

Article ID: 1003 - 6326(2003)02 - 0320 - 05

Investigation of exfoliation corrosion of rolled AA8090 Al-Li alloy using electrochemical impedance spectroscopy^①

LI Jir-feng(李劲风)¹, ZHANG Zhao(张昭)¹, CAO Fa-he(曹发和)¹,
CHENG Ying-liang(程英亮)¹, ZHANG Jian-qing(张鉴清)^{1, 2}, CAO Chu-nan(曹楚南)^{1, 2}
(1. Department of Chemistry, Zhejiang University, Hangzhou 310027, China;
2. State Key Laboratory for Corrosion and Protection, Institute of Metal Research,
Chinese Academy of Sciences, Shenyang 110016, China)

Abstract: The exfoliation morphologies and electrochemical impedance spectroscopy (EIS) features of as-received rolled AA8090 Al-Li alloy in EXCO solution were studied. The EIS was simulated using an equivalent circuit. The results show that once the exfoliation occurs, the EIS is composed of two capacitive arcs at high frequency and medium low frequency; among them, the capacitance corresponding to high frequency (C_1) is originated from original flat alloy surface, while the capacitance corresponding to medium low frequency (C_2) from new interface exposed to EXCO solution due to the exfoliation and the ratio of C_2 to C_1 increases with exfoliation degree. It is advanced that the exfoliation degree can be quantitatively judged through this ratio.

Key words: rolled AA8090 Al-Li alloy; exfoliation degree; electrochemical impedance spectroscopy (EIS)

CLC number: TG 174.3

Document code: A

1 INTRODUCTION

Al-Li alloys, compared to traditional Al alloys, have more excellent properties, such as lower density, greater elastic modulus and higher specific strength^[1, 2]. In the near future, they will 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 exfoliation depth from this resistance. The exfoliation susceptibility of LY12-T3 and LY12-T6 alloys was distinguished through the exfoliation depth.

It is generally thought that exfoliation corrosion is developed from intergranular attack. During corrosion process, the corrosion product accumulates on 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 AA2090 and AA8090

alloys in EXCO solution and found that the highest force is different due to various heat treatments. 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.

The purpose of this work is to study the exfoliation of rolled AA8090 Al-Li alloy using electrochemical impedance spectroscopy (EIS), try to find out some regular relationships between exfoliation degree and EIS features, and develop an electrochemical method for judging exfoliation degree quantitatively.

2 EXPERIMENTAL

The alloy used for this study was as-received rolled AA8090 plate with a thickness of 3 mm. Specimens were cut from the alloy plate, connected to a copper wire, then mounted on epoxy with a surface exposed. The exposed surface with an area of approximate 3 cm × 2 cm was ground using abrasive papers through 500 grit to 1 200 grit, polished with diamond paste, rinsed using acetone, degreased with deionized water and then dried in air. The accelerated exfoliation test was performed according to EXCO test of ASTM G 34 - 79^[9]. The EXCO solution of 4.0 mol/L NaCl + 0.5 mol/L KNO₃ + 0.1 mol/L HNO₃ (pH = 0.4) was used and solution temperature was maintained at 25 °C in a thermostat water bath.

① **Foundation item:** Project (50271066) supported by the National Natural Science Foundation of China; Project (G19990650) supported by the State Key Fundamental Research and Development Program of China

Received date: 2002 - 05 - 08; **Accepted date:** 2002 - 10 - 28

Correspondence: Dr. LI Jir-feng, Tel: + 86-571-87952318, E-mail: jfli2000@163.net

The volume of EXCO solution was about 150 mL, providing ratio of solution volume to metal surface of 25 mL/cm².

The test specimens were continuously immersed in the EXCO solution for different durations. Before the end of immersion, EIS was measured with a CHI660A Electrochemical Workstation at the open-circuit potential and always carried out from high frequency of 20 kHz to low frequency of 5 μHz. Then the exfoliation morphologies were recorded by a Nikon Coolpix995 Digital Camera and the ratings were judged by naked eyes according to ASTM G34–79. Meanwhile, the EIS was simulated through a Zview Program.

3 RESULTS AND DISCUSSION

3.1 Corrosion morphology

Due to the low pH of the EXCO solution, corrosion occurs on the rolled alloy rapidly. After 12 h of immersion, some blisters appear on specific zones of the surface, which can be distinguished through naked eyes, as can be seen in Fig. 1(a). After 24 h, delamination with exfoliation degree EB is produced (Fig. 1(b)). While after 36 h and 48 h, the exfoliation is very severe (Figs. 1(c), (d)), the exfoliation degree is ED according to ASTM G34–79. So it is indicated that the exfoliation is aggravated with the increase of immersion time, though some corrosion morphologies for different immersion time are not displayed.

3.2 EIS features

The EIS patterns of the rolled alloy in EXCO solution are shown in Figs. 2, 3 and 4. It is clearly seen that the Nyquist plots are mainly comprised by a depressed capacitive arc at high-mediate frequency and an inductive loop at low frequency at the beginning of immersion. 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 low frequency^[10]. 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 2 h of immersion. The inductive component also disappears slowly, due to the same reason^[10]. 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^[11].

With prolonging the immersion time up to 12 h, exfoliation with degree EA is produced, another capacitive arc appears at mediate-low frequency.

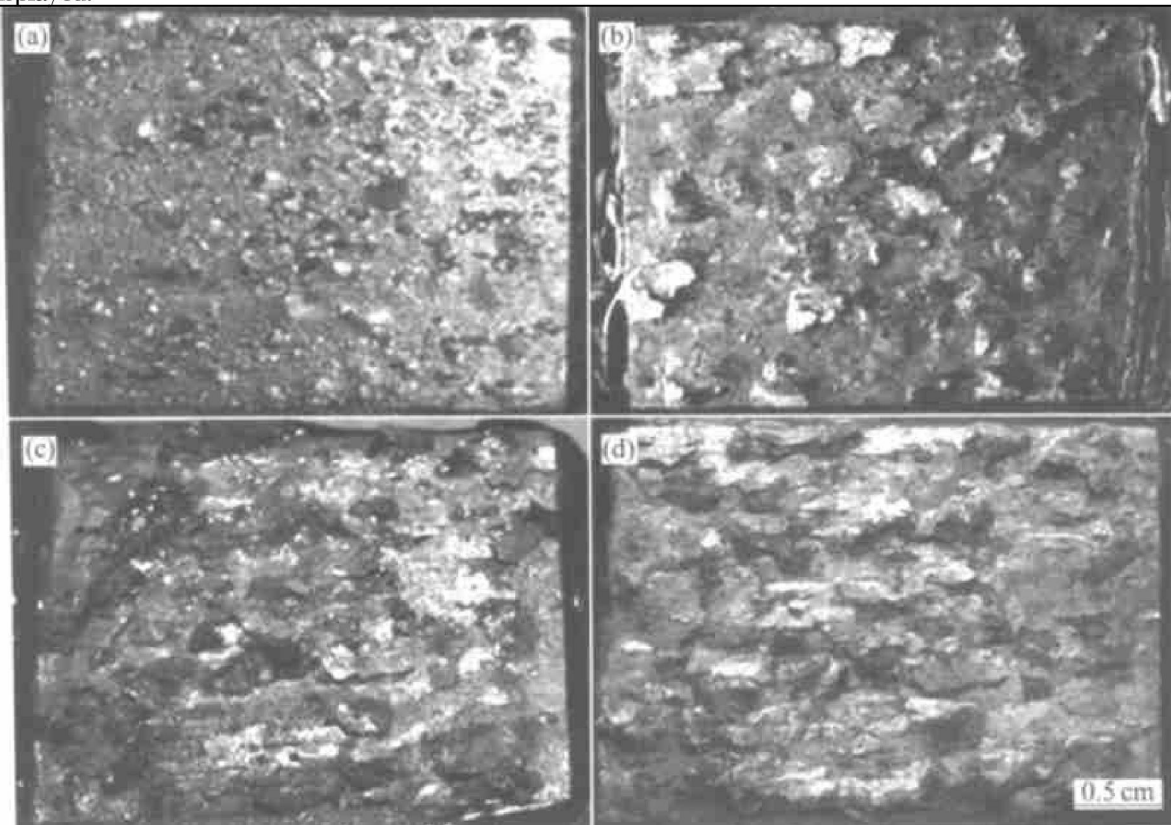


Fig. 1 Corrosion morphologies of rolled AA8090 alloy in EXCO solution for different immersion durations (sample dimension 3 cm × 2 cm)
(a) –12 h; (b) –24 h; (c) –36 h; (d) –48 h

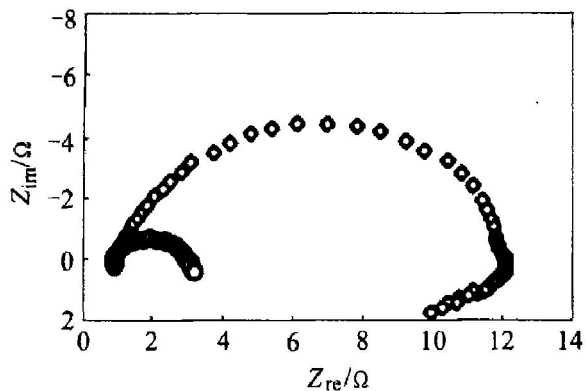


Fig. 2 Nyquist plots of rolled AA8090 alloy in EXCO solution for different durations
 ◇—10 min, ○—2 h

Though these two capacitive arcs overlap partly, they still can be distinguished from each other through the Nyquist plots and the Bode diagrams in Fig. 3 and Fig. 4. The exfoliation-attacked surface is obviously composed of two parts, one is an original flat alloy surface, the other is a new interface exposed to the EXCO solution due to the exfoliation. According to Refs. [11, 12], the capacitive arc at high frequency is originated from the original flat surface, while that at mediate-low frequency from the new interface.

3.3 EIS simulation and discussion

The schematic diagram of exfoliation-corroded surface is presented in Fig. 5. Usually the original flat surface is covered with a thin oxide film or corrosion product film. According to this exfoliation structure, an equivalent circuit model is designed as Fig. 6^[10, 11]. In this equivalent circuit, R_s is the electrolyte resistance, which can be negligible. The resistance corresponding to the original flat surface is represented by R_1 and the capacitance corresponding to this surface is defined by C_1 . The charge transfer resistance and the capacitance from the new interface are described as R_2 and C_2 respectively, while R_{po} is the resistance through the pore.

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

$$Z_{CPE} = Z_0 / (j\omega)^\alpha \quad \text{or} \quad Y_{CPE} = 1 / Y_0 \cdot (j\omega)^\alpha$$

where Z_0 (or Y_0) and α are constants, ω is angular frequency, and $j = \sqrt{-1}$. For $\alpha = 1$, Z_{CPE} represents an ideal capacitance; $\alpha = 0$, a resistance; $\alpha = -1$, an inductance; and $\alpha = 0.5$, a Warburg impedance.

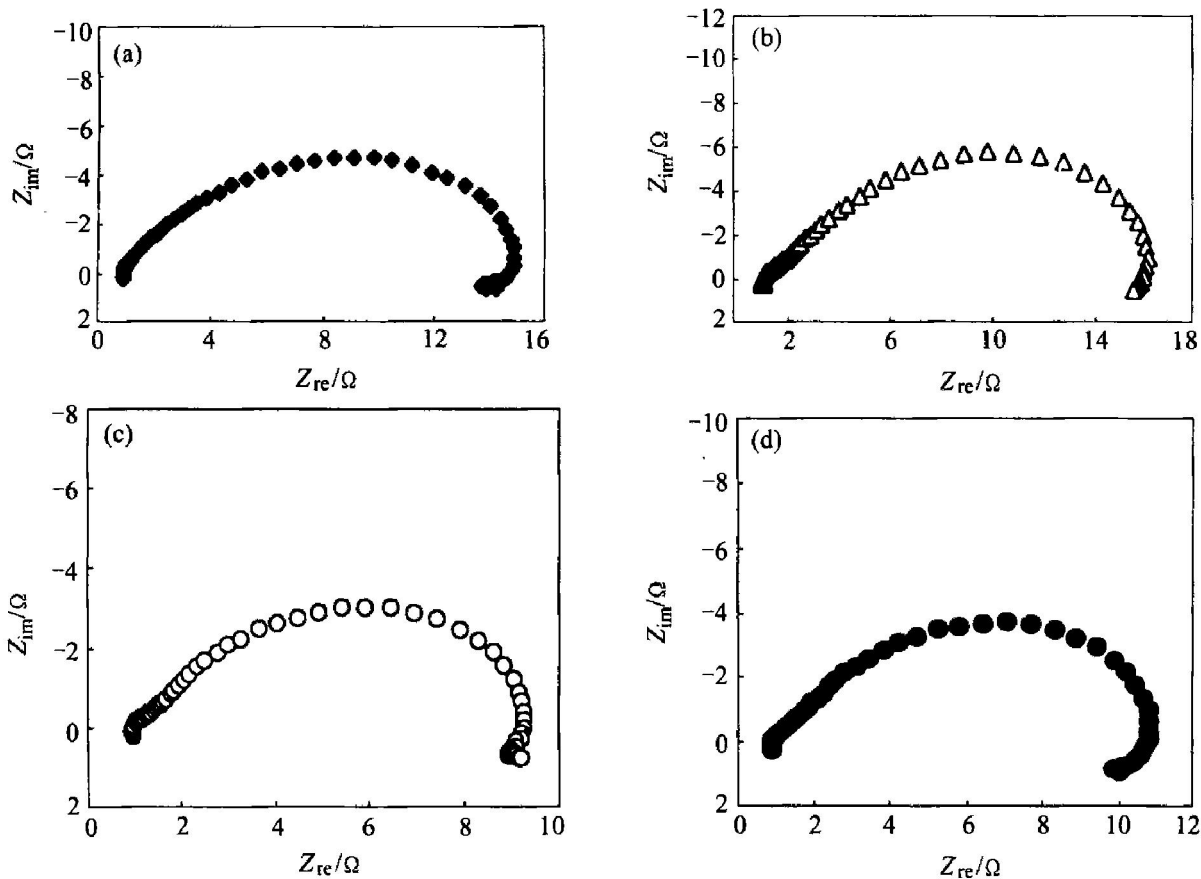


Fig. 3 Nyquist plots of rolled AA8090 alloy in EXCO solution for different durations
 (a) —12 h; (b) —24 h; (c) —36 h; (d) —48 h

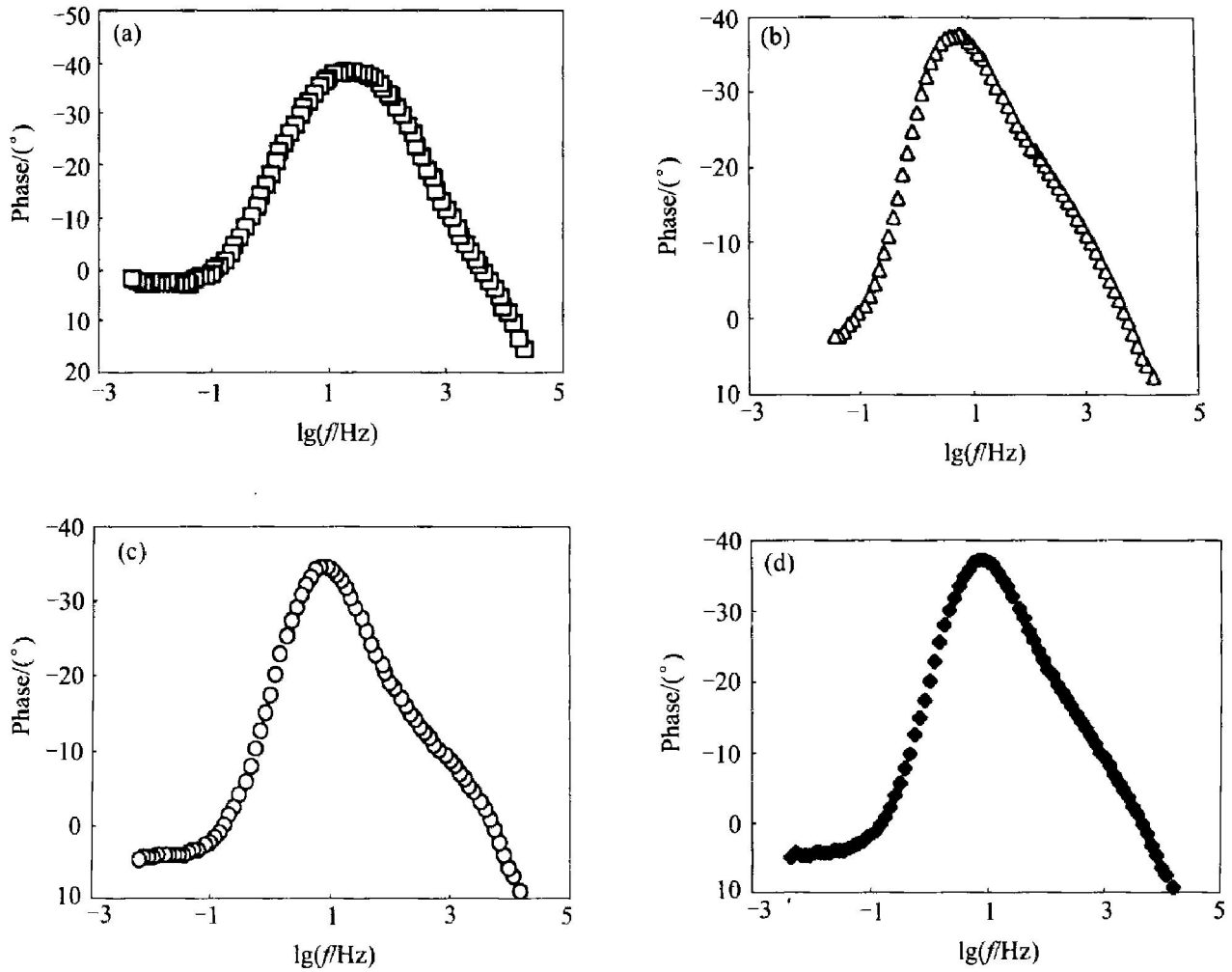


Fig. 4 Bode (phase) diagrams corresponding to relevant Nyquist plots
(a) -12 h; (b) -24 h; (c) -36 h; (d) -48 h

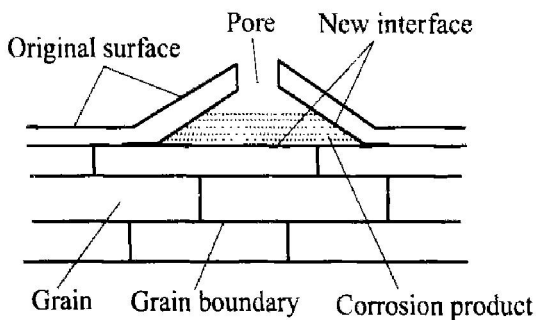


Fig. 5 Schematic diagram of exfoliation structure

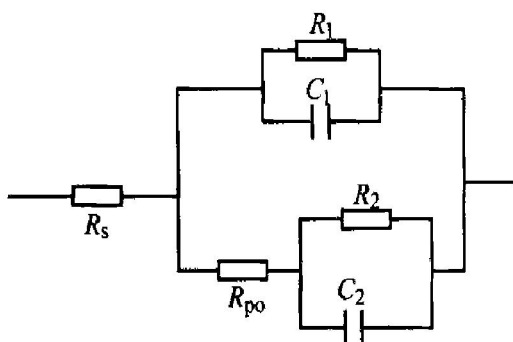


Fig. 6 Equivalent circuit used for this study

The simulated results are consistent with Conde's view^[11, 12] on the origin of capacitive components at high frequency and mediate-low frequency. The simulated parameter values are displayed in Table 1. It is found that C_1 decreases with immersion time, indicating the decrease of the original flat surface area or the thickening of the film due to corrosion. A trend, that C_2 increases with the immersion time, also can be found. Maybe because of loss of some delaminated surface layer, C_2 value at 47 h is a little less than that at 36 h.

It is known that capacitance is defined by the following equation:

$$C = \epsilon \cdot S / d \tag{1}$$

where ϵ is dielectric constant, S is the area of surface or interface, and d is the thickness of the film or the double-layer. Then

$$C_1 = \epsilon_1 \cdot S_1 / d_1 \tag{2}$$

$$C_2 = \epsilon_2 \cdot S_2 / d_2 \tag{3}$$

where S_1 and S_2 are the areas of the original flat surface and the new interface respectively, while d_1 and d_2 represent the thickness of the film and the double-layer. So

Table 1 Simulated EIS information for exfoliation corroded alloy in EXCO solution

Time/h	R_1/Ω	$10^3 C_1/F$	α_1	R_2/Ω	$10^3 C_2/F$	α_2	C_2/C_1
12	31	6.0	0.67	16.00	5.6	0.82	0.93
24	30	5.4	0.75	11.00	8.0	0.80	1.48
36	39	4.2	0.82	10.05	12.0	0.77	2.85
47	57	3.3	0.83	10.90	10.0	0.80	3.03

$$C_2/C_1 = k \cdot \frac{S_2}{S_1} \quad (4)$$

$$\text{where } k = \frac{\varepsilon_2}{\varepsilon_1} \cdot \frac{d_1}{d_2}$$

That is to say, the ratio of C_2 to C_1 (C_2/C_1) is in direct proportion to the ratio of the new interface area to the original surface area. An enlargement in C_2 will indicate the increase of exfoliation degree. So it is possible that exfoliation degree can be judged through the value of C_2/C_1 . In this case, this ratio at 12 h of immersion time is about 0.93 and the corresponding exfoliation degree is EA. At 24 h of immersion, it is increased to 1.48 with exfoliation degree EB. While it is 2.85 and 3.03 at 36 h and 47 h respectively, corresponding to exfoliation degree ED. This means that the value of C_2/C_1 increases with the increase of exfoliation degree or immersion time. Thus, it seems that the EIS technique can provide quantitative information on the exfoliation degree. To develop this new method, a substantial amount of research work is being done on different aluminium alloys with various heat treatments.

4 CONCLUSIONS

1) The rolled AA8090 alloy undergoes severe exfoliation after 36 h of immersion in EXCO solution. At the beginning of immersion, the Nyquist plot is mainly comprised by a depressed capacitive arc at high/mediate frequency and an inductive arc at low frequency. When exfoliation occurs, it is composed of two capacitive arcs at high frequency and mediate/low frequency respectively.

2) The exfoliation corroded alloy surface consists of two parts, an original flat alloy surface and a new interface exposed to the aggressive EXCO solution due to the exfoliation. The capacitance at high frequency (C_1) is originated from the original flat alloy surface, and the capacitance at mediate/low frequency (C_2) from the new interface.

3) The ratio of C_2 to C_1 increases with the increase of exfoliation degree, due to the change of the new interface area and original surface area. It is rational that exfoliation degree can be judged through this ratio.

REFERENCES

- [1] HUANG Guang-jie, WANG Ling-yun. Development, application and prospect of aluminium-lithium alloys [J]. Materials Review, 1997, 11(2): 21 - 24. (in Chinese)
- [2] CUI Cheng-song, FAN Hong-bo, LAI Zhong-hong, et al. Fracture behaviour of rapidly solidified Al-2.15Li-1.28Mg-1.26Cu-0.10Zr alloy by spray deposition processing [J]. The Chinese Journal of Nonferrous Metals, 1997, 7(1): 138 - 142. (in Chinese)
- [3] HE Jiarping, CHEN Wen-Li, XU Wei, et al. Effect of exfoliation on structure and tensile strength of LC4CS aluminium alloy at constant temperature [J]. Journal of Nanjing University of Aeronautics and Astronautics, 1999, 31(5): 575 - 579. (in Chinese)
- [4] HE Bin, SUN You-chao, FAN Weixun. Influence of exfoliation corrosion on the fatigue of aluminium alloy [J]. Journal of Nanjing University of Aeronautics and Astronautics, 1998, 30(3): 306 - 310. (in Chinese)
- [5] TAN Cheng-yu, ZHENG Ziqiao, PAN Yin, et al. Effect of exfoliation corrosion on mechanical properties of Al-Li alloy [A]. ZHENG Ziqiao. Proceedings of the 2nd National Symposium on Al-Li alloys [C]. Changsha: Central South University of Technology Press, 1993. 154 - 157. (in Chinese)
- [6] LI Di, ZUO Shang-zhi, GUO Bao-lan. Study on the exfoliation corrosion behaviour of LY12 aluminium alloy [J]. Journal of Chinese Society of Corrosion and Protection, 1995, 15(3): 203 - 208. (in Chinese)
- [7] Kelly D J, Robinson M J. Influence of heat treatment and grain shape on exfoliation corrosion of Al-Li alloy 8090 [J]. Corrosion, 1993, 49(10): 787 - 795.
- [8] Habashi M, Bonte E, Galland J, et al. Quantitative measurements of the degree of the exfoliation on aluminum alloys [J]. Corrosion Science, 1993, 35(4): 168 - 183.
- [9] ASTM G34-79. Standard Test Method for Exfoliation Corrosion Susceptibility in $2 \times \times \times$ and $7 \times \times \times$ Series Aluminum Alloys (EXCO test) [S].
- [10] CAO Chun-nan, WANG Jia, LIN Hai-chao. Effect of Cl⁻ ion on the impedance of passive film covered electrodes [J]. Journal of Chinese Society of Corrosion and Protection, 1989, 9(4): 261 - 270. (in Chinese)
- [11] Conde A, de Damborenea J. Evaluation of exfoliation susceptibility by means of the electrochemical spectroscopy [J]. Corrosion Science, 2000, 42(8): 1363 - 1377.
- [12] Conde A, de Damborenea J. Electrochemical modeling of exfoliation corrosion behavior of 8090 alloy [J]. Electrochimica Acta, 1997, 43(8): 849 - 860.

(Edited by HUANG Jirong)