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The Influence of the Aerobic Bacterium on the Electrochemical Corrosion Behavior of B10 Alloys

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A comparative study about the electrochemical corrosion behavior of the B10 alloys in a nutrient-rich seawater-based medium in the presence and the absence of marine aerobic microorganism was carried out by electrochemical experiments and surface analytical techniques. The OCP of the B10 alloys in the inoculated medium shifted to cathodic direction more quickly than these in sterile medium. By compared studies, the results of EIS indicate that aerobic microorganism slows down the formation progress of the passive film on the surface and then accelerates the breakdown of the passive film. Cyclic polarization plots show that the aerobic microorganism accelerates the corrosion and the B10 alloys are no tendency for pitting both in inoculated medium and sterile medium. The biofilms formed on the B10 alloys surface have the same FT-IR spectrum with the inoculated medium and the presence of possible acidic groups may increase the corrosion of B10 alloys.

Keywords: Cu-Ni alloy; Aerobic bacterium; Microbial corrosion; Electrochemical impedance spectroscopy

1. INTRODUCTION

Cu–Ni alloys as engineering materials are used widely as pipelines, heat exchangers, offshore oil structures, ship hulls in seawater due to their corrosion resistance, machinability, thermal and electrical conductivity. Originally, Cu–Ni alloys were widely used and the microbial corrosion is insignificant for the toxicity of copper to microorganisms[1]. In fact Cu–Ni alloys are easily attacked by microorganism that results in the materials failure. The microbiologically-influenced corrosion (MIC) of Cu–Ni alloys has been studied extensively[2]. The early studies about the microbial corrosion of Cu-Ni alloys mainly focus on the anaerobic bacterium such as SRB (sulfate-reducing bacteria)[3-5]. Actually the microorganisms are diversity and the marine microbial corrosion is

complicated. I. B. Beech found there were a large population of both anaerobic bacterium and aerobic bacterium in heat exchanger internals. And the most is the *Pseudomonad* genus [6]. So it is significant to investigate the wide range of microorganisms influenced corrosion, which may provide helpful insight in controlling biofouling and MIC in aquatic environments. Aerobic bacteria are widely existent in the seawater and have been found to be involved in the corrosion process of many metal materials, such as mild steel, stainless steel, aluminum alloys and Cu-Ni alloys[7-9].

In this presentation, the influence of aerobic bacterium on B10 Cu-Ni alloys corrosion was studied to gain a better understanding on the aerobic microbial corrosion behavior of B10 Cu-Ni alloys using electrochemical experimental and surface analytical techniques. The results show that the aerobic bacterium accelerates the corrosion of B10 alloys.

2. EXPERIMENTAL PART

2.1. Materials

A 1mm-thick B10 Cu-Ni alloy specimen (Mn, 0.63; Ni, 9.5; Fe, 1.2; balance copper) was mechanically cut into 10×15 mm^2 (drilling a φ=2 mm hole in the edge) rectangle and 10×10 mm^2 square specimens. The square specimens were exposed only by one side, sealed with epoxy resin and connected with copper lead. All the specimens were polished with SiC papers up to 1200 grade, washed in distilled water, degreased ultrasonically in acetone, and sterilized using 75% ethanol just before immersion test.

2.2 Microorganism and culture

Test microorganism was isolated from the biofilms formed on the B10 alloys specimens exposed to seawater of Qingdao seashore for 30 days. The microorganism was cultured in Zobell 2216E culture medium on thermostatic incubator. The composition is as follows: peptone, 5 g; yeast extract, 1 g; Fe_3PO_4, 0.01 g; aged seawater, 1 l. The pH was adjusted to 7.6 with 5% (m/v) NaOH. And the medium was autoclaved at 121 ℃ and 20 psi for 30 min. The sterile Zobell 2216E culture medium inoculated with 5 % (v/v) microorganism-enriched medium was used as experimental medium and the sterile culture medium was used as a control for all the experiments.

2.3 Microscope observation

The B10 specimens were removed from the culture medium at different time, washed three times in 15 ml sterile seawater, fixed with 4% glutaraldehyde (GTA) (diluted by sterile seawater), and then stained with 0.1% acridine orange (AO). After air-drying in darkness, each of the B10 specimens with stained cells was placed on a glass slide and observed with epifluorescence microscope (Leica DM2500, Germany).

After cyclic polarization experiments, the morphology of B10 electrodes was pictured by inverted metallurgical microscope (Leica DMI 5000M, Germany).

2.4 Biochemical analysis

For assessing the extra-cellular polymeric substance (EPS), the test bacteria were inoculated in the Zobell 2216E medium containing B10 alloy coupons (10 mm×15 mm) at room temperature (25 °C). After 7 days, the liquid was centrifuged at 10,000 rpm at 4 °C for 10 min and filtered (0.2 μm membrane filter paper) to separate the bacterial cells. The filtered solid mass was washed thrice with sterile 2216E solution and again filtered. 1 ml of the filtrate was used for assessing EPS production by fourier transform infrared (FT-IR) spectroscopy (Thermo Fisher, Nicolet 8700, American). The B10 coupons with biofilms were taken out, dried and analyzed using FT-IR microspectrography.

2.5 Electrochemical experiments

The Electrochemical experiments were performed in a conventional three electrodes cell, B10 alloys as working electrodes, a platinum - niobium stick as counter electrode, and a saturated calomel electrode (SCE) provided with a Luggin capillary as reference electrode. Measurements were performed at room temperature (25 °C) with PARSTAT 2273 Potentiostat/Galvanostat (Princeton Applied Research).

The Electrochemical impendence spectroscopy (EIS) was performed on steady state open circuit potential (OCP) disturbed with amplitude of 10 mV a.c. sine wave at frequencies between 100 kHz and 10 MHz. The frequency range was 100 kHz–10 MHz. And the cyclic polarization curves were obtained from $-100mV_{SCE}$ versus OCP to a vertex potential of 100 mV_{SCE} and then reversed to OCP with a scan rate of 0.5 mV/s. The softwares in the test were CorrWare with CorrView 2.0 for collection and analysis of cyclic polarization curve data and ZPlot with ZSIMPWIN for EIS data.

3. RESULTS AND DISCUSSION

3.1 Characterization of aerobic bacteria

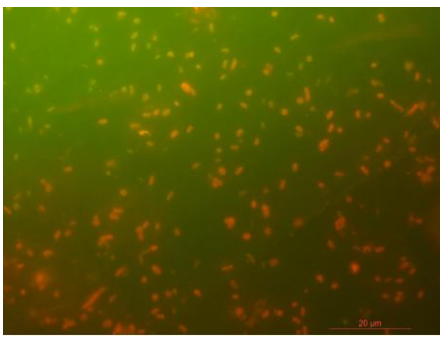

Figure 1. the epifluorescence microscope picture of aerobic bacterium on the surface of specimens after immersion for three days.

The epifluorescence microscope picture of aerobic bacteria on the surface of B10 samples immersion for three days was showed in figure 1. It exhibited that colonization existed with a higher number of microorganisms about 2 μm.

3.2 Electrochemical measurement

The OCP of the B10 alloys exposed in sterile medium and in inoculated medium was shown in figure 2. The OCP of the B10 alloys in the inoculated medium shifted to cathodic direction more quickly than these in sterile medium. The result can be attributed to the adsorption of aerobic biofilms. From the results it can be speculated that the existence of the aerobic biofilms increased the corrosion tendency of B10 alloys[10].

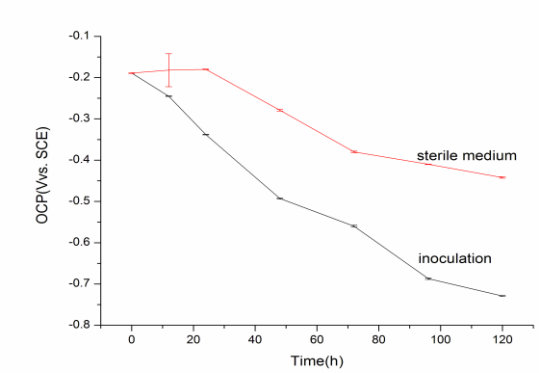

Figure 2. Variation of OCP of B10 electrodes with time in sterile medium and inoculated medium.

Figure 3 shows the EIS and the equivalent circuits used in the analysis of B10 alloys in the sterile and inoculated medium. Based on the equivalent circuit (with Z_w in inoculated medium and without Z_w in sterile medium), the fitting parameters of the EIS are given in table 1. In the circuit, R_s is the resistance of solution, R_{ct} is the charge transfer resistance and R_p is resistance of the passive film. Q_{dl} and Q_p are the CPE parameters for the electric double layer and the passive film, Y and n are CPE parameters. Warburg impedance (Z_w) was introduced to the circuit in the presence of bacteria representing the diffusion process due to biofilms influence. Figure 3B shows the Nyquist plots of B10 alloys in sterile medium. From figure 3B and table 1 we can see that the diameter of Nyquist semicircle and the values of R_p in sterile medium increase with time which indicates the corrosion rate decreases. And it can be contributed to the formation of the passive film on the B10 alloys surface. Figure 3A shows the Nyquist plots of B10 alloys in inoculated medium. From figure 3A and table 1, we can see that the diameter of Nyquist semicircle and the values of R_p increase at the first three days, and then on the following days the diameter of Nyquist semicircle and the values of R_p begin to decrease that indicates the corrosion rate decreases at the first three days and then increases. The results indicate that the adsorption of aerobic microorganism slows down the formation progress of the passive film on the surface and then accelerated the breakdown of the passive film. From figure 3A we can see that the Nyquist diagrams tend to straight line with time that indicates the electrochemical

behavior is controlled by diffusion process with time in inoculated medium. The decrease of Z_w value will cause Q_p to increase which will increase the rate of corrosion[11]. Q_{dl} can be seen as the parameter of surface biofilm adsorption, and its increase is connected with an adsorption progress. The values of Q_b from the 3th day to the 5th day are almost stable that indicates microorganism adsorption achieves balance[12].

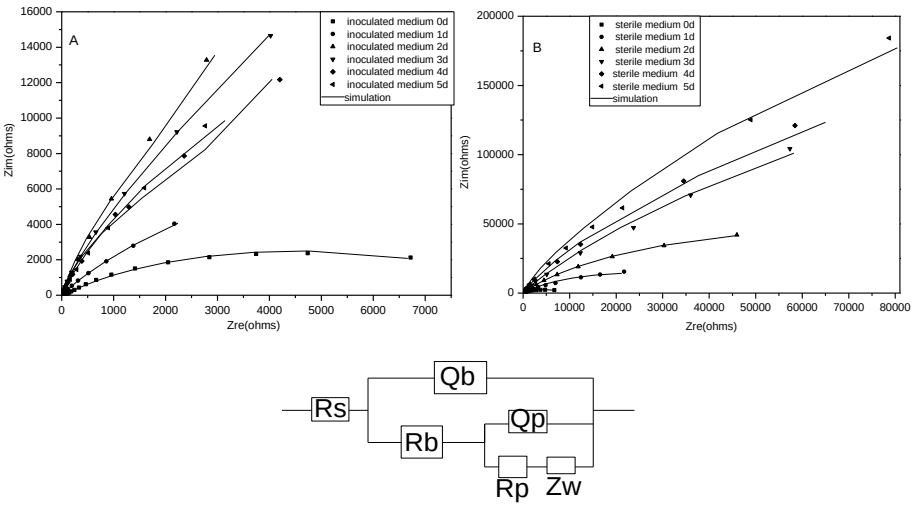

Figure 3. The EIS and equivalent circuit of B10 alloys in inoculated medium (A) and sterile medium (B): the symbol, measured data; the line, calculated data.

Table 1. Electrochemical model impedance parameters of the B10 alloys in the sterile medium (SM) and inoculated medium (IM).

t (days)		*Rs* (Ωcm^2)	Q_b		R_b (Ωcm^2)	Q_p		R_p (Ωcm^2)	Z_w ($\Omega s^{-1/2} cm^2$)	*Chi-square* χ^2
			$Y_0(\Omega^{-1}cm^{-2}s^{-n})$	n_1		$Y_0(\Omega^{-1}cm^{-2}s^{-n})$	n_2			
0	SM	1.762	2.45E-4	0.932	58.9	2.08	0.637	9068		1.02E-2
1	SM	7.522	1.87E-5	0.833	105.4	1.52E-4	0.6815	4.74E4		1.71E-3
	IM	5.325	1.27E-3	0.880	301	0.526	0.709	9764	4.00E-4	1.46E-3
2	SM	7.731	8.16E-6	0.966	112	8.58E-5	0.732	1.36E5		1.07E-3
	IM	6.196	3.45E-3	1	1.75	5.00E-5	0.893	3.41E4	5.39E-5	1.88E-3
3	SM	7.617	5.59E-5	0.880	1.66E4	1.99E-5	0.638	6.41E5		1.21E-3
	IM	7.166	3.28E-4	1	2.671	3.73E-4	0.899	1633	7.03E-5	6.88E-4
4	SM	6.890	5.28E-5	0.899	1.33E5	5.74E-5	1	6.31E5		1.79E-2
	IM	6.529	7.62E-4	0.941	2.81	6.15E-4	1	419.6	7.82E-6	7.81E-3
5	SM	7.661	5.30E-5	0.902	3.95E5	1.77E-5	0.713	6.94E5		6.77E-3
	IM	6.753	3.22E-4	1	3.137	7.23E-4	0.8901	358.2	9.88E-6	9.59E-4

Figure 4 shows the results of cyclic polarization scans for B10 electrodes in sterile medium (a) and inoculated medium (b) for 5 days. Analysis of the data shows that curve a has a smaller corrosion current than curve b which indicates that the aerobic microorganism increases the corrosion rate of the

B10 alloys. The smaller current with no hysteresis loop on the reverse scan indicates that there is no tendency for pitting[13, 14]. Both in sterile medium and inoculated medium the B10 alloys have no indication of pitting. The electrochemical experiments studies reveal that the results obtained from EIS and cyclic polarization are in reasonably good agreement.

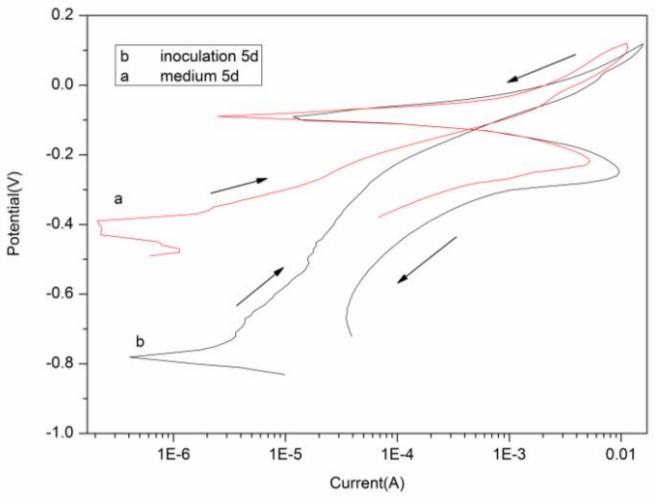

Figure 4. Cyclic polarization plots for B10 electrodes in sterile medium (a) and inoculated medium (b) after immersion for 5 days.

3.3 Metallurgical microscope investigation

After cyclic polarization experiments, B10 alloys surface was analyzed by inverted metallurgical microscope and the results were shown in figure 5. From figure 5a it can be seen that there is a good passive protective film on the surface against corrosion. From figure 5b we can see obviously that the B10 alloys in inoculated medium have been strongly damaged because of the existence of aerobic bacterium[15].

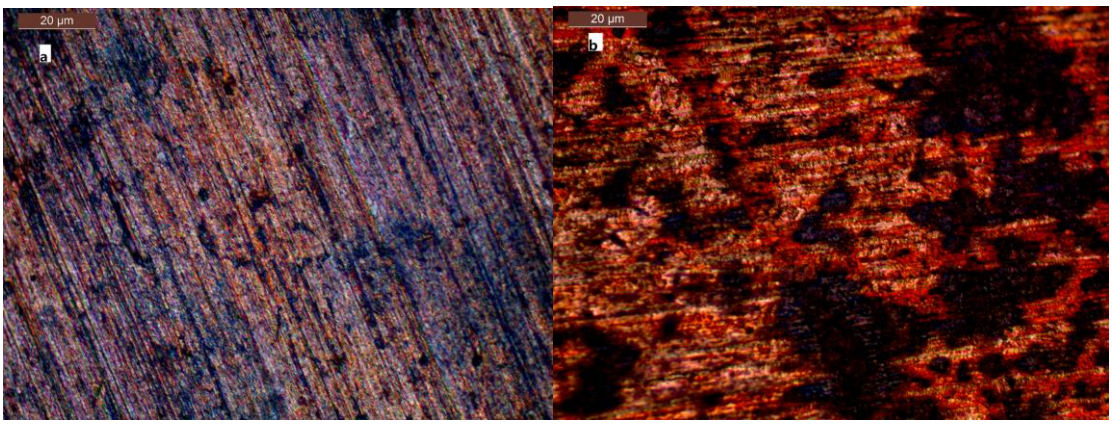

Figure 5. The metallurgical microscope picture of B10 alloys immersed in sterile medium (a) and inoculated medium (b) after cyclic polarization.

3.4 FT-IR analysis

Many literatures have reported that the microorganisms can secrete highly corrosive acid whilst metabolizing organic matter[16]. In order to better understand the influence of the aerobic bacterium metabolites on the corrosion of B10 alloys, the FT-IR spectrums of biofilms on specimens after immersion in inoculated medium for 5 days, inoculated medium for 5 days and sterile medium for 5 days were analyzed and shown in figure 6. From figure 6, we can see that the compounds in sterile medium were mainly peptone with the peak at 3200 cm^{-1}, 1520cm^{-1} and 1100cm^{-1} without EPS. The FT-IR spectrum of inoculated medium is basically consistent with that of biofilms. In consideration of the possible groups located in EPS being polysaccharides, proteins and hydrocarbons[17], the peaks observed at 1700 cm^{-1} and 1600 cm^{-1} are attributed to C=O and C-N, respectively. Additionally the peaks from 1500 cm^{-1} to 1000 cm^{-1} are attributable to polysaccharides as C-O, P=O, or C-O-C. Compared with the sterile medium the inoculated medium and the biofims contain more metabolites. And the metabolites accelerate the corrosion of B10 alloys.

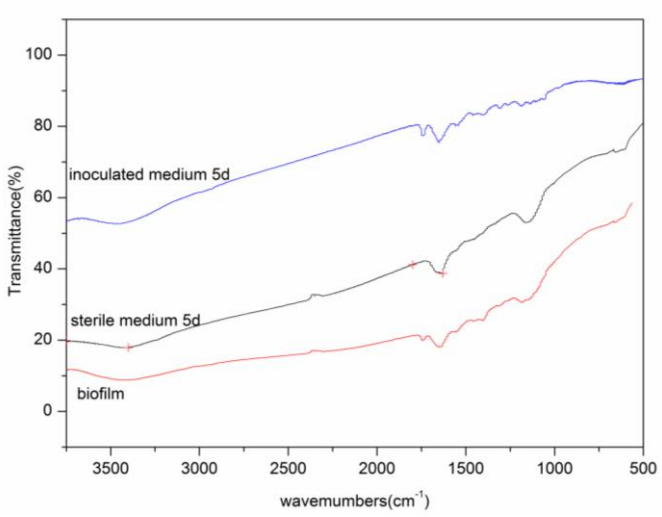

Figure 6. FT-IR spectrum of biofilms, inoculated medium and sterile medium.

4. CONCLUSIONS

In this paper, the electrochemical corrosion behavior of B10 alloys influenced by aerobic microorganism was studied by electrochemical experiments and surface analytical techniques. The aerobic microorganism was isolated from the biofilms formed on the B10 alloys specimens that exposed to seawater of Qingdao seashore for 30 days. The OCP of the B10 alloys in the inoculated medium shifted to cathodic direction more quickly than these in sterile medium. By compared studies, the results of EIS indicate that aerobic microorganism slows down the formation progress of the passive film on the surface and then accelerates the breakdown of the passive film. Cyclic polarization plots shows that the aerobic microorganism accelerates the corrosion rate and the B10 alloys are no

tendency for pitting both in inoculated medium and sterile medium. All results indicated that the aerobic bacterium increased the corrosion of B10 alloys. The biofilm formed on the B10 alloys surface have the same FT-IR spectrum with the inoculated medium and the presence of possible acidic groups may increase the corrosion of B10 alloys. The characterization of the aerobic microorganism and the MIC mechanisms of B10 alloys need to be studied further.

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