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Corrosion behavior of LY12CZ aluminum alloy in simulated acid rain solution^①

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Abstract: The variations of corrosion potential, electrochemical impedance and surface morphology of LY12 aluminum alloy with pH of simulated acidic rain solutions were investigated with EIS and SEM. It is found that corrosion potential shifts to less noble value with increasing pH in the solutions of pH lower than 3.1 and shifts to more noble value in the solutions of pH higher than 3.1. In the solutions of pH lower than 3.1, the electrochemical impedance diagram has a capacitive loop at higher frequency and an inductive loop at lower frequency and the magnitude of high frequency loop decreases with decreasing pH and increasing period of immersion. However, in the solutions of pH higher than 3.4 two capacitive loops appear and the magnitude of high frequency loops increases with pH and period of immersion. Observation of SEM shows that the pitting intensity increases with decreasing pH in the range of pH 2.0~3.4, no evident pits are observed at pH higher than 3.4. The experiment results were discussed from resistance of oxide film and adsorption processes of anions in simulated acid rain solution.

Key words: acid rain; aluminum alloy; impedance; SEM

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1 INTRODUCTION

Aluminum and aluminum alloy represent an important category of material due to high technology value and wide range of industrial application, especially in aerospace and household industries. Aluminum and its alloy, however, are active materials and are prone to corrosion whether in atmosphere or bulk solution environment.

Atmospheric corrosion is mainly deterioration type of aluminum and its alloys which can be accelerated by atmospheric pollutants. Atmospheric pollutants are transported principally in two ways to the surface of metals, namely by dry and wet deposition processes. This leads to the fact that the atmospheric constituents found on the metal surface are as abundant as in the atmosphere. Among them sulfates, nitrates, chlorides, carbonates, hydrogen ions, ammonium, metal ions, atmospheric particles and also organic compounds are commonly found constituents of electrolytes or corrosion layers and have an effect on the corrosion processes. Acid rain is a wet deposition due to atmospheric pollution which dissolved many kinds of aggressive ions such as Cl^- , SO_4^{2-} , NO_3^- , H^+ . There were many investigations on the effects of atmospheric pollutants such as SO_2 , NO_2 , NO , Cl^- or their

solutions respectively on corrosion of aluminum^[1-4], however, the investigations were less relatively on corrosion behavior of aluminum alloys in acid rain dissolving several aggressive ions^[5, 6]. The effects of pH of simulated acid rain on corrosion behavior of aluminum alloy with EIS and SEM are studied in the present paper.

2 EXPERIMENTAL

Experimental specimens were made of LY12CZ aluminum alloy, which were mounted with epoxy resin and area exposed is 1 cm^2 . The specimen surface was prepared by wet abrading with silicon carbide paper of 350, 600, 1 000 grit in turn and then washed with acetone and bidistilled water, dried and kept in desiccator for 24 h to keep the oxide film to be formed.

The simulated rain solutions were prepared from bidistilled water and analytical grade reagents. Composition of simulated acid rain solution is shown in Table 1^[7]. The pH of simulated acid rain solutions ranged from 2.0 to 4.5 with the addition of sulfuric acid. The temperature of solution was maintained at $25 \pm 0.5 \text{ }^\circ\text{C}$ through the whole experiment.

Electrochemical impedance was measured by a So-

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lartron 1260 frequency response analyzer connected with a Solartron 1286 potentiostat. The amplitude of potential modulation was 10 mV. Impedance measurements were done at the rest potential in the frequency range of 0.02 ~ 20 000 Hz. SCE was employed as the reference electrode and platinum electrode as counter electrode. The specimens were immersed in solution for 1 h and 2 h respectively and then the EIS was determined.

The specimens for SEM observation were immersed in solutions with different pH values for 72 h. The Philips XL30 scanning electron microscopy was used to investigate the variation of surface morphology of LY12 aluminum alloy with pH value of solutions.

Table 1 Composition of solution employed as simulated acid rain^[7] (10^{-3} g/dm⁻³)

SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺
0.274	0.099	0.052	0.223	0.126	0.045	0.055	0.212

3 RESULTS AND DISCUSSION

3.1 Relation of corrosion potential with pH value of acid rain solutions

Fig. 1 shows the relation between the corrosion potential and pH value of simulated acid rain solutions, which is similar to the result obtained by Magaino that zinc corrosion in simulated acid rain was tested^[6]. It is seen that the corrosion potential shifts to less noble value with increasing pH in the range of pH 2.0~ 2.7 and shifts to more noble value in the solutions of pH higher than 3.1. According to the mixed potential theory, the corrosion potential shifts to more noble value with increasing concentration of oxidizing agent while the corrosion rate is determined by the charge transfer processes. The variation of corrosion potential in the pH range of 2.0~ 2.7 observed in the present work is explained by considering the above model. If the thickness of oxide film, through which metal ions diffusion increases with increasing pH and decay of local anodic current, exceeds that of a local cathodic current, then the corrosion potential will certainly shift to more noble value. Thus, the corrosion potential shift observed in the pH range of 3.4~ 4.5 might be due to the phenomenon described above.

3.2 Electrochemical impedance

Fig. 2 shows the variation of the electrochemical impedance diagram with the pH value of simulated acid rain solutions. It is seen from Fig. 1 that the EIS comprises a capacitive loop at higher frequency and an inductive loop at lower frequency in the range of pH 2.0~ 3.1; at pH 3.4 the inductive loop is not very evident. However,

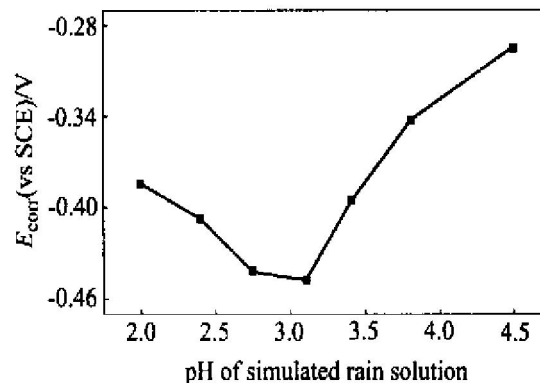


Fig. 1 Relation between corrosion potential and pH value of solution

there are a capacitive loop at low and high frequency respectively in the solutions of pH 3.8 and 4.5.

It is well known that inductive loops are obtained under the specific conditions of adsorption and desorption^[8, 9]. There are many kinds of anions in simulated acid rain solutions employed here whose adsorption and desorption processes can occur through forming the intermediates^[10]. For aluminum and aluminum alloys, the inductive loop can be connected with the pitting processes^[11]. Thus it can be deduced from impedance that aluminum alloy pitting corrosion will occur in simulated acid rain of pH 2.0~ 3.1.

It also can be seen from Fig. 2 that the magnitude of impedance diagram at higher frequency decreases with decreasing pH in the whole range of pH investigated, the magnitude of higher frequency loop decreases with increasing immersion time in the range of pH 2.0~ 2.7. This is contrary to the situation following the immersion in the solutions of pH higher than 3.4. Its magnitude value increases with increasing immersion time. The variation of magnitude of impedance diagram with immersion time at pH 3.1 might be due to the fact that the immersion was too short to be differed. It had been reported that higher frequency loop corresponds to Faradic impedance and is caused by charge transfer resistance in parallel arrangement with the double layer capacitance and represents corrosion rate^[12]. On the other hand, the lower frequency capacitive loop probably arises from the diffusion process at relatively higher pH^[13]. The oxide film resistance and the composition of solutions decide the high frequency impedance. The high frequency impedance in the whole range of investigated pH will be influenced by the composition of solution employed here. In this work of low pH range, it is confirmed that hydrogen evolution is the predominant cathodic process using solution containing oxygen and those with oxygen being removed^[4]. Thus the low frequency capacitive loop may give rise to the diffusion process of hydrogen ion. The oxide film

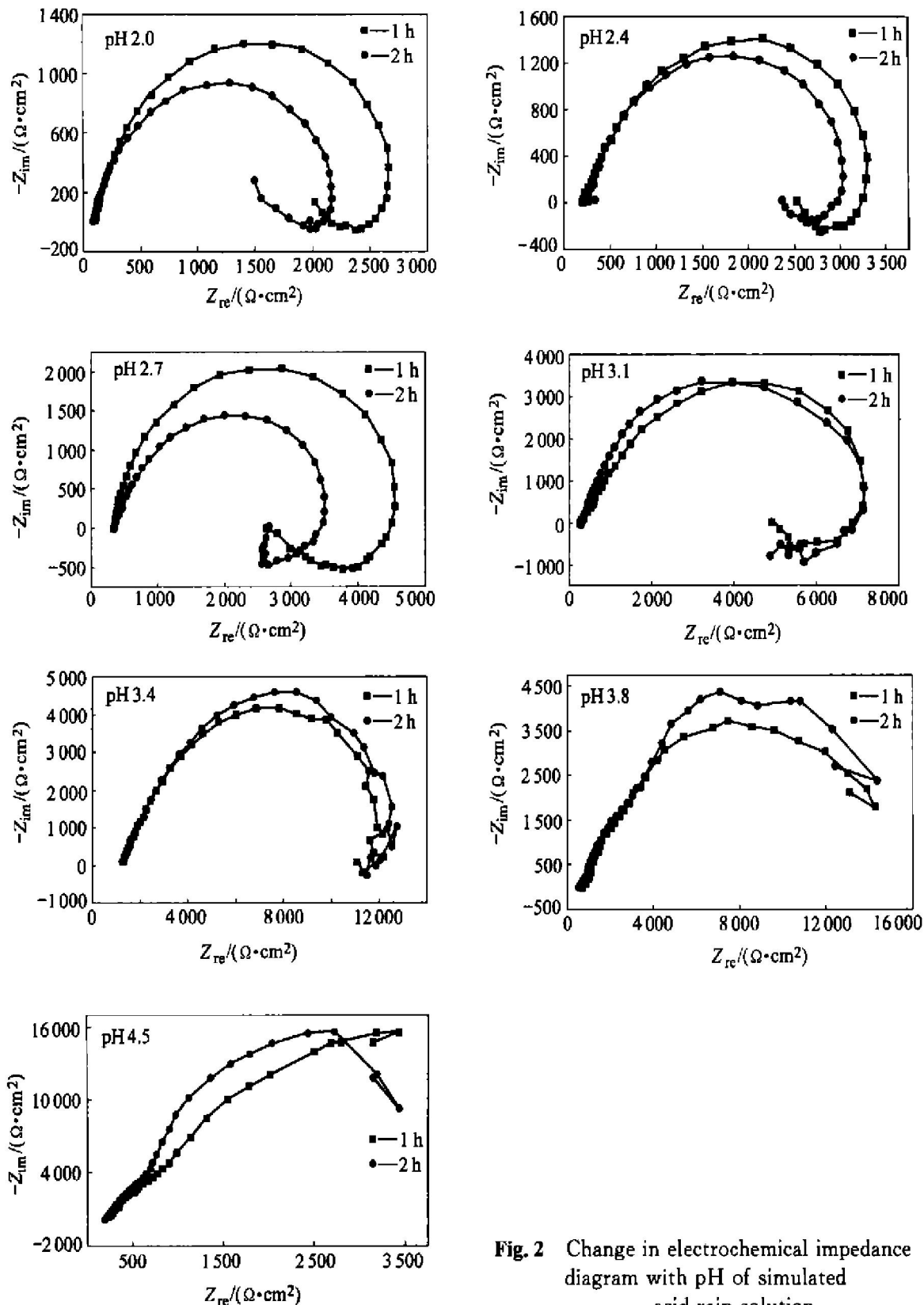


Fig. 2 Change in electrochemical impedance diagram with pH of simulated acid rain solution

resistance is mainly influenced by the thickness of oxide film and area of defect sites in oxide film with low ionic resistance. In the range of pH 2.0~ 2.7, oxide film resistance was mainly determined by the above two ways. The variation of high frequency impedance with pH and immersion time may be due to the fact that the oxide film was thinned locally and defect site increased with decreasing pH namely increasing oxidizing hydrogen ion concentration and immersion time. A thin oxide layer can give

rise to a high electric field strength permitting the occurrence of ionic migration across the oxide film, thus the pitting corrosion is intensified and corrosion rate will be accelerated.

However, in the solution of pH higher than 3.4, high frequency impedance magnitude increases with increasing immersion time. Because the oxide film of aluminum is relatively more stable in the solution whose pH value is between 4~ 9, the oxide film growth is almost

not probably in the range of pH 3.8~ 4.5, the magnitude of impedance increasing is more probably attributable to the adsorption of aggressive anions on the defect site and formation of resistive compounds. It is well known that the anions such as SO_4^{2-} , NO_3^- can occur adsorption and the adsorption will be enhanced at defective site locally which will reduce the reacting surface area and hence inhibit the pitting corrosion of aluminum alloy^[3].

3.3 SEM observation

Fig. 3 and Fig. 4 show the results of SEM observation of those specimens immersed in solutions of pH 2.0~ 3.8 for 72 h. It can be seen from Fig. 3 that the pitting corrosion is intensified with decreasing pH of simulated acid rain solutions in the range of pH 2.0~ 3.4, however, no evident pits are observed in the solutions of pH 3.8. In the range of pH 2.0~ 2.7, the pits become larger and the pits adjoined merge each other gradually with decreasing pH. While the pits formed in the solutions of pH 3.1 and 3.4 are more shallow. This can be seen more clearly from Fig. 4 that the enlarged morphology of a single pit, especially the morphology of pits in the solution of pH 3.4. The caps of pits are confirmed to be the corrosion product of aluminum alloy by other authors^[14].

The corrosion mechanism has been discussed according to the nature of oxide film from the variation of

impedance with pH above. The result of SEM observation can also be explained by it. In the solutions of lower pH value, the thinned oxide film and high hydrogen ion concentration ensure the dissolved metal ions pass through oxide film and the pit attack continues to occur, thus the pitting intensity increases with decreasing pH and increasing immersion time. However, in the solution of relatively higher pH, due to the formation of resistive compounds the pitting corrosion rate will be reduced and pitting intensity become low.

4 CONCLUSIONS

1) In the solutions of pH lower than 3.1, the electrochemical impedance diagram has a capacitive loop at higher frequency and an inductive loop at lower frequency, the magnitude of high frequency loop decreases with decreasing pH and increasing period of immersion, which can be attributed to the dissolution of oxide film locally and defective site increasing on oxide film. However, in the solutions of pH higher than 3.4, the electrochemical impedance diagram is represented by two capacitive loops, the magnitude of high frequency loop increases with increasing pH and immersion time, which is due to anions adsorption and the formation of resistive compounds on the defective sites of oxide film.

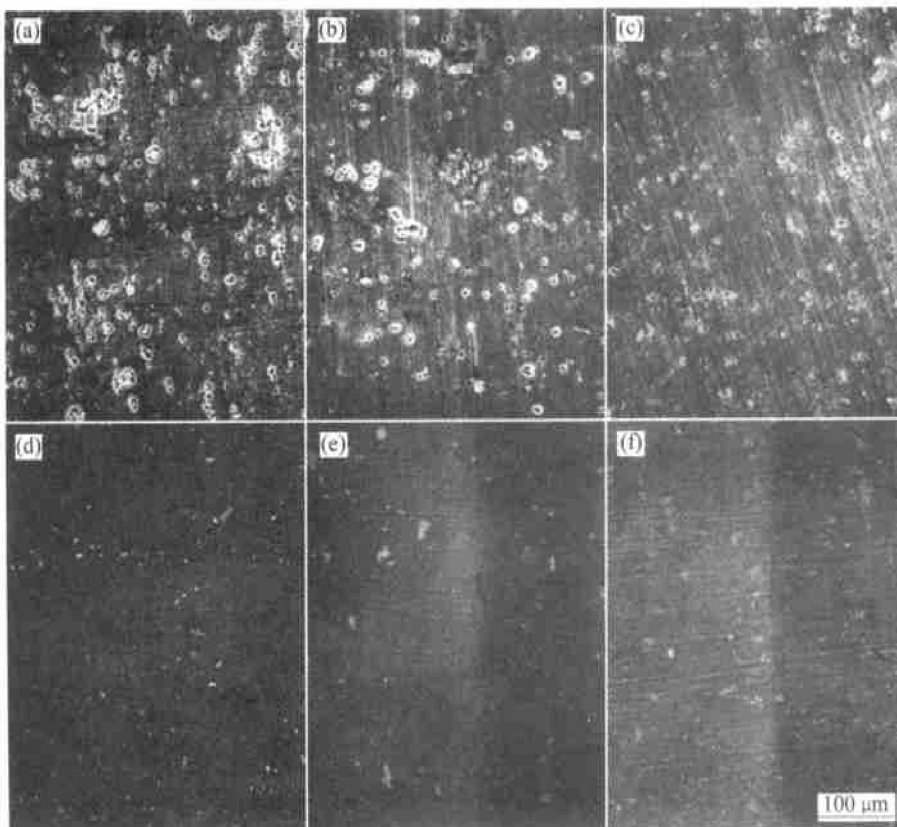


Fig. 3 Surface morphologies of LY12 aluminum alloy immersed for 72 h in simulated acid rain solutions with different pH values
(a) —pH 2.0; (b) —pH 2.4; (c) —pH 2.7; (d) —pH 3.1; (e) —pH 3.4; (f) —pH 3.8

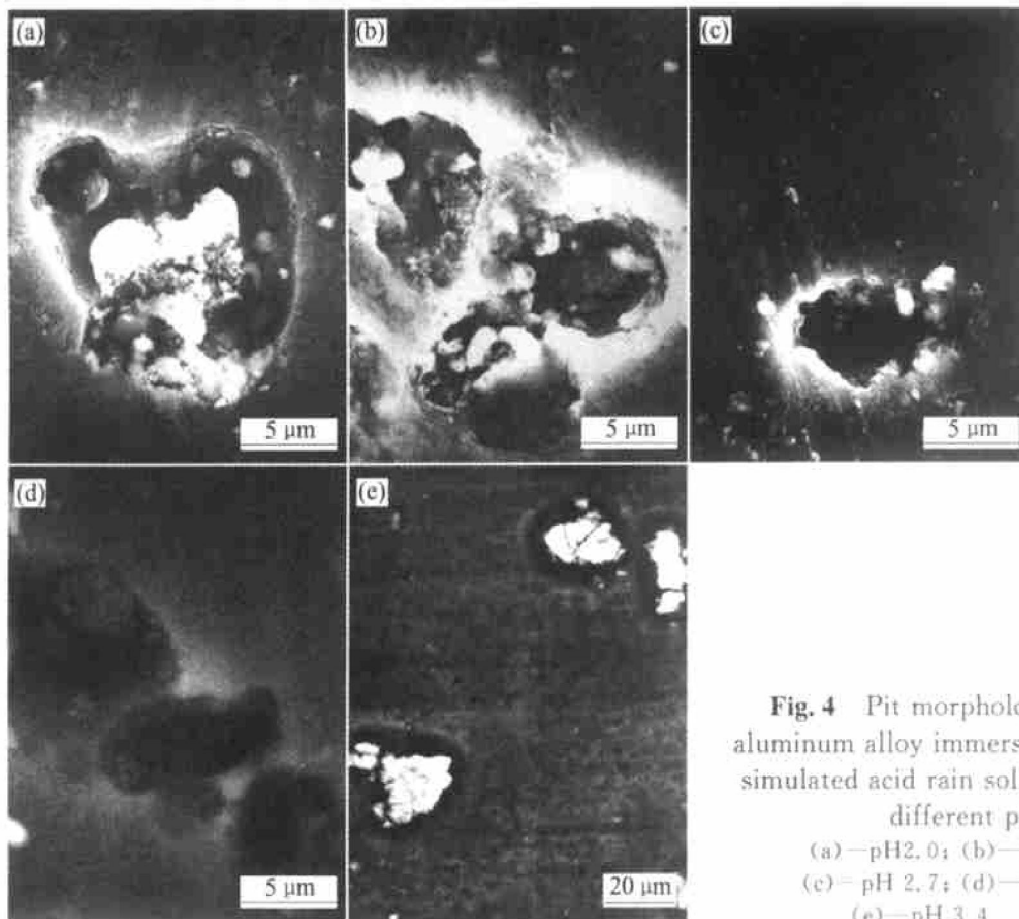


Fig. 4 Pit morphologies of LY12 aluminum alloy immersed for 72 h in simulated acid rain solutions with different pH values
 (a)—pH 2.0; (b)—pH 2.4;
 (c)—pH 2.7; (d)—pH 3.1;
 (e)—pH 3.4

2) The results of SEM observation show that the pitting intensity increases with decreasing pH in the range of pH 2.0~3.4, no apparent pits have been observed in the solutions of pH higher than 3.8. In the range of pH 2.0~2.7, because the oxide film is dissolved and thinned locally, the pitting density and intensity are higher than that in the solutions of pH 3.4~3.8, in which the pits are more shallow and covered by caps of corrosion product. It can be attributed to the anions adsorption and formation of resistive compounds which reduce the reactive surface area of aluminum alloy.

REFERENCES

- [1] Oesch S, Faller M. Environmental effects on materials: The effect of the air pollutants SO_2 , NO_2 , NO and O_3 on the corrosion of copper, zinc and aluminum. A short literature survey and results of laboratory exposures[J]. *Corros Sci*, 1997, 39(9): 1505 - 1530.
- [2] Christopher M, Brett A. On the electrochemical behavior of aluminum in acidic chloride solution[J]. *Corros Sci*, 1992, 33(2): 203 - 210.
- [3] Pyun S I, Moon S M, Ahn S H, et al. Effects of Cl^- , NO_3^- and SO_4^{2-} ions on anodic dissolution of pure aluminum in alkaline solution[J]. *Corros Sci*, 1999, 41: 653 - 667.
- [4] Wu T I, Wu J K. Effect of sulfate ions on corrosion inhibition of AA7075 aluminum alloy in sodium chloride solutions[J]. *Corrosion*, 1995, 51(3): 185 - 190.
- [5] Magaino S, Soga M, Sobue K, et al. Zinc corrosion in simulated acid rain[J]. *Electrochimica Acta*, 1999, 44: 4307 - 4312.
- [6] Magaino S. Corrosion rate of copper rotating disk-electrode in simulated acid rain[J]. *Electrochimica Acta*, 1997, 42(3): 377 - 382.
- [7] TANG Guir-gang, BAI Nar-bin. An analysis of precipitation chemistry data in China with genetic neural network[J]. *Acta Scientiae Circumstantiae*, 2000, 20(5): 542 - 547.
- [8] Epelboin I, Keddam M. Faradic impedances: diffusion impedance and reaction impedance[J]. *J Electrochem Soc*, 1970, 117: 1052 - 1056.
- [9] Keddam M, Mattos O R, Takenouti H. Reaction model for iron diffusion studied by electrode impedance[J]. *J Electrochem Soc*, 1981, 128: 257 - 266.
- [10] Foley R T. Localized corrosion of aluminum alloys—A review[J]. *Corrosion*, 1986, 42(5): 277 - 288.
- [11] Bessone J B, Mayer C E, Eber M, et al. An EIS study of aluminum barrier-type oxide films formed in different media [J]. *Electrochim Acta*, 1992, 37(12): 2283 - 2290.
- [12] Epelboin I, Gabrielli G, Keddam M, et al. A model of the anodic behavior of iron in sulfuric acid medium[J]. *Electrochim Acta*, 1975, 20: 913 - 916.
- [13] Cachet C, Saidani B, Wiat R. The behavior of Zinc electrode in alkaline electrolytes II. Akinetic analysis of anodic dissolution[J]. *J Electrochem Soc*, 1992, 139: 644 - 654.
- [14] Richardson J A, Wood G C. A study of the pitting of Al by scanning electron microscopy[J]. *Corros Sci*, 1970, 10: 313 - 323.