MICROBIOLOGICALLY INFLENCED CORROSION OF ALUMINIUM ALLOYS IN WATER--FUEL SYSTEMS

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ABSTRACT Microbiologically influenced corrosion (MIC) of three aluminum alloys (LC4, LC9 and LY12) in simulated aircraft water-fuel systems was studied by using electrochemical polarization techniques, SEM and EPMA. The action of metabolism of the microorganisms and the susceptibility of the alloys to pitting corrosion were discussed. It was found that the free corrosion potential (E_{corr}) and pitting potential (E_{br}) shifted negatively about 15-20mV for the alloys in the solutions with microorganisms than that without microorganisms, respectively. Of three tested aluminum alloys, LY12 alloy showed the greatest resistance to MIC.

Keyword: *Microbiologically influenced corrosion (MIC), aluminum alloys, pitting corrosion*

1. INTRODUCTON

Microbiologically influenced corrosion (MIC) of metallic materials placed in the ground and water has been recognized[1,2]. The authors have indicated that aluminum and its alloys were subjected to MIC easily[3,4]. In recent investigation, aluminum alloys used in aircraft tanks has been found as a serious problem[5].

The microorganisms in aircraft tanks were always found in the inner bottom of the fuel tanks and have been detected to be consisted of fungus such as Cladosporium Resinae, sulfate-reducing bacteria (SRB) and others[4]. The faulty tanks must be discarded because serious corrosion pit, intergranular attack and exfoliation were formed. Many researchers tried to study the mechanism of MIC to obtain the protective methods to solve these problems. In previous works, the cultivation, isolation, purification and identification of the microorganisms sampled from a fuel tank, which has been corroded, has been tried in our laboratory[5]. MIC in the fuel-water system has been observed. Electrochemical polarization techniques, SEM and EPMA were demonstrated as the useful methods to study MIC of metals[5-8].

In this paper, MIC of three aluminum alloys, LY12, LC4 and LC9, tested in fuel-water system containing sodium chloride were studied by methods of immersion tests, electrochemical polarization techniques and surface analysis. The corrosion processes of MIC of three aluminum alloys were discussed.

2. EXPERIMENTAL

2.1 Materials and reagents

The chemical composition of three tested aluminum alloys (LY12, LC4 and LC9) are Table 1. The corrosion coupons (25×50×5 mm) were cut from the metal sheet. After al scale on the surface of the coupons was removed with a common chemical method, the c were washed with 33% nitric acid and water. Then the coupons were mechanically grou silicon carbide papers and cleaned with distill water. Finally, the coupons were rinsed on with anhydrous alcohol to disinfect.

The Bushnell and Haas aqueous culture medium (B-H medium) [5,7], its compositio in Table 2, was employed to study on MIC of aluminum alloys in fuel-water system. Two the mixture solution of 3.5% NaCl + B-H medium as Solution 1 and the solution of So added with aircraft fuel as Solution 2, were used for the immersion test. Solution 2 was a system (3/1, v/v) of Solution 1 with fuel obtained directly from an aircraft fuel tank in Airport in Beijing of China. The pH values of the solutions were adjusted to about 6.0.

Table 1 Chemical composition of alloys (% , weight percent)

Alloy	Cu	Fe	Mg	Zn	Mn	Si
LY12	3.8~4.9	0.2~0.5	1.2~1.8	--	0.3~0.9	1.0
LC4	1.4~1.6	--	1.2~1.6	5.0~7.0	0.2~0.6	1.1
LC9	1.6~2.0	0.4~0.8	2.0~3.0	5.1~6.1	0.2~0.4	0.8

Table 2 Chemical composition of B-H aqueous culture medium

Compound	Concentration
$CaCl_2$	1.8×10^{-4} mol/l
$MgSO_4$	1.7×10^{-3} mol/l
K_2HPO_4	5.7×10^{-3} mol/l
KH_2PO_4	7.3×10^{-3} mol/l
NH_4NO_3	1.3×10^{-2} mol/l
$(NH_4)_2SO_4$	7.6×10^{-3} mol/l
$FeCl_3$	3.1×10^{-4} mol/l

2.2 Electrochemical measurements

A conventional three electrode systems were used for the electrochemical test, where s calomel electrode with a Luggin capillary was used as the reference electrode, platinum e as the auxiliary electrode and aluminum electrodes (1cm^2) as the working electr potentiodynamic polarization was measured by using a potentionstat (TYPE HDV-7, S China) and a potential scanner (TYPE DCG-2, Changchun, China) at a scan rate of 18 The polarization curves were plotted by a X-Y plot recorder. The pH of the solutions was with a Microcomputer pH/mV Meter (F-13, Beijing, China). The corrosion morpholog alloys was investigated by scanning electron microscopy (SEM). The contents of e elements in the alloys were determined with an Electron Probe X-ray Microanalyzer (EP

Electrochemical measurements and the morphology observation of the attacks were carried out once every five days during a 40 day test duration.

3 RESULTS AND DISCUSSION

3.1 Immersion tests

The immersion tests of the coupons for three tested aluminum alloys in two solutions described above were carried out for forty days. During the period, the surface change of coupons and the contents of microorganisms were observed once per five days. It was found that the microorganisms began to proliferate rapidly in the first 5～6th day in Solution 2, and the color changed of the solution from transparentness to brown. Some tawny precipitates were formed on the bottom of the vessels and the surface of the coupons. White flocculate emerged at the interface of water and fuel. Corrosion pits were found after removing bacterial colonies from the metal surface. However, these phenomena above were not found in Solution 1 except slight pitting on the coupons .

The corrosion morphology of alloys in two solutions after different immersion time was investigated. Fig.1 gives the results of SEM for alloy LC9 after 10 days immersed in two solutions.

a) b)

Fig1 Scanning electron micrograph (× 100) of alloy LC9 after immersion of 10 days in:
a) Solution 1; b) Solution 2

3.2 Electrochemical Measurement

The same water in Solution 2 as electrolyte was used for electrochemical corrosion measurements. The anodic polarization curves of the alloys in Solution 2 at the different time of the culture were measured by potentiodynamic sweep technique, respectively. The polarization curves of LY12 alloy in Solution 2 of the culture time of 10 days were measured as shown in Fig.2.

There were some different shape on the polarization curves in Fig.2(b) with Fig.2 (a). Pitting potential (E_{br}) moved negatively about 25mV in Fig.2(b) in comparison with that in Fig.1(a). It was considered that the microorganisms influenced the electrode reactions and complicated the electrode processes. Sequentially the corrosion attack of the alloy was accelerated due to the existence of the microorganisms. Moreover, corrosion current of the alloy in Solution 2 was higher than that in Solution 1. The similar results were obtained for LC4 and LC9 alloys. It was found

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for the alloys in the solutions with microorganisms than that without microorganisms, respe

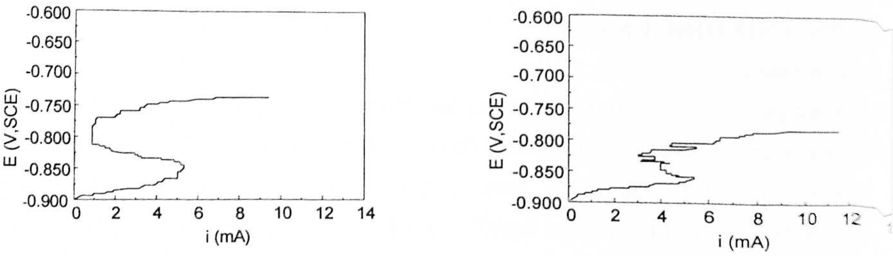

Fig.2 Anodic polarization curves of LY12 in:
a) Solution 1; b) Solution 2

The polarization curves for LC9 alloy at different culture intervals in Solution investigated. It was found that the corrosion current on the curves increased with the cultu and reached a maximum value on the 10th day, then decreased gradually with the microor culture time. The similar results were found for alloys LC4 and LY12. The changes of the of free corrosion potential (E_{corr}) and pH in Solution 2 with the time were investigated an in Fig.3. It was known that the values of free corrosion potential decreased gradually values of pH increased with the microorganism culture time. But, such changes were not f the alloys in Solution 1.

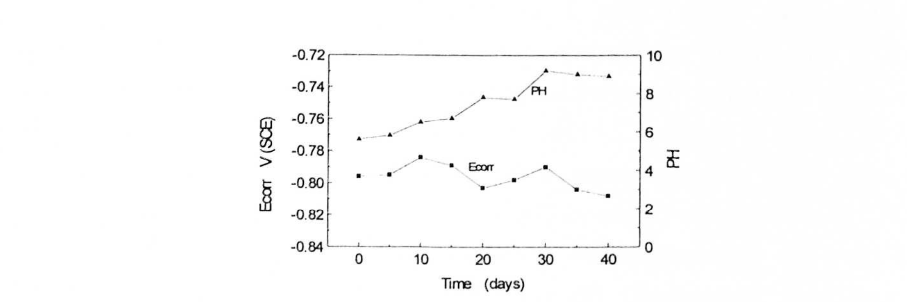

Fig.3--Time dependence of E_{corr} and pH for : a) LC9; b) LC4; c) LY12 during exposure to Soluti

The changes of corrosion current (i_{corr}), corrosion potential (E_{corr}) and pH in Solution 2 were considered to be referred to metabolism of the microorganisms. It has been known that fungus Cladosporium Riesinae generally produce organic-acid (citric acid and fatty acid etc.)[4], which lowered pH of the solutions. On the other hand sulfate-reduced bacteria consumed hydrogen in their metabolism processes. Anaerobic respiration of SRB reduced sulfate to sulfide in the solutions and accelerated cathodic depolarization reaction[8]. So there was a competition between the consuming and producing of H^+ ions. As a consequence of the cathodic depolarization reaction, the corrosion current (i_{corr}) increased and corrosion potential (E_{corr}) decreased. On the other hand, it was possible that S^{2-} anions produced by reduction of SRB were reacted with metal cations such as Al^{3+} or other ions dissolved from the alloys, and formed insoluble sulfides deposited in the pits. The products were strongly aggressive and thus caused corrosion on aluminum alloys directly. This is similar with that of the corrosion phenomena observed above.

Additionally, the insoluble corrosion products deposited on the surface of the coupons acted as small anodics of aluminum alloys and accelerated simultaneously anodic dissolution reactions. Table 3 gives the changes of the pitting potential (E_{br}) of three alloys with the test time. It was known that the values(E_{br}) for the same materials in Solution 2 always showed more negative than

Table 3 Pitting potentials(E_{br}) of three tested aluminum alloys

	Medium	Time (day)								
		0	5	10	15	20	25	30	35	40
LC9	Solution 1	-0.750	-0.763	-0.750	-0.737	-0.763	-0.754	-0.752	-0.751	-0.750
	Solution 2	-0.753	-0.767	-0.769	-0.745	-0.759	-0.768	-0.769	-0.768	-0.760
LC4	Solution 1	-0.718	-0.720	-0.725	-0.741	-0.733	-0.729	-0.728	-0.726	-0.720
	Solution 2	-0.719	-0.739	-0.750	-0.753	-0.741	-0.761	-0.764	-0.760	-0.755
LY12	Solution 1	-0.751	-0.767	-0.753	-0.745	-0.747	-0.756	-0.747	-0.748	-0.751
	Solution 2	-0.755	-0.765	-0.773	-0.748	-0.749	-0.759	-0.759	-0.756	-0.754

that in Solution 1. The minimum values of E_{br} on the 10th and 30th days were also observed. The results were identified with the changes of the contents of the microorganisms and pH of solutions measured in this work. Table 3 illustrated that aluminum alloys in Solution 2 containing microorganisms were easier to produce pitting attack than in Solution 1.

The effects of the concentrations of sodium chloride, nitrate and phosphate on the metabolism of the microorganisms and the corrosion processes were also investigated. The concentrations of phosphate and nitrate anions were lowered. In other words, because of the microorganism activation, the concentration of chloride anions inducing to pitting attack was decreased.

3.3 Surface analysis and discussion

The results of element analysis of sulfur and chlorine in the corrosion sites on the 10th day and the 40th day are given in Table 4. The serious pitting was found below microorganism precipitates. As shown in Fig1 there were larger, deeper and denser pits on the surface of the coupons immersed in Solution 2 than those in Solution 1. The contents of sulfur in all coupons immersed in Solution 2 were much higher than that in Solution 1 and increased with the time, especially 10th day and

40th day, as shown in Table 4. The contents of chlorine increased also with immersion time solutions, but there are more chlorine in Solution 1.

Table 4 Element analysis results for the alloys

Alloy	Time (day)	Contents of sulfur(%)		Contents of chlorine(%)	
		Solution 1	Solution 2	Solution 1	Solution 2
LC4	10	0.21	0.60	0.37	0.36
	40	0.12	0.77	0.51	0.48
LC9	10	0.22	0.36	0.40	0.32
	40	0.10	0.84	0.83	0.69
LY12	10	0.12	0.17	0.37	0.10
	40	0.11	0.62	1.15	0.64

It was found that the order of the corrosion resistance were given as LY12>LC4 Solution 2, and LY12 < LC9 < LC4 in Solution 1. It may be refereed to the alloy comp microorganism action and the pitting potentials. It needs to be studied continuously.

Acknowledgments

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