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Characterization of pitting corrosion of 7A60 aluminum alloy by EN and EIS techniques

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Abstract: The pitting corrosion behaviors of 7A60 aluminum alloy in the retrogression and re-aging (RRA) temper were investigated by electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques, and the microstructure and the second phase content of the alloy were observed and determined by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The results show that there exist two different corrosion stages for 7A60 alloy in 3.5% NaCl solution, and the corrosion process can be detected by the appearance of EIS spectrum with two capacitive time constants and the wavelet fractal dimension D extracted from EN. SEM and EDS results also demonstrate that severe pitting corrosion in 7A60 alloy is mainly caused by electrochemical active MgZn₂ particles, secondly by Al₂MgCu and Mg₂Si. Al₇Cu₂Fe particles make little contribution to the pitting corrosion of 7A60 alloy.

Key words: 7A60 aluminum alloy; constituent particles; pitting corrosion; electrochemical impedance spectroscopy; electrochemical noise; wavelet fractal dimension

1 Introduction

7xxx series aluminum alloys are widely used in military and aerospace industries for their low density and favorable mechanical properties [1]. However, these alloys are often suffered from pitting corrosion and stress corrosion cracking (SCC) when subjected to aggressive environments such as salt water spray and/or salt fog [2,3]. It has been reported that a superior balance of SCC resistance and strength can be obtained by retrogression and re-aging (RRA) treatment [4–6]. And our previous study has also proved that the SCC resistance of 7A60 aluminum alloy in 3.5% NaCl solution is improved by RRA treatment [7].

Al–Zn–Mg–Cu alloys contain numerous constituent particles with electrochemical potentials different from those of the matrix, then corrosion pits can readily develop in these particles [8,9]. The initiation of SCC cracks can be basically associated with intensive localized corrosion around constituent particles [10,11]. The electrochemical characteristics of intermetallic phases in Al–Zn–Mg–Cu series alloys have been studied by BIRBILIS and BUCHHEIT [12]. It is concluded that Al₇Cu₂Fe and Al₂Cu phases are noble particles while MgZn₂ phase is active particle with high self-dissolution rates. Nevertheless, the dealloying and incongruent dissolution of Al₂CuMg particles may lead to polarity reversal. The pitting behaviors of 7150 and 7075 alloys under solution heat treatment and laser surface treatment have been discussed [9,10]. It is demonstrated that the pitting resistance of 7150 alloy can be improved due to the removal of active constituent particles such as η (MgZn₂) and *S*(Al₂MgCu) phases.

7A60 alloy is a new developed ultra-high strength aluminum alloy, and its SCC behaviors in RRA tempers have been studied [7]. In this work, the pitting corrosion behavior of 7A60 alloy in the RRA temper was investigated by using electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) methods, and their corroded micrographs were observed and determined by scanning electron microscopy (SEM)

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and energy dispersive spectrometer (EDS).

2 Experimental

2.1 Material and heat treatment

7A60 alloy used was composed of 8.0%–9.0% Zn, 2.3%–3.0% Mg, 2.0%–2.6% Cu, 0.1%–0.2% Zr, 0.09% Fe, 0.06% Si, 0.002% Be and balanced Al. The alloy was prepared by conventional casting, hot rolling and annealing at 470 °C for 2 h. And then, the hot rolled plates with a thickness of 2 mm were RRA-treated in the following sequences: 1) pre-aged at 120 °C for 24 h; 2) retrogressed at 195 °C for 180 min and 3) re-aged at 120 °C for 24 h.

2.2 Immersion test

7A60 specimens were mounted in epoxy resin with an exposed area of 2 cm². Then, they were abraded with silicon carbide paper (from 400 to 2000 grade) and polished. The immersion test was carried out in 3.5%NaCl solution for 72 h at room temperature to evaluate the pitting corrosion behavior. The microstructure and corroded surface were observed by a TDCLS4800 scanning electron microscope, and the chemical compositions of the constituent particles were analyzed by energy dispersive spectrometer.

2.3 EIS measurements

EIS measurements of 7A60 alloy in 3.5% NaCl solution at different immersion time were carried out by using a VersaSTAT 4 electrochemical workstation with three-electrode system at open circuit potential with a 10 mV sine perturbation to the cell. The working electrode was 7A60 alloy with an exposed area of 2 cm^2 . The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum plat. The measuring frequency range was 10^{5} – 10^{-2} Hz. The experimental data of the impedance were analyzed in terms of an appropriate equivalent circuit using the ZSimpWin program, and the values of the parameters were determined by the simulation. In the circuit, capacitance was mathematically modeled using a constant phase element Q in order to obtain a better simulation between the model and the experimental data. Then, the impedance was defined by [13,14]

$$Z(j\omega) = (Y_0)^{-1} j\omega^{-n}$$
(1)

where Y_0 is the *Q*-constant; j is the imaginary unit; ω is the angular frequency ($\omega = 2\pi f, f$ is the frequency); *n* the *Q*-power ranging from -1 to 1.

2.4 EN measurements

Electrochemical noise data of 7A60 alloy in 3.5% NaCl solution was measured by using two nominally

identical 7A60 alloys with an exposed area of 2 cm^2 as working electrodes and a saturated calomel electrode as reference electrode. The EN system used was specifically described in Ref. [15]. The sampling frequency used in this study was 2 Hz and each time record consisted of 512 s. The standard deviations (STD) of the potential and current noise were given to evaluate the corrosion activity. Before STD analysis, the direct current (DC) component was removed from the original EN data by a 5-order polynomial fitting every 512 s interval.

Wavelet transformation was also used to analyze EN signals [16]. By using the wavelet transformation technique based on orthogonal db2 wavelet, the collected electrochemical potential noise data were decomposed to seven levels (d1-d7) [17]. Then, for orthonormal discrete wavelet decomposition, the following power law was used [18,19]:

$$\sigma_j^2 = \frac{\sigma^2}{(2^j)^{-\beta}} \quad (j=1, 2, \dots, 7)$$
(2)

where σ^2 is the variance of EN signal; σ_j^2 is the variance of detail crystal d_j , which can be calculated by the following equation:

$$\sigma_j^2 = \frac{1}{N/2^j - 1} \sum_{k=1}^{N/2^j} (d_{j,k} - d_j)^2 \quad (j=1, 2, \dots, 7)$$
(3)

where N is the number of data record, $k=1, 2, \dots, N/2^{j}$.

The slope β was obtained from the plot $\log_2 \sigma_j^2$ versus level *j*:

$$\log_2 \sigma_j^2 = \beta j + \log_2 \sigma^2 \tag{4}$$

Finally, the fractal dimension *D* was obtained by

$$D = 2.5 - 0.5\beta$$
(5)

3 Results

3.1 Surface morphology

The microstructure and EDS spectra of 7A60 alloy before immersion are shown in Fig. 1. From Fig. 1 it can be observed that the round constituent particles were rich in Mg and Si elements (33.34% Mg and 15.7% Si in Fig. 1(b)), and could be related as β (Mg₂Si) phase. The constituent particles with irregular shape were composed of 76.15% Al, 15.87% Cu and 7.98% Fe (Fig. 1(c)), and could be referred to as ternary phase Al₇Cu₂Fe. The oval particles should be *S* phase (Al₂MgCu) with the composition of 50.17% Al, 24.59% Mg and 20.93% Cu (Fig. 1(d)). The particles with high contents of Mg and Zn in Fig. 1(e) could be related as η phase (MgZn₂) [9,12,20].

The surface morphology of 7A60 alloy after immersion is shown in Fig. 2. During the initial 2 h of immersion, there were no visible pits. However, it was



clearly seen that the oxide layer rupture (pits nucleation) was mainly localized at the constituent particles (Fig. 2(a)). As immersion time increased to 3 h, the corrosion pits with an average size of 20 μ m were observed, and the particles in pits rich in Mg and Zn could be related as MgZn₂ phase (Fig. 2(b)). After 10 h of immersion, some stable pits grew up and the alloy surface was covered with corrosion product of mud structure (Fig. 2(c)). For up to 48 h and 72 h of immersion, the size and depth of corrosion pits were further increased with the diameter of 100 μ m for 48 h and 200 μ m for 72 h (Figs. 2(d) and (e)).

The magnified morphologies of corrosion pits induced by constituent particles are shown in Fig. 3, and the EDS spectra of the related constituent particles are also shown in Fig. 3. Around Al₇Cu₂Fe particles, the size of corrosion pits was much larger than that of the particles. It indicated that during the corrosion process

the surrounding Al matrix was dissolved as anode whereas Al_7Cu_2Fe particle was cathode (Fig. 3(a)). And EDS result revealed that the Al_7Cu_2Fe particles were stable (Fig. 3(b)).

For Al₂MgCu particle, obvious corrosion trenches at the interface of Al₂MgCu particles and Al matrix were observed (Fig. 3(c)). However, after corrosion the Al₂MgCu particle was rich in Al and Cu, but Mg element was hardly detected (Fig. 3(d)). These results proved that preferential dissolution of Mg element occurred in the Al₂MgCu particles during immersion test.

Apart from the above corrosion pits and constituents, the round constituent particle mainly composed of Si element was observed and anodic dissolution of Al matrix around the Si-rich particle was obvious (Figs. 3(e) and (f)). Based on a comparison with the Mg₂Si particle shown in Figs. 1(a) and (b), it was indicated that very active Mg was selectively dissolved from Mg₂Si, leaving



Si-enriched remnants. It was similar to the dealloying of Al₂MgCu particle [21,22].

As for $MgZn_2$ particle, no corrosion pits containing $MgZn_2$ particle were found. The possible reason was that $MgZn_2$ particle was dissolved completely due to its anodic nature, and thus only deep corrosion pits left as shown in Figs. 2(d) and (e) [9].

3.2 EIS characterization

EIS plots of 7A60 alloy at different immersion time were determined and shown in Fig. 4. During the initial 2 h, EIS plots showed a capacitive impedance arc at high frequency and an inductive impedance arc at low frequency (Fig. 4(a)). The inductive arc could be related with pitting nucleation in the pitting model for Al alloys [13, 23]. With increasing immersion time to 3 h, 7A60 alloy had a capacitive impedance arc at high frequency, and the inductive impedance arc at low frequency, and the inductive impedance arc at low frequency disappeared (Fig. 4(b)). The capacitive arc at high frequency corresponded to the original surface while the one at low frequency was associated to the new generated surface in pits. Meanwhile, the radius of the capacitive arc at low frequency decreased with the increase of immersion time due to the anodic corrosion process in stable pits.

Figure 5 shows the phase angle plots of 7A60 alloy obtained from Fig. 4. During the initial 2 h, only one capacitive time constant was observed (Fig. 5(a)). After immersion for 2 h, two capacitive time constants could be found (Fig. 5(b)). Moreover, the phase angle peak at 0.01-0.1 Hz in Fig. 5(b) tended to depress with increasing time, which suggested that the pitting corrosion activity increased [14,24]. While the phase angle peak at 10-100 Hz showed no obvious tendency.

In order to analyze the EIS spectrum of 7A60 alloy, the corresponding equivalent circuits are shown in Fig. 6. In Fig. 6, R_{sol} represented solution resistance; R_t and Q_p were defined as the charge transfer resistance and oxide-layer capacitance of the original flat surface (or the



Fig. 3 Morphologies of corrosion pits and EDS spectra of constituent particles of 7A60 alloy: (a, b) Al₇Cu₂Fe; (c, d) Al₂MgCu; (e, f) Mg₂Si



Fig. 4 Nyquist plots of 7A60 alloy during immersion in 3.5% NaCl solution: (a) At different immersion time in initial 2 h; (b) At different immersion time after 2 h of immersion

double-layer capacitance of the original corrosion product surface), respectively, while $R_{t(pit)}$ and $Q_{dl(pit)}$ were the charge transfer resistance and double-layer capacitance corresponding to the new generated surface in pits, respectively; R_0 and L were the inductive parameters.

The fitting parameters of 7A60 alloy are listed in Tables 1 and 2. For a capacitance element, the derivation of *n* from the unit was due to the heterogeneous effect. n_1 and n_2 were around 0.9, showing a deviation from the ideal capacitive behavior. It could be attributed to the formation of an inhomogeneous corroded surface because of the dissolution of particles or Al matrix. And

 R_t increased slightly due to the formation of corrosion product on the metal surface [24,25]. After 2 h of immersion, $R_{t(pit)}$ decreased markedly with increasing immersion time because of the propagation of stable pits in breadth and depth.

3.3 EN characterization

EN signals of 7A60 alloy in 3.5% NaCl solution at different immersion time are shown Fig. 7. During the initial 2 h of immersion, the potential and current noise signals showed high frequency fluctuations consisted of lots of overlapped transients with low amplitude (Fig. 7(a)). It illustrated that the oxide layer rupture of



Fig. 5 Phase angle plots of 7A60 alloy during immersion in 3.5% NaCl solution: (a) At different immersion time in initial 2 h; (b) At different immersion time after 2 h of immersion



Fig. 6 Equivalent circuit of 7A60 alloy: (a) At initial 2 h; (b) After 2 h of immersion

Table 1 EIS fitting parameters of 7A60 alloy at different immersion time in initial 2 h

Immersion time/h	$R_{\rm sol}/(\Omega \cdot {\rm cm}^2)$	$Q_{\rm p}/(\Omega^{-1}\cdot {\rm cm}^{-2}\cdot {\rm s}^{-1})$	n_1	$R_{\rm t}/(\Omega \cdot {\rm cm}^2)$	$R_0/(\Omega \cdot \mathrm{cm}^2)$	$L/(\mathrm{H}\cdot\mathrm{cm}^2)$	Error/%
0.5	2.34	4.35×10 ⁻⁵	0.91	1392	179.9	910.7	0.7
1	2.29	3.68×10 ⁻⁵	0.92	1471	211.2	794.1	0.3
1.5	2.25	7.84×10^{-5}	0.90	1419	236.4	562.0	0.4
2	3.57	4.09×10 ⁻⁵	0.93	1245	392.5	418.8	0.1

Table 2 EIS fitting parameters of 7A60 alloy at different immersion time after 2 h of immersion

Immersion time/h	$R_{\rm sol}/(\Omega \cdot {\rm cm}^2)$	$Q_{\rm p}/(\Omega^{-1} \cdot {\rm cm}^{-2} \cdot {\rm s}^{-1})$	n_1	$R_{\rm t}/(\Omega \cdot {\rm cm}^2)$	$Q_{\rm dl(pit)}/(\Omega^{-1} \cdot \rm cm^{-2} \cdot \rm s^{-1})$	n_2	$R_{t(pit)}/(\Omega \cdot cm^2)$	Error/%
3	2.39	8.47×10^{-5}	0.92	1567	4.83×10^{-4}	0.89	20038	0.9
4	4.67	9.24×10 ⁻⁵	0.91	1462	5.33×10 ⁻⁴	0.89	20388	4
5	2.77	1.60×10^{-4}	0.92	1508	6.21×10^{-4}	0.87	18248	4
10	3.04	1.96×10^{-4}	0.90	1561	8.24×10^{-4}	0.90	13588	0.7
20	3.00	2.20×10^{-4}	0.87	1858	4.01×10^{-4}	0.82	15580	5
48	3.12	2.30×10^{-4}	0.88	1763	3.98×10^{-4}	0.89	6885	3
72 h	2.68	2.36×10^{-4}	0.86	1716	3.81×10^{-4}	0.83	4085	3

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7A60 alloy around the constituent particles occurred on the whole surface, and no visible pits could be observed (Fig. 2(a)). At the immersion time of 3 h, the potential and current noise signals showed low frequency fluctuations consisted of some transients with a long time width, and the potential amplitude was an order of magnitude higher than that of the initial 2 h (Fig. 7(b)). It indicated the onset of a pitting type of corrosion on the active sites (Fig. 2(b)). When immersion time was prolonged to 10 and 72 h, the EN signals all showed low frequency fluctuations with large transients, and the current amplitude also increased (Figs. 7(c) and (d)). It was corresponding to the development of corrosion pits on the alloy surface (Figs. 2(c)-(e)).

The STD of potential (STD_{φ}) and current noise (STD_I) , and the wavelet fractal dimension *D* were calculated and shown in Fig. 8. During the initial 2 h, The STD_{φ} and STD_{*I*} were relatively small, and the fractal dimension *D* was in the range of 1.7–1.8. With the increase of immersion time, the STD_{φ} and STD_I of 7A60 alloy increased significantly (Fig. 8(a)) [26,27], whereas the fractal dimension *D* decreased steeply and then reached a constant value around 1.4 (Fig. 8(b)).



Fig. 7 EN signals of 7A60 alloy in 3.5% NaCl solution at immersion time of 2 h (a), 3 h (b), 10 h (c) and 72 h (d) after DC removal



Fig. 8 Variation of STD_{φ} and $STD_{I}(a)$, and fractal dimension D (b) of 7A60 alloy with immersion time

4 Discussion

4.1 Effect of constituent particles

The microstructures of 7xxx series aluminum alloys incorporate a combination of constituent particles: Mg₂Si, MgZn₂, Al₇Cu₂Fe, Al₂Cu, Al₂MgCu and Al₃Fe [12]. The constituent particles did not precipitate for the purpose of strength development specifically. Generally, these particles lead to rather severe micro-galvanic corrosion in NaCl solution, as they are rich in alloying elements and their electrochemical behavior is significantly different from the surrounding Al matrix [28]. The main constituent particles in 7A60 alloy are η (MgZn₂), $S(Al_2MgCu)$, $\beta(Mg_2Si)$ and Al_7Cu_2Fe (Fig. 1). They exhibit either anodic or cathodic characteristics relative to the matrix. Since these particles can be formed during alloy solidification at high temperature, they are unaffected by the subsequent aging treatment at low temperatures.

The corrosion potential of MgZn₂ phase in 3.5% NaCl solution is -1095 mV (vs SCE) [12], while the corrosion potential of 7A60 alloy in this study is -767 mV (vs SCE). Therefore, η (MgZn₂) phases are electrochemically active particles with high anodic dissolution ability. Before immersion, η (MgZn₂) phases have high concentration of Mg and Zn elements (Figs. 1(a) and (e)). After immersion for 3 h, MgZn₂ remnants in pits still can be seen (Fig. 2(b)). However, after 72 h of immersion, no MgZn₂ particles can be observed because MgZn₂ particles have been dissolved completely due to its anodic nature. It is reported that the dissolution of anodic particles can form pits which are very deep [29]. Pits of this type will propagate by self-catalyzed reaction [30]. As a result, the dissolution of anodic MgZn₂ particles results in the occurrence of deep corrosion pits as shown in Figs. 2(d) and (e) [9].

The corrosion potentials of Al₂MgCu and Mg₂Si phases in 3.5% NaCl solution are -1061 and -1536 mV respectively [12]. As a result, $S(Al_2MgCu)$ and $\beta(Mg_2Si)$ particles are anodic relative to the Al matrix during the initial corrosion process, and they are rich in Mg (Figs. 1(b) and (d)). Nevertheless, the evidence of so-called peripheral matrix dissolution is observed around $S(Al_2MgCu)$ and $\beta(Mg_2Si)$ particles after 72 h of immersion (Figs. 3(c) and (e)). This is because dealloying and incongruent dissolution of Mg allow $S(Al_2MgCu)$ and $\beta(Mg_2Si)$ intermetallic particles to behave as a local cathode after some unknown time (Figs. 3(d) and (f)) [22,31].

Since Al_7Cu_2Fe particles are nobler than the aluminum matrix with corrosion potential of -654 mV in 3.5% NaCl solution [12], the aluminum matrix around Al_7Cu_2Fe particles is preferentially dissolved and the size

of corrosion pits is larger than that of Al_7Cu_2Fe particles (Fig. 3(a)). Dissolution of the matrix around the cathodic particles continues as long as the particles retain electrical contact with the matrix [32]. Once the particles are detached from the pits, the corrosion process is stopped [33]. Therefore, the pits caused by Al_7Cu_2Fe can be re-passivated.

Consequently, the presence of the highly active η (MgZn₂) is seen to make a very large contribution to the severe pitting corrosion damage, secondly *S*(Al₂MgCu) and β (Mg₂Si) [9].

4.2 Corrosion process

In general, there are two pitting corrosion stages for pitting corrosion of aluminum alloy: pitting initiation stage and pitting propagation stage. During the initial 2 h of immersion of 7A60 alloy in 3.5% NaCl solution, lots of oxide film rupture events are located around constituent particles (Fig. 2(a)). Consequently, EIS shows a capacitive arc at high frequency and an inductive arc at low frequency (Fig. 4(a)), the capacitive arc is an indication of the corrosion process for original surface under activation control, and the inductive behavior is attributed to the relaxation processes induced by Cl^- ion adsorption [34].

From our previous study it can be deduced that the fractal dimension D can be used to distinguish the corrosion type and evaluate the localized degree of corrosion [35]. Since the oxide film rupture events are dispersed at lots of locations on the metal surface, and no pitting corrosion occurs, EN shows high frequency signal and high D value of about 1.7–1.8 (Figs. 7(a) and Fig. 8(b)).

As the immersion time increases, the inductive arc in EIS decreases and then disappears (Fig. 4). This indicates that the oxide layer is absent and the bare metal is attacked [36]. When the immersion time increases to 3 h, corrosion pits with a size of 20 μ m can be observed (Fig. 2(b)). This process can be termed as pitting propagation stage. At the same time, EIS is characterized by double capacitive arcs (Fig. 4(b)). The capacitive arc at high frequency represents the oxide layer or corrosion products on metal surface, while the other at low frequency represents the new surface in pits [37]. Meanwhile, EN signal shows obvious large transients (Fig. 7(b)), the STD_{φ} and STD_{*I*} increase and *D* decreases due to the onset of local pitting corrosion (Fig. 8).

As the immersion time further increases to 10, 48 and 72 h, respectively, the stable pits are propagated in breadth and depth (Figs. 2(c)–(e)). Therefore, EN signal still shows obvious large transients, and the *D* value calculated from EN continues to decrease and reaches a steady state value of around 1.4 finally. This is in the range of *D* values for pitting corrosion (Fig. 8(b)) [35].

In addition, STD_{φ} and STD_{I} increase with immersion time for the enhanced anodic dissolution in deep pits (Fig. 8(a)). Meanwhile, for EIS, the increase of R_t (Tables 1 and 2) is ascribed to the corrosion products covered on the surface. And the decrease of $R_{t(pit)}$ is caused by pitting propagation.

On the basis of the above discussion, the two pitting corrosion stages of 7A60 alloy in 3.5% NaCl solution can be distinguished by the appearance of two capacitive time constants in EIS and the wavelet fractal dimension D extracted from EN.

5 Conclusions

1) $MgZn_2$ particles show high anodic dissolution ability. Preferential dissolution of Mg can occur in Al_2MgCu and Mg_2Si particles during immersion, showing evidence of dealloying. Al_7Cu_2Fe particles are noble and stable.

2) Severe pitting corrosion in 7A60 alloy is mainly induced by active $MgZn_2$ particles, secondly Al_2MgCu and Mg_2Si particles. And Al_7Cu_2Fe particles make little contribution to pitting corrosion.

3) At the pitting initiation stage of 7A60 alloy in 3.5% NaCl solution, EIS shows a capacitive arc at high frequency and an inductive arc at low frequency, and the fractal dimension D value extracted from EN is about 1.7–1.8. At the pitting propagation stage, EIS shows double capacitive arcs with D value of around 1.4.

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7A60 铝合金点蚀行为的电化学噪声和 电化学阻抗谱表征

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摘 要:采用电化学阻抗谱(EIS)和电化学噪声(EN)方法研究回归再时效(RRA)热处理状态下 7A60 铝合金的点蚀 行为,通过扫描电子显微镜(SEM)和能谱仪(EDS)观察和分析合金的组织和第二相颗粒成分。结果表明,7A60 铝 合金在 3.5% NaCl 溶液中存在两个腐蚀阶段,并且可以用 EIS 出现两个电容时间常数的时间和由 EN 计算出的小 波分形维数 D 的变化来表征。SEM 和 EDS 分析结果表明,在 7A60 铝合金中,严重的点蚀主要是由阳极相 MgZn₂ 引起的,其次是 Al₂MgCu 和 Mg₂Si 相, Al₇Cu₂Fe 相对 7A60 铝合金点蚀行为的影响不大。 关键词: 7A60 铝合金;金属间化合物;点蚀;电化学阻抗谱;电化学噪声;小波分形维数

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