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Exfoliation corrosion susceptibility of 8090 Al-Li alloy examined by electrochemical impedance spectroscopy ①

CAI Chao(蔡 超)[1, 2], LI Jin-feng(李劲风)[3], ZHENG Zi-qiao(郑子樵)[3], ZHANG Zhao(张 昭)[1],
(1. Department of Chemistry, Zhejiang University, Hangzhou 310027, China;
2. Key Laboratory of Energy Resource and Chemical Engineering, Ningxia University, Yinchuan 750021, China;
3. School of Materials Science and Engineering, Central South University, Changsha 410083, China)

Abstract: The exfoliation corrosion susceptibility and electrochemical impedance spectroscopy(EIS) of rolled and peak-aged 8090 Al-Li alloys in EXCO solution were studied, and the EIS after exfoliation was simulated. Once exfoliation occurs, two capacitive arcs appear in the EIS at high-mediate frequency and mediate-low frequency respectively. The exfoliation-attacked alloy surface consists of two parts, an original flat alloy surface and a new inter-face exposed to EXCO solution due to the exfoliation. The capacitance corresponding to the new exfoliation inter-face increases approximately linearly with time at early exfoliation stage, due to the enlargement of the new inter-face. Then it maintains stable, due to the corrosion product covering on the new inter-face. The exfoliation susceptibility can be judged through the average slope of the capacitance vs time curve of the early exfoliation stage. This average slope of the rolled 8090 alloy is much higher than that of the peak-aged 8090 alloy, accordingly the rolled 8090 alloy is more susceptible to exfoliation than the peak-aged 8090 alloy.

Key words: exfoliation corrosion; 8090 Al-Li alloy; electrochemical impedance spectroscopy(EIS)

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1 INTRODUCTION

Al-Li alloys, compared to traditional Al alloys, have more excellent properties, such as lower density, greater elastic modulus and higher ratio of strength to mass[1, 2]. In the near future, they would be widely applied to airplane structures. While, exfoliation, a main kind of localized corrosion, lowers their strength, plasticity and fatigue properties, and also decreases their service life[3-5]. So investigating their exfoliation will be very important to their application.

Usually, the exfoliation ratings are observed by naked eyes. Hence, they are subject to variation among inspectors. It is essential to find out other ways to judge exfoliation degree. Li et al[6] measured the electricity resistance of exfoliation-corroded LY12 alloy, and calculated the corrosion depth from this resistance. The exfoliation susceptibility of LY12 alloys with various aging treatment was distinguished through the corrosion depth.

It is generally thought that exfoliation corrosion is developed from intergranular attack. During corrosion process, the corrosion product accumulates in grain boundary, resulting in a wedging force and finally lifting the alloy surface. So it is possible to judge the exfoliation degree through this wedging force. Kelly et al[7, 8] measured the corrosion product force of 2090 and 8090 Al-Li alloys in EXCO solution and found that the highest force was different due to various heat treatment. Meanwhile, an incubation period in the corrosion product force vs time curve was found. They suggested that the exfoliation susceptibility be quantitatively represented by the highest force and incubation period.

Although electrochemical impedance spectroscopy(EIS) has been widely used to study corrosion[9, 10], it has not been applied for exfoliation research until later 1990s. Conde et al[11-13] found that the EIS of exfoliation-attacked alloy electrode was composed of two capacitive arcs, and suggested that the exfoliation susceptibility be judged through the appearance time of the two capacitive arcs. However, severe pitting corrosion on the alloy surface also could cause a capacitive arc, which would cause our misunderstanding about the beginning of exfoliation. Further research into EIS of exfoliation is essential.

The purpose of this work is to study the exfoliation and EIS features of rolled and peak-aged 8090 Al-Li alloys, and to establish a method to judge exfoliation susceptibility of the alloys through EIS simulation analysis.

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Correspondence: ZHANG Zhao, PhD; Tel: +86-571-87952318; E-mail: eaglezzy@zjuem.zju.edu.cn

2 EXPERIMENTAL

The alloys used for this study were as-received rolled and peak-aged 8090 Al-Li alloy plates with a thickness of 3 mm. Specimens were cut from the alloy plates, connected to a copper wire, then mounted in epoxy with a surface exposed. The exposed surface with an area of approximate 6 cm^2 (3 cm × 2 cm) was ground using abrasive papers through 500-grade to 1200-grade, polished with diamond paste, rinsed using acetone, degreased with de-ionized water and then dried in air. The accelerated exfoliation test was performed according to EXCO test of ASTM G34-79[12]. The EXCO solution of 4.0 mol/L NaCl+ 0.5 mol/L KNO_3+ 0.1 mol/L HNO_3 (pH = 0.4) was used and the solution temperature was maintained at 25 ℃ in a thermostat water bath. The volume of EXCO solution was about 150 mL, providing a ratio of solution volume to metal surface of 25 mL/cm^2.

The test specimens were continuously immersed in the EXCO solution. During the immersion process, electrochemical impedance spectroscopy (EIS) was measured with a Model 273A Potentiostat/Galvanostat at the open-circuit potential and always carried out from high frequency of 20 000 Hz to low frequency of 0.1 Hz. After immersion, the ratings were judged by naked eyes according to ASTM G34-79. Meanwhile, the EIS was simulated through a Z-view Program.

3 RESULTS AND DISCUSSION

The corrosion development of the rolled and peak-aged 8090 alloys is presented in Table 1 and Table 2. It is clearly seen that the exfoliation on the rolled alloy surface develops more quickly than that on the peak-aged alloy surface, indicating that the rolled alloy is more susceptible to exfoliation than the peak-aged alloy.

The EIS patterns of the peak-aged 8090 alloy at the beginning of immersion in EXCO solution are shown in Fig. 1. It is clearly seen that the Nyquist plot is mainly comprised by a depressed capacitive arc at high-mediate frequency and an inductive loop at mediate-low frequency. Usually, aluminium alloy surface is covered with an oxide film in air. At the beginning of immersion, due to the protection of this oxide film, the reaction resistance is high and the corrosion rate is slow. However, once the alloy is immersed in the EXCO solution, the dissolution of the oxide film occurs. The weakening of the protection of the oxide film leads to the appearance of the inductive arc at mediate-low frequency[15]. When the oxide film is fully dissolved and bare metal is exposed to the solution, the reaction resistance decreases, being represented by the steep decrease of the capacitive arc radius at 6.1 h of immersion, as shown in Fig. 1. The inductive component also disappears slowly, due to the same reason[13]. Meanwhile, the corrosion process causes an increase in the surface irregularity and leads to the surface roughness, which can explain why the capacitive semi-circle is depressed[9]. The EIS feature of the rolled 8090 alloy is similar to that of the peak-aged 8090 alloy at the beginning of immersion.

Table 1 Corrosion development of rolled 8090 alloy at different immersion time

Immersion time/h	8	11.5	19.5	24.5	29.5	36	48.5
Exfoliation degree	EA	EA	EB	≥EC	ED	ED	ED

Table 2 Corrosion development of peak-aged 8090 alloy at different immersion time

Immersion time/h	12.3	24	48	72	96	120
Exfoliation degree	P	EA	EB	≥EC	> EC	ED

P: Pitting corrosion; EA: Superficial exfoliation; EB: Moderate corrosion; EC: Severe exfoliation; ED: Very severe exfoliation[14]

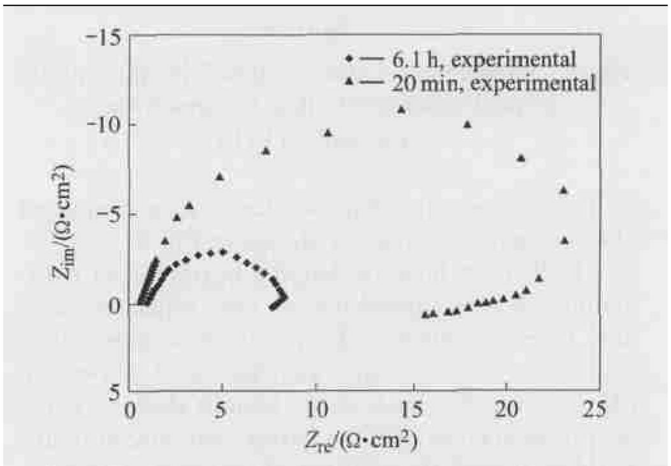

Fig. 1 Nyquist plots of peak-aged 8090 alloy without exfoliation

With prolonging the immersion time up to 8 h, exfoliation occurs on the rolled 8090 alloy surface, and two capacitive arcs appear in the EIS pattern at high-mediate frequency and mediate-low frequency respectively, as shown in Fig. 2(a). Though these two capacitive arcs overlap partially, they still can be distinguished from each other through its Bode diagram which is omitted. The exfoliation degree is increased with immersion time increasing, while the Nyquist plot is still composed of two capacitive arcs, as presented in Fig. 2(b).

At about 29.8 h of immersion, exfoliation is produced on the peak-aged 8090 alloy surface. After

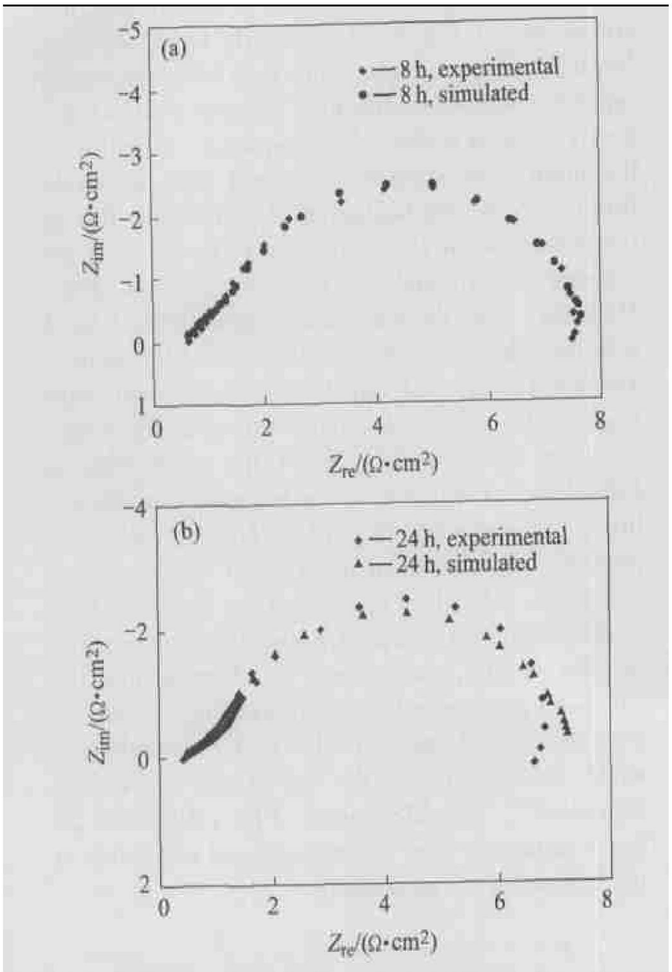

Fig. 2 Experimental and simulated Nyquist plots of peak-aged 8090 alloy immersed for 8 h(a) and 24 h(b)

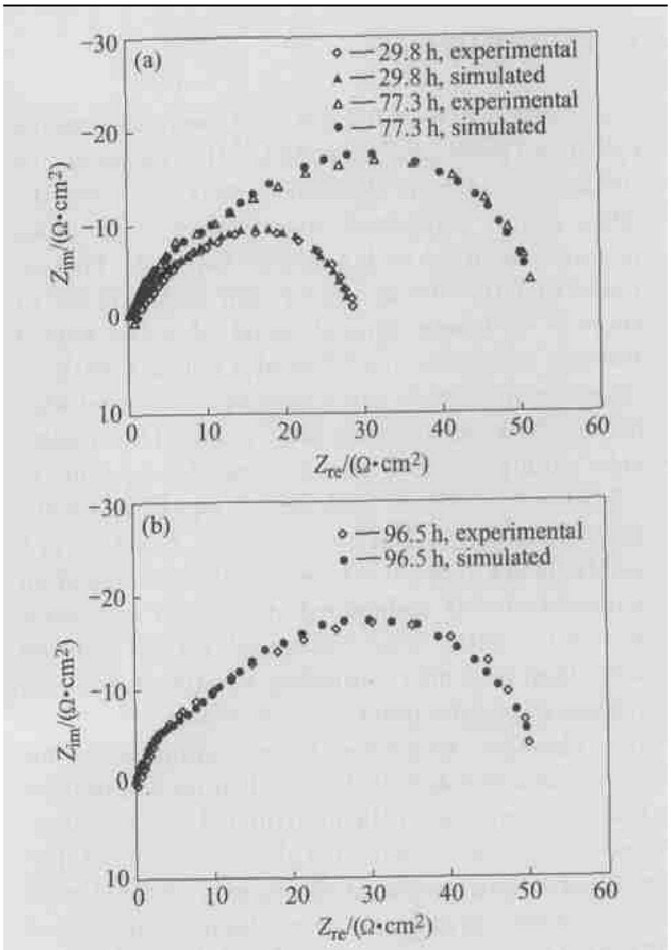

Fig. 3 Experimental and simulated Nyquist plots of peak-aged 8090 Al-Li alloy immersed for 29.8 h, 77.3 h(a) and 96.5 h(b)

exfoliation, the Nyquist ploy is also composed of two capacitive arcs, as shown in Fig. 3.

It also can be seen that the beginning of exfoliation and the appearance of two capacitive arcs have time consistency. That is to say, once exfoliation is produced, two capacitive arcs appear in EIS pattern. So Conde et al thought that the exfoliation occurrence and the exfoliation susceptibility could be judged through the appearance of two capacitive arcs in the EIS pattern[11, 12], and this method is applicable to these two 8090 alloys. In this case, two capacitive arcs appear in the EIS of the rolled 8090 alloy at 8 h of immersion, while for the peak-aged 8090 alloy, they do not appear until 29.8 h of immersion. Accordingly, the rolled 8090 alloy is more susceptible to exfoliation than the peak-aged 8090 alloy.

The exfoliation-attacked 8090 alloy surface is composed of two parts, an original flat alloy surface and a new inter-face exposed to the outside EXCO solution through a pore or gape, as shown in Fig. 4. According to this exfoliation structure, an equivalent circuit model is designed as Fig. 5[11, 12]. In this equivalent circuit, R_s is the electrolyte resistance, which can be neglected. The capacitance correspond-

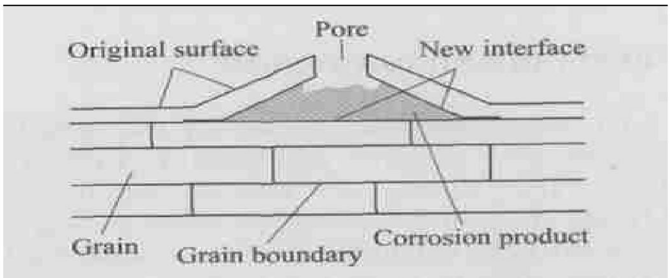

Fig. 4 Schematic diagram of exfoliation-attacked 8090 Al-Li alloy surface

ing to the flat surface is defined by C_1. The resistance and the capacitance corresponding to the new inter-face are described as R_2 and C_2 respectively, while R_{po} is the resistance through the pore or gape.

A better simulation between the model and the experimental data can be obtained if the capacitance in this circuit is replaced with constant-phase element (CPE), which is defined by the following equation:

$$Z_{CPE} = Z_0/(j\omega)^{\alpha} \qquad (1)$$

where Z_0 and α are constants, ω is the angular frequency, and $j=\sqrt{-1}$. For $\alpha=1$, Z_{CPE} represents

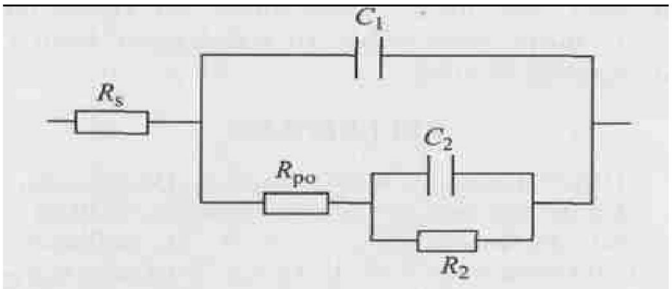

Fig. 5 Equivalent circuit used for this study

an ideal capacitance; α= 0, a resistance; α= − 1, an inductance; and α= 0.5, a Warburg impedance.

Table 3 and Table 4 list the simulated data of the rolled and peak-aged 8090 Al-Li alloys respectively. For these two alloys, R_s is very low and maintains stable. However, R_{po} of the peak-aged 8090 alloy is ten times higher than that of the rolled alloy. It is known that the new inter-face of exfoliation is connected to the outside EXCO solution through a pore or gape, and R_{po} is the resistance through this pore or gape. It is found that the pore on the peak-aged 8090 alloy surface is small, while, the wedge-shaped gape on the rolled 8090 alloy surface is much larger. This can explain why R_{po} of the rolled 8090 alloy is much lower than that of the peak-aged 8090 alloy.

R_2 and C_2 have direct relation to the new inter-face area of exfoliation. Higher C_2 and lower R_2 indicate larger new inter-face of exfoliation or greater exfoliation degree. So C_2 of the rolled 8090 alloy is higher than that of the peak-aged 8090 alloy.

Fig. 6 shows the regular relationship between simulated capacitance C_2 and immersion time. For these two alloys, after exfoliation, the C_2 vs time curve is divided into two parts. C_2 is increased approximately linearly with time at the first, and then maintains stable at a later immersion stage.

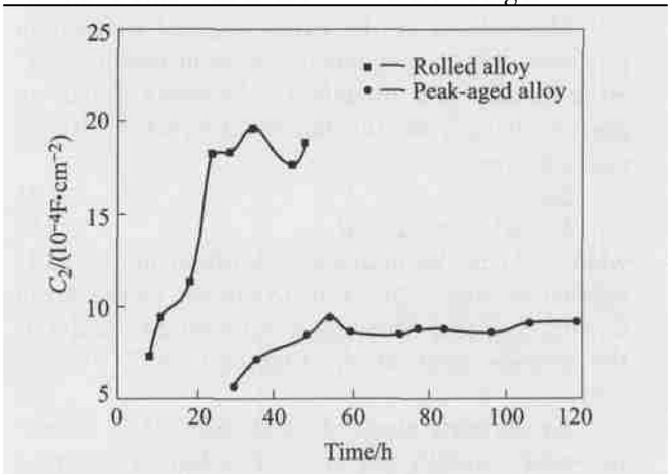

Fig. 6 Regular relationship between simulated capacitance and immersion time

Table 3 Simulated data for EIS of rolled 8090 alloy

Time/h	R_s/(Ω•cm^2)	C_1/(F•cm^{-2})	$α_1$	R_{po}/(Ω•cm^2)	C_2/(F•cm^{-2})	$α_2$	R_2/(Ω•cm^2)
8	4.16	1.22×10^{-3}	0.722	10.85	7.24×10^{-4}	0.899	38.48
11	2.63	1.0×10^{-3}	0.650	11.39	9.39×10^{-4}	0.818	71.4
18.8	2.63	7.82×10^{-4}	0.689	6.19	1.12×10^{-3}	0.842	70.8
24	2.80	6.02×10^{-4}	0.725	3.56	1.82×10^{-3}	0.758	41.39
29	6.48	8.91×10^{-4}	0.662	4.04	1.83×10^{-3}	0.802	38.89
35	2.77	1.19×10^{-3}	0.665	5.41	1.95×10^{-3}	0.787	41.92
45	2.78	1.45×10^{-3}	0.630	7.21	1.75×10^{-3}	0.801	51.05
48	3.98	1.28×10^{-3}	0.627	7.45	1.88×10^{-3}	0.772	49.17

Table 4 Simulated data for EIS of peak-aged 8090 alloy

Time/h	R_s/(Ω•cm^2)	C_1/(F•cm^{-2})	$α_1$	R_{po}/(Ω•cm^2)	C_2/(F•cm^{-2})	$α_2$	R_2/(Ω•cm^2)
29.8	4.31	9.439×10^{-4}	0.777	102	5.570×10^{-4}	0.976	67.68
35.8	5.07	3.757×10^{-4}	0.807	125.46	7.022×10^{-4}	0.905	162.96
48.3	6.02	3.324×10^{-4}	0.817	135.18	8.462×10^{-4}	0.867	164.76
54.7	4.23	3.259×10^{-4}	0.823	110.22	9.287×10^{-4}	0.887	120.66
60.3	4.03	2.982×10^{-4}	0.830	131.16	8.515×10^{-4}	0.890	159.06
72.5	5.34	3.328×10^{-4}	0.818	121.50	8.433×10^{-4}	0.880	145.92
77.3	5.20	2.824×10^{-4}	0.834	126.12	8.710×10^{-4}	0.873	185.10
84	5.87	2.782×10^{-4}	0.836	127.20	8.701×10^{-4}	0.853	198.72
96.5	4.35	2.809×10^{-4}	0.837	112.92	8.531×10^{-4}	0.856	194.88
106	5.1	2.513×10^{-4}	0.847	117.12	9.038×10^{-4}	0.743	306.12
119	8.95	2.371×10^{-4}	0.850	129.60	9.073×10^{-4}	0.738	357.0

It is known that capacitance C_2 can be defined by the following equation:

$$C = \varepsilon \cdot S/d \quad (2)$$

where ε is the dielectric constant, S is the new inter-face area of exfoliation, and d is the thickness of the double-layer or corrosion product on the new inter-face. C_2 is in direct proportion to the new inter-face area and in inverse proportion to the thickness d. It is rational that the exfoliation degree should be increased with S increasing. That is to say, exfoliation also should be increased with C_2 increasing.

Meanwhile, at the early stage of exfoliation process, there is not much corrosion product covering on the new inter-face, thickness d has no greater change, so the following equation can be easily deduced.

$$\Delta C_s \propto \Delta S \quad (3)$$

$$k = \Delta C_s / \Delta t \propto \Delta S / \Delta t \quad (4)$$

where Δt is the immersion duration of the early exfoliation stage, ΔC_2 and ΔS are the increment of C_2 and S during immersion duration Δt, and k is the average slope of the first part of C_2 vs time curve.

At the early stage of exfoliation, if C_2 increases more rapidly, the new inter-face is enlarged more quickly, and exfoliation should also develop more quickly. So, the exfoliation susceptibility would be judged through the average slope k of the first part of C_2 vs time curve. In this study, the slope k of the rolled 8090 alloy is about 6.85×10^{-5} F/(cm^2·h), much higher than that of the peak-aged 8090 alloy, 1.56×10^{-5} F/(cm^2·h). Accordingly, the rolled 8090 alloy is more susceptible to exfoliation than the peak-aged 8090 alloy.

4 CONCLUSIONS

1) At the beginning of immersion in EXCO solution, the Nyquist plot of rolled and peak-aged 8090 Al-Li alloys is comprised by a depressed capacitive arc at high-mediate frequency and an inductive arc at mediate-low frequency. Once exfoliation occurs, two capacitive arcs appear at high-mediate frequency and mediate-low frequency respectively.

2) The exfoliation-corroded alloy surface consists of two parts, an original flat alloy surface and a new inter-face exposed to the outside EXCO solution due to the exfoliation. The capacitance(C_2) corresponding to the new inter-face is increased approximately linearly with time prolonging at early exfoliation stage, due to the enlargement of the new inter-face of exfoliation; then it maintains stable at a later immersion stage, due to the corrosion product covering on the new inter-face.

3) The exfoliation susceptibility can be judged through the average slope of the first part of C_2 vs immersion time curve. The average slope of the rolled 8090 alloy is much higher than that of the peak-aged 8090 alloy, accordingly the rolled 8090 alloy is more susceptible to exfoliation than the peak-aged 8090 alloy.

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