospace and automotive industries [1]. Owing to the wide application of aluminum alloys, considerable attention has been devoted to the corrosion behavior of the alloys in various corrosive environments. Zor et al [2] reported that the increase of Cu content increased the volume fraction of β-phase particles and decreased the corrosion rate of Al-Si eutectic alloy in acidic solution. Barros et al [3] reported that the addition of Mg to the Al-Cu alloy resulted in a lower polarization resistance and higher corrosion current density of the alloy, which accelerated the corrosion of the alloy in 0.5 M NaCl solution. Yang et al [4] reported that the addition of Be to the A357 alloy improved the microstructure of the 3-Al5FeSi and Si phases, which increased the corrosion resistance of the alloy. Yu et al [5] reported that the addition of rare earth La refined the microstructure of the AlSi5Cu1Mg alloy, which improved the corrosion resistance in 3.5 wt% NaCl solution.

In addition to adding alloy elements, the corrosion resistance of aluminum alloy can also be improved by heat treatment. Osório et al [6] reported that T4 heat treatment could effectively improve the corrosion resistance of an Al-9 wt% Si casting alloy. Heat treatment can not only improve the corrosion resistance of the alloy, but also improve the microhardness of the alloy. Chen et al [7] reported that both long-term solution treatment and short-term aging treatment would reduce the volume fraction of the hard phase precipitated in Al-7Si-Mg alloy after T6 heat treatment, thereby reducing the hardness of the alloy. Barbosa et al [8] reported that the microhardness of Al7Si0.3Mg alloy increases with increasing aging time.

Heat treatment and addition of alloying elements can improve the corrosion resistance of the aluminum alloy. So, the researchers focused on combining the two processes. Peng et al [9] reported that the synergistic effects of Sc and Zr microalloying and heat treatment increased corrosion resistance and decreased corrosion current density of Al-Mg-Mn alloys. For Al-Si alloys, many researchers had a focus on the addition of rare earth...
elements and heat treatment to increase the mechanical properties of the alloy [10, 11]. AlSi5Cu1Mg alloy has an attached passive oxide film on the surface, which has good corrosion resistance in various environments [12]. The hydrochloric acid medium will accelerate the corrosion of the alloy, so that the addition of rare earth elements and heat treatment process can better reflect its improvement ability in a short time. However, little research has been done on its corrosion resistance in acid solution. Our previous work [13] showed that the addition of 0.6 wt% (Pr + CePr + Ce) had the best refinement effect on the microstructure of AlSi5Cu1Mg alloy. The corrosion resistance of the alloy depends on the morphology of the microstructure [5, 14]. In this paper, our aim is to investigate the effect of (Pr + Ce) addition and T6 heat treatment on microhardness and corrosion of AlSi5Cu1Mg alloy. Microstructure analysis and electrochemical techniques were used to analyze the corrosion mechanism on the alloy surface by T6 heat treatment and 0.6 wt% (Pr + Ce) addition.

2. Experimental procedure

2.1. Preparation of materials

The materials used to prepare the specimens mainly included commercial AlSi5Cu1Mg alloys and Al-5Pr-5Ce ternary master alloy in the study. The AlSi5Cu1Mg alloy was placed in a preheated graphite crucible and heated to 740 °C in an electric resistance furnace to melt the alloy. Then, the Al-5Pr-5Ce ternary master alloy was added to fabricate AlSi5Cu1Mg-\(x\)Pr(Pr + Ce)0 = 0 and 0.6 wt%) alloy (table 1) after degassing and removal of slag. The melts were held at 740 °C for 30 min. Finally, molten alloys were poured into a preheated (200 °C) metal mold and cooled to room temperature.

The center position of the AlSi5Cu1Mg-\(x\)Pr(Pr + Ce) alloy was cut into nine groups of cylindrical specimens of the same size (12 mm in diameter and 2 mm in height). Six groups of specimens were placed into an SX24-13 type resistance furnace for T6 heat treatment. The solution temperature was set at 520 °C and held for 6 h, then the specimens were quenched in water at 60 °C. The specimens were then subjected to an aging treatment (175 °C, 6 h) and finally placed in air to cooling.

2.2. Microstructure characterization

The morphological changes of the main phase in the AlSi5Cu1Mg alloy were studied by T6 heat treatment and the addition of (Pr + Ce). The surfaces of the specimens were sequentially ground with 400–2000 grit SiC abrasive paper and polished. Then, the specimen surface was etched with 0.5 wt% hydrofluoric acid solution. Finally, the microstructure characteristics of the specimens were observed via optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS). Different phases in the AlSi5Cu1Mg and AlSi5Cu1Mg+0.6 wt% (Pr + Ce)/T6 alloys were identified using x-ray diffraction (XRD). The average grain size and average area of the eutectic Si phase were measured via Image-Pro Plus 6.0 analyzer software (IPP), and approximately 20 different areas were measured to minimize errors.

2.3. Microhardness testing

The Vickers hardness (HV) of the specimens was measured using HVS-1000A hardness tester device. The applied load was 0.3 kg, and the load time was 10 s. At least five hardness points were collected at different positions on the specimens, and the average value was taken.

2.4. Immersion testing and electrochemical measurements

The corrosion resistance of the specimens was evaluated by immersing in 0.1 M HCl solution for 12 h. All specimens were sequentially ground with 400–2000 grit SiC abrasive paper, polished, and ultrasonically cleaned using an ethanol solution (95 wt%) for 5 min. During corrosion, the volume of HCl overflow was recorded by reading the change in the liquid level scale of the inverted acid burette above the specimens. Specimens were cleaned using a mixed solution of 20 g l\(^{-1}\) chromic oxides (CrO\(_3\)), phosphoric acid (H\(_3\)PO\(_4\)), and distilled water at 80 °C for 2–3 min. Subsequently, the specimens were dried, and weighed by using an electronic balance with an accuracy of 0.0001 g. To reduce errors, each test was repeated five times under the same corrosion parameters. The calculation formulas of the weight loss and hydrogen evolution rates are as follows [15, 16]:

| Elements | Si  | Cu  | Mg  | Fe  | Mn  | Zn  | Pr  | Ce  | Al  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0        | 5.40| 1.05| 0.43| 0.59| 0.32| 0.14| —   | —   | Bal.|
| 0.6 wt%  | 5.20| 1.01| 0.44| 0.61| 0.32| 0.16| 0.28| 0.31| Bal.|

Table 1. Main chemical composition of the AlSi5Cu1Mg-\(x\)Pr(Pr + Ce) alloy (wt%).
3.1. Microstructure and Microhardness of AlSi5Cu1Mg alloys under T6 heat treatment and (Pr + Ce) addition

Figure 1 shows the microstructures of AlSi5Cu1Mg alloys with the addition of 0.6 wt% (Pr + Ce) and T6 heat treatment. From Figure 1, it can be found that the dendritic α-Al and long-needle-like eutectic Si phases are gradually refined, and the α-Al phase distribution is more regular. The synergistic effect of T6 heat treatment and (Pr + Ce) results in the best refining effect of the α-Al and eutectic Si phases. The eutectic Si phase is granular and short rod, and the α-Al phase is elliptic (Figure 1(c)). Studies have shown that the morphological changes of eutectic Si are mainly the spheroidization of solution treatment and fine grain strengthening of rare earth [11, 13, 17]. Figure 2 shows the morphological changes of eutectic Si with or without 0.6 wt% (Pr + Ce) addition under T6 heat treatment conditions.

Table 2 shows microhardness, average grain size, and the average area of Si phase of the AlSi5Cu1Mg alloys under different modification conditions. Both T6 heat treatment and the addition of 0.6 wt% (Pr + Ce) can decrease the average grain size and increase the microhardness of the alloy. The microhardness of the AlSi5Cu1Mg + 0.6 wt% (Pr + Ce)/T6 was 27.8% higher than that of the matrix.

Back scattered SEM images of the AlSi5Cu1Mg alloys with the addition of 0.6 wt% (Pr + Ce) and T6 heat treatment is shown in Figure 3. Researchers have reported that as-cast AlSi5Cu1Mg alloys contained many intermetallic phases containing Fe, such as Al4Fe, γ-Al2FeSi, α-Al5Fe2Si, β-Al5FeSi, and Al12FeMnSi phase [13, 18]. From the results of Figure 3(d), it can be seen that the fish-bone-like phase at point 1 may be Al4FeMnSi phase, and the bright block-like at point 2 may be Al6Cu phase. After the alloy was subjected to T6 heat treatment, the fish-bone-like Al12FeMnSi phase was decreased relative to the matrix, and gradually became short rod or small block-like (Figure 3(b)). When 0.6 wt% (Pr + Ce) was added to the AlSi5Cu1Mg alloys and T6 heat treatment was performed, the Al12FeMnSi phase was long needle-like (Figures 3(c) and (e)). From Figures 3(a)–(c), it can be found that the distribution of Al2Cu phase is gradually uniform. By adding 0.6 wt% (Pr + Ce) and

\[
V_W = \frac{M_1 - M_2}{A \times T}
\]

(1)

\[
V_H = \frac{H_1 - H_2}{A \times T}
\]

(2)

where \(V_W (\mu g \ cm^{-2} \ h^{-1})\) represents the weight loss rate, \(V_H (ml \ cm^{-2} \ h^{-1})\) represents the hydrogen evolution rate, \(M_1 (\mu g)\) represents the initial weight, \(M_2 (\mu g)\) represents the weight after corrosion for 12 h, \(H_1 (ml)\) represents the liquid level of the acid burette before corrosion, \(H_2 (ml)\) represents the liquid level after corrosion for 12 h, \(A (cm^2)\) represents the total area of the specimen immersed in the solution, and \(T = 12 \ h\) represents the corrosion time.

The specimens were ground to 2000 grit SiC abrasive paper, cleaned with ethanol, and air dried before testing. Electrochemical measurements were conducted on a standard three-electrode flat cell, electrochemical workstation (PARSTAT 4000), and 0.1 M HCl electrolyte. The flat cell consisted of the working electrode with 1 cm² test area, the counter electrode (platinum mesh), and the reference electrode (Ag/AgCl in 3 M KCl). Tafel polarization curves were obtained at a scanning rate of 2 mV s⁻¹ in the range of ±250 mV after the specimens were immersion in the 0.1 M HCl electrolyte for 1 h to stabilize the free corrosion potential. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 100 kHz to 10 MHz, with an amplitude of 5 mV. Electrochemical analysis software (Versa Studio software) and electrochemical impedance fitting software Zview (Scribner Associates Inc.) were used to analyze the Tafel polarization curves and impedance spectra, respectively. All measurements were repeated no less than five times.

3. Results

3.1. Microstructure and Microhardness of AlSi5Cu1Mg alloys under T6 heat treatment and (Pr + Ce) addition

Figure 1. Optical microstructures of uncorroded alloys: (a) AlSi5Cu1Mg, (b) AlSi5Cu1Mg + T6, and (c) AlSi5Cu1Mg + 0.6 wt% (Pr + Ce)/T6.

Figure 1. Optical microstructures of uncorroded alloys: (a) AlSi5Cu1Mg, (b) AlSi5Cu1Mg + T6, and (c) AlSi5Cu1Mg + 0.6 wt% (Pr + Ce)/T6.
T6 heat treatment, the distribution of Al2Cu phase and the refining of Al12FeMnSi phase were significantly improved. From the point scanning of results of the alloy, it can be found that the bright needle-like phase at point 3 may be composed of Al, Si, Cu, Pr, and Ce, forming the Al-Si-Cu-Pr-Ce intermetallic compound. To determine the composition of AlSi5Cu1Mg and AlSi5Cu1Mg + 0.6 wt% (Pr + Ce)/T6 alloys, XRD patterns are shown in figure 4. The RE-rich intermetallic compound was confirmed as Al3Ce and Al2Pr. Meanwhile, the matrix contains mainly Al, Si, Al12FeMnSi, and Al2Cu phases.

3.2. Weight loss and hydrogen evolution tests
Figure 5 shows the weight loss and hydrogen evolution rates of AlSi5Cu1Mg alloys under different modification conditions immersed in 0.1 M HCl solution for 12 h. When the AlSi5Cu1Mg alloy was subjected to T6 heat treatment, the weight loss and hydrogen evolution rates of the alloy were 67.2% and 55.3% lower than that of the matrix. In addition, when the alloy was modified by the addition of (Pr + Ce) and T6 heat treatment, the weight loss and hydrogen evolution rates of the alloy reached the minimum values of 12.7 μg cm⁻² h⁻¹ and 1.66 × 10⁻³ ml cm⁻² h⁻¹, respectively.

3.3. Tafel polarization curves
Tafel polarization curve analyzes the corrosion mechanism of the alloy surface by the polarization reaction of the anode part and the cathode part. Figure 6 shows the Tafel polarization curves for the AlSi5Cu1Mg, AlSi5Cu1Mg + T6, and AlSi5Cu1Mg + 0.6 wt% (Pr + Ce)/T6 alloys after 1 h of immersion in 0.1 M HCl solution. The results show that the cathode portion gradually moves to the left, while the anode portion remained similar. The values of corrosion potential (Ecorr) and corrosion current density (Icorr) for different specimens are shown in table 3. The corrosion potential of the modified alloy is relatively lower than that of the matrix, but the corrosion current density is significantly decreased. The corrosion current density of the AlSi5Cu1Mg + 0.6 wt% (Pr + Ce)/T6 alloy (38.1 μA cm⁻²) is 86.9% lower than that of the matrix (294.9 μA cm⁻²). And the corrosion current density of the alloy was 64.8 μA cm⁻² after T6 heat treatment. The combination of T6 heat treatment and the addition of (Pr + Ce) minimizes the corrosion current density of the alloy.

3.4. Electrochemical impedance spectroscopy
Figure 7 shows EIS plots obtained for different specimens after 1 h of immersion in 0.1 M HCl solution. The AlSi5Cu1Mg has the lowest resistance against corrosion in the Nyquist plots, which increased gradually with T6 heat treatment and 0.6 wt% (Pr + Ce) addition (figure 7(a)). The combination of T6 heat treatment and (Pr + Ce) addition results in the best corrosion resistance of the alloy. Bode phase plots and Bode magnitude plots (two typical spectra) are shown in figures 7(b) and (c), respectively. Different specimens have significant
differences in the middle and low frequency bands. The alloy treated with 0.6 wt% \((\text{Pr} + \text{CePr} + \text{Ce})\) and T6 heat treatment have the highest impedance value at a frequency of approximately 1 HZ. The Bode phase plot has obvious peaks in the middle frequency, while the peaks are not obvious at low frequency. This indicates that the specimens have two well-defined time constants in this frequency range.

All experimental impedance spectra can be quantified by appropriate equivalent circuits to characterize the corrosion process. The impedance spectrum consists of a high frequency capacitive loop and a low frequency inductor loop. The equivalent circuit is shown in figure 7(d). \(R_s\) represents the solution resistance in 0.1 M HCl solution, \(R_1\) represents a thin film resistance which is related to the presence of a native oxide layer and the inhibition layer on the alloy surface \([19]\), \(C\) represents the capacitance of the film, \(R_2\) represents the charge transfer resistance, and \(\text{CPE} - T\) represents the capacitance of the double layer at the interface on the metal/solution interface \([20]\). According to the equivalent circuit model, the values obtained by fitting the experimental
Figure 4. XRD patterns of AlSi5Cu1Mg and AlSi5Cu1Mg+0.6 wt% (Pr + CePr + Ce)/T6 alloys.

Figure 5. Weight loss and hydrogen evolution rates of AlSi5Cu1Mg alloys under different modification conditions immersed in 0.1 M HCl solution for 12 h.

Figure 6. Tafel polarization curves for different specimens after 1 h of immersion in 0.1 M HCl solution.
EIS data are shown in Table 4. The Chi-Squared values are less than 0.01. The solution resistance of different specimens in 0.1 M HCl solution is basically unchanged. The values of CPE-P are close to 1, indicating that CPE corresponds nearly to an ideal capacitor \( [21] \). The polarization resistance \( (R_p) \) of the alloys is equal to the addition of \( R_1 \) and \( R_2 \). The \( R_p \) value of the \( \text{AlSi5CuMg} \) alloy treated with is greater than that of the matrix. In particular, the \( R_p \) value of the alloy by 0.6 wt% \((\text{Pr + Ce})/\text{T6}\) addition and T6 heat treatment is 182.22 \( \Omega \) cm\(^2\), which is about three times that of the matrix (59.76 \( \Omega \) cm\(^2\)). The \( C \) and CPE-T values for the \( \text{AlSi5Cu1Mg} + 0.6 \text{ wt\% (Pr + Ce)/T6} \) alloy were higher than those of the \( \text{AlSi5Cu1Mg} + \text{T6} \) alloy, and the \( C \) and CPE-T values of the matrix are the minima.

### Table 3. \( E_{corr} \) and \( I_{corr} \) values obtained from Tafel fit analyses in figure 6.

| Specimen                          | \( E_{corr} \) (mV versus Ag/AgCl) | \( I_{corr} \) (\( \mu A \) cm\(^{-2}\)) |
|-----------------------------------|-------------------------------------|------------------------------------------|
| \( \text{AlSi5Cu1Mg} \)           | -639.3                              | 294.9                                    |
| \( \text{AlSi5Cu1Mg} + \text{T6} \) | -650.4                              | 64.8                                     |
| \( \text{AlSi5Cu1Mg} + 0.6 \text{ wt\% (Pr + Ce)/T6} \) | -649.2                              | 38.4                                     |

### Table 4. Simulated parameters of the EIS data obtained for different specimens in 0.1 M HCl solution after 1 h.

| Specimen                          | \( R_s \) (\( \Omega \) cm\(^2\)) | \( R_1 \) (\( \Omega \) cm\(^2\)) | \( C \) (F cm\(^{-2}\)) | \( R_2 \) (\( \Omega \) cm\(^2\)) | \( \text{CPE-T} \) (F\(^4\) cm\(^{-2}\)) | \( \text{CPE-P} \) | Chi-Squared |
|-----------------------------------|-------------------------------------|-------------------------------------|--------------------------|-------------------------------------|------------------------------------------|----------------|-------------|
| \( \text{AlSi5Cu1Mg} \)           | 10.08                               | 5.06                                | 6.70E-5                  | 54.7                                | 3.31E-4                                  | 0.886         | 0.006       |
| \( \text{AlSi5Cu1Mg} + \text{T6} \) | 9.85                                | 10.47                               | 1.20E-5                  | 146.6                               | 2.70E-4                                  | 0.810         | 0.005       |
| \( \text{AlSi5Cu1Mg} + 0.6 \text{ wt\% (Pr + Ce)/T6} \) | 10.91                               | 12.12                               | 0.45E-5                  | 176.1                               | 2.13E-4                                  | 0.863         | 0.008       |

EIS data are shown in Table 4. The Chi-Squared values are less than 0.01. The solution resistance of different specimens in 0.1 M HCl solution is basically unchanged. The values of CPE-P are close to 1, indicating that CPE corresponds nearly to an ideal capacitor \( [21] \). The polarization resistance \( (R_p) \) of the alloys is equal to the addition of \( R_1 \) and \( R_2 \). The \( R_p \) value of the \( \text{AlSi5CuMg} \) alloy treated with is greater than that of the matrix. In particular, the \( R_p \) value of the alloy by 0.6 wt% \((\text{Pr + Ce})\) addition and T6 heat treatment is 182.22 \( \Omega \) cm\(^2\), which is about three times that of the matrix (59.76 \( \Omega \) cm\(^2\)). The \( C \) and CPE-T values for the \( \text{AlSi5Cu1Mg} + 0.6 \text{ wt\% (Pr + Ce)/T6} \) alloy were higher than those of the \( \text{AlSi5Cu1Mg} + \text{T6} \) alloy, and the \( C \) and CPE-T values of the matrix are the minima.
3.5. Microscopic characteristics of corroded surfaces

Figure 8 shows corrosion morphology of different specimens in 0.1 M HCl solution after 1 h. The results show that the corrosion of the AlSi5Cu1Mg alloy gradually evolves from intergranular corrosion to exfoliation corrosion. The α-Al of the unmodified AlSi5Cu1Mg alloy surface layer is completely etched away, and many and large corrosion pits are formed, leaving only the surface layer to be peeled off (figure 8(a)). When the alloy was treated with T6 heat treatment, the corrosion pits gradually decreased and became smaller relative to the matrix. However, the alloy still has significant exfoliation corrosion (figure 8(b)). T6 tempering led to the low Cu content and continuous distribution at grain boundaries, increasing the sensitivity of the alloy to exfoliation corrosion. When 0.6 wt% (Pr + Ce) was added to the alloy and T6 heat treatment was performed, only α-Al at the grain boundary was etched away (figure 8(c)). The combination of (Pr + Ce) and T6 heat treatment can effectively improve the corrosion resistance of the AlSi5Cu1Mg alloy.

4. Discussion

The T6 and 0.6 wt% (Pr + Ce)/T6 can effectively refine the α-Al, eutectic Si and Al12FeMnSi phases of the AlSi5Cu1Mg alloy. When the AlSi5Cu1Mg alloy was treated with solid solution, the Al2Cu particles were dissolved into the alloy matrix [17]. From the HV results presented in table 2, it has allowed to deduce that the Al2Cu particles gradually precipitated after the aging treatment. T6 heat treatment affects the distribution and refinement of the Al2Cu phases in the alloy. Figure 3 shows that the bright white Al2Cu phase in the alloy after T6 heat treatment is more evenly distributed and refined relative to the matrix. The modification of T6 and 0.6 wt% (Pr + Ce) results in the best improvement of Al2Cu. Figure 6 shows that the peak value of Al2Cu phase is lower than that of the matrix after modification of T6 and 0.6 wt% (Pr + Ce), indicating that Al2Cu phase is refined. The increased microhardness of modified samples with T6 and 0.6 wt% (Pr + Ce) can be attributed to two reasons. One is the refinement of eutectic Si phases, another is the dissolution of Al2Cu phases. When the average area of the eutectic Si phase gradually decreases, the microhardness of the alloy gradually decreases (table 2). The microhardness variation is related to the average grain size using the Hall-Petch equation [22, 23]:

$$HV = H_0 + k_1d^{-1/2}$$

(3)

where HV represents the microhardness of the specimens, $H_0$ and $k_1$ represent appropriate constants associated with the microhardness measurements, and $d$ (μm) represents the average grain size of the specimens. Figure 9 shows variation in microhardness with $d$ for AlSi5Cu1Mg alloy under different modification conditions. The average grain size of the alloy has a great effect on the microhardness of the alloy. The finer the average grain of the alloy, the higher the microhardness of the alloy. The microhardness of AlSi5Cu1Mg alloy is improved by T6 heat treatment and (Pr + Ce) addition.

When the AlSi5Cu1Mg alloy was immersed in 0.1 M HCl solution, Cl− corroded a native oxide layer on the surface of the alloy. The Si phase and the intermetallic compounds (Al2Cu and Al12FeMnSi phases) are nobler than the α-Al matrix [24–26]. After the oxide film on the surface was destroyed, micro-galvanic couple occurred on the matrix. According to the results of the immersion testing and electrochemical measurements, T6 and 0.6 wt% (Pr + Ce)/T6 can effectively improve the corrosion resistance of the alloy. The weight loss and hydrogen evolution rates of the alloy gradually decreased with the change of the modification conditions (figure 5). As shown in figure 6 and table 3, the corrosion current density of the AlSi5Cu1Mg alloy after T6 heat treatment decreases, and the corrosion current density of the alloy after the addition of (Pr + Ce) and T6 heat treatment further decreases. Studies have shown that the corrosion resistance of alloys is related to grain refinement [27]. Therefore, the change in grain size of the alloy affects the corrosion rate. The relationship
The relationship between the corrosion current density and the average grain size is expressed as [28–30]:

\[ i_{\text{corr}} = A + Bd^{-1/2} \]  

(4)

\[ i_{\text{corr}} = Cd^{3.16} \]  

(5)

where \( i_{\text{corr}} \) (A cm\(^{-2}\)) represents the corrosion current density of the alloy, the constant \( A, B \) and \( C \) represent constants, and \( d \) (\( \mu m \)) represents the average grain size of the specimens. Figure 10 shows grain size effect on corrosion properties for AlSi5Cu1Mg alloy under different modification conditions. The finer the average grain of the alloy, the lower the corrosion current density of the alloy. The AlSi5Cu1Mg alloy has the best corrosion resistance under the combination of T6 heat treatment and \((\text{Pr} + \text{Ce})\) addition.

The refinement and uniform distribution of the Al\(_2\)Cu phase can decrease the Cu-depleted zone and preferentially pitting corrosion. Figure 8 shows that the distribution and particle size of both Si phase affect the corrosion of the AlSi5Cu1Mg alloy. The concentration distribution of Si phase can accelerate the corrosion of the alloys due to the increase of the local cathode area. The Si phase acts as the cathode phase, and the coarse Si phase forms a large surface potential with the \( \alpha \)-Al matrix to accelerate the corrosion of the alloy.

To further analyze the corrosion effect of T6 heat treatment and the addition of 0.6 wt\% \((\text{Pr} + \text{Ce})\) in the AlSi5Cu1Mg alloy, the corrosion mechanism of the alloy is shown in figure 11. When the specimens were immersed in 0.1 M HCl solution, the native oxide film on the surface was destroyed. The \( \alpha \)-Al would undergo an oxidation reaction and be dissolved as an anode phase. The hydrogen evolution reaction mainly occurs in the Si phase because the Si phase acts as the main cathode phase, while the Al\(_2\)Cu and Al\(_{12}\)FeMnSi phases act as the secondary cathode phase. Figure 11(d) shows that severe localized corrosion occurs around the coarse Si, Al\(_2\)Cu...
and Al$_2$FeMnSi phases, and further corrosion occurs along with these phases. A layer of Si phase and intermetallic compound is formed on the surface of the alloy. After the T6 heat treatment, the migration of Al$_2$Cu particles from the grain boundary into the matrix like finer and better distributed, thereby destroying the strong electrolyte cell that exists between the grains. The cathodic reduction reaction mainly occurs on the Al$_2$Cu phase as the preferred cathode. This result promotes pitting of the alloy during the corrosion process, without causing severe local corrosion (figures 11(b) and (e)). After the addition of 0.6 wt% (Pr + Ce) and T6 heat treatment, each phase of the alloy is further refined and evenly distributed (figure 11(c)). Only α-Al at the grain boundary is corroded, forming a smaller corrosion pit (figure 11(f)). The grain refinement and uniform distribution increase the pitting formation site for the corrosion of the alloy, so as to avoid serious local corrosion and exfoliation corrosion. Al$_2$Pr and Al$_3$Ce phases act as cathode phases, increasing the cathode area. However, the increase of cathode area has no obvious effect on the corrosion of alloy, because Al$_2$Pr and Al$_3$Ce phases increase pitting formation position. The corrosion resistance of the alloy is related to the grain size and distribution of the alloy. The combination of T6 heat treatment and (Pr + Ce) addition results in the best corrosion resistance of the alloy.

5. Conclusion

In this study, the microstructure, microhardness and corrosion behavior of AlSi5Cu1Mg alloy processed by the combination of T6 heat treatment and (Pr + Ce) addition were investigated. Microhardness, weight loss, hydrogen evolution, Tafel polarization, and EIS tests were used to reveal the effects of different microstructures on the hardness and corrosion resistance of the alloy. The main results of this study are as follows.

1. After T6 heat treatment and 0.6 wt% (Pr + Ce) addition, the dendritic α-Al, coarse-needle-like eutectic Si, fish-bone-like Al$_2$FeMnSi and block-like Al$_2$Cu phases in the alloy were significantly refined and evenly distributed. The RE-rich intermetallic compound was confirmed as Al$_3$Ce and Al$_2$Pr.

2. The microhardness of the AlSi5Cu1Mg+0.6 wt% (Pr + Ce)/T6 (115 HV) was 27.8% higher than that of the matrix (90 HV). The finer the average grain of the alloy, the higher the microhardness of the alloy.

3. Under the combined action of T6 heat treatment and 0.6 wt% (Pr + Ce), the weight loss and hydrogen evolution rates of the alloy reached the minimum values of 12.7 $\mu$g cm$^{-2}$ h$^{-1}$ and $1.66 \times 10^{-3}$ ml cm$^{-2}$ h$^{-1}$, respectively. At the same time, the corrosion current density of the alloy also reached the minimum value (38.4 $\mu$A cm$^{-2}$). In addition, the Rp value of the alloy by 0.6 wt% (Pr + Ce) addition and T6 heat treatment is 182.22 $\Omega$ cm$^2$, which is about three times that of the matrix (59.76 $\Omega$ cm$^2$).
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