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Corrosion Performance of Zn-Al-Cd Alloy in Amphora-containing f/2 Culture Medium

Jie Zhang[1,*], *Xiumin Ma*[1], *Zhenhua Yu*[2], *Jie Yang*[3,*], *Caixia Sun*[1,4], *Wenzuo Li*[4]

[1] Key Laboratory of Marine Environmental Corrosion and Biofouling, Institute of Oceanology, Chinese Academy of Sciences. Qingdao 266071, China
[2] Qingdao Municipal Center for Disease Control and Prevention, Qingdao 266033, China
[3] School of Naval Architecture and Ocean Engineering, Zhejiang Ocean University, Zhoushan 316022, China
[4] College of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, China
[*]E-mail: zhangjie@qdio.ac.cn, kittyangj@163.com

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The corrosion properties of Zn-Al-Cd alloy in Amphora-containing culture media were investigated by using electrochemical AC impedance method, polarization curve research, and surface microstructure analysis methods. The results showed that the corrosion rate of Zn-Al-Cd alloy in f/2 culture medium with Amphora was greater than that of samples in sterilized culture medium. SEM micrographs proved that many corrosion pits occurred on the surface of the anode in the Amphora-containing environment. Amphora adhered on the surface of the specimen could produce oxygen, which increased the corrosion of Zn-Al-Cd alloy.

Keywords: Amphora; corrosion; Zn-Al-Cd sacrificial anode; electrochemical impedance spectroscopy (EIS); scanning electron microscopy (SEM)

1. INTRODUCTION

Cathodic protection by sacrificial anodes is often applied to prevent immerged metallic structures from corrosion, among which, zinc-base anode has a wide range of applications because of their high current efficiency [1-4]. Zn-Al-Cd sacrificial anode is the most widely used in all kinds of zinc alloy sacrificial anodes home and abroad, which is mainly used in cathodic protection of ships, oil platform, port terminals, submarine oil pipeline, etc [5]. When the metal material immersed in the complex seawater environment, it will face all kinds of corrosion problems, among which microbial

corrosion is one of the most important aspects. Microbiologically influenced corrosion is not a specific corrosion process, but a corrosion process induced by microorganisms or an accelerated corrosion [6-7]. Microorganisms here mainly refer to the microalgae and bacteria which adhered on the surface of metal material, and participated in the formation of biofilms. It will have an important impact on the local environment of metal material surface change the corrosion process of metal material.

Marine biofouling has attracted more attention from many researchers all over the word, and caused a huge loss in vessels and marine equipments. In which, the attachment of microalgae on material surface is an initial stage and important process. Amphora is one of the widely distributed benthic diatoms species in the world, which has a strong environmental adaptability and rapid growth. The anti-fouling researches of Amphora have attracted many people's attentions [8-11]. However, few papers about the relationship between Amphora with the corrosion of Zn-Al-Cd alloy can be found. In this study, the impact of Amphora isolated from Huanghai seawater on the corrosion performance of Zn-Al-Cd alloy was studied by using electrochemical AC impedance method, polarization curve analysis, and surface microstructure analysis methods. The mechanism of Amphora on the corrosion performance of Zn-Al-Cd alloy sacrificial anode was also discussed, which is benefit to evaluate the performance and life prediction of sacrificial anode.

2. EXPERIMENTAL

2.1 Enrichment Purification of Amphora

The experimental algae species were gotten from the Huanghai Sea near Qingdao. The f/2 culture solutions were used to enrich the microalgae for many times (Figure 1). The composition of f/2 trace element solution was the following: 23 mg $ZnSO_4 \cdot 4H_2O$, 10 mg $CuSO_4 \cdot 5H_2O$, 3.9 mg $FeC_6H_5O_7 \cdot 5H_2O$, 7.3 mg $Na_2MoO_4 \cdot 2H_2O$, 12 mg $CoCl_2 \cdot 6H_2O$, 4.35 mg Na_2EDTA, and 1000 ml purified water. The composition of f/2 Vitamin solution was the following: 0.5 mg Vitamin 12, 100 mg Vitamin B1, 0.5 mg Vitamin H, and 1000 ml purified water.

Figure 1. Microscopy figure of Amphora and the enrichment culture of Amphora

The composition of f/2 culture medium was the following: 74.8 mg $NaNO_3$, 4.4 mg NaH_2PO_4, 10 mg $Na_2SiO_3 \cdot 9H_2O$, 1mL f/2 trace element solution, 1mL f/2 Vitamin solution, and 1000 ml aged seawater. The medium was autoclaved at 121°C for 30 min. After cooling, 10 ml of microalgae was

added to 100 ml of culture medium, placed at 25 ℃ light incubator culture for 10 days to culture, the light intensity is 4000lx..

2.2 Determination of Amphora Growth Curve

The suspension concentration of Amphora is proportional to the optical density (OD), and so the optical density was determined to study the Amphora growth curve by spectrophotometer [12].The specific operation steps were as follows:

First, 310 mL f/2 culture solutions were sterilized in an autoclave for 30 min under the temperature of 121 ℃, and then 10 ml of sterilization f/2 culture solutions were chosen and injected into a 15 mL sterile centrifuge tube as a reference solution and stored in a refrigerator at 4 ℃. After which 15mL overnight broth cultured solutions were applied into the remaining 300mL f/2 sterilized culture solutions and shook well, then the solutions were uniformly dispersed into thirty 15mL centrifugal tubes, and cultured in a 30 ℃ constant temperature incubator. Three test tubes were taken out from the constant temperature incubator at the same time every day and then stored in refrigerator at 4 ℃. After 10 days, the absorbance values of these thirty test tubes were measured by using ultraviolet spectrophotometer at the same time. The biggest characteristic absorption wavelength of Amphora in the ultraviolet–visible light range is determined as 690 nm by use of spectrophotometric scanning method. 3 mL Amphora-containing culture medium of different growth times (from 1 day to 10 day), which taken previously from the refrigerator,was measured sequentially at the wavelength of 690 nm. The absorbance of each sample was continuously measured three times , and then the average OD value was chosen. The growth curve of Amphora was drawn according to the OD values.

2.3 The Experimental Materials and Medium

Zn-Al-Cd alloy anode is used in this experiment, the chemical composition (mass fraction / %) is：Al:0.36，Cd:0.045，Pb:0.00092，Cu:0.0012，Fe:0.0021，the rest is Zn. The specimens were cut into 10 mm × 10 mm × 6 mm for electrochemical tests and surface analysis. After the copper wire welding on the end of electrochemical test samples, one side was reserved as the working face, the other side surface was sealed by using epoxy resin in a PVC tube. All samples were abraded with emery papers of a grit size from 200 # to 2000# according to the national standard of China (GB 5776-86) and degreased in an ethanol solution with an ultrasonic bath. Afterward, three samples were selected and rinsed with deionised water for three times, then dried by using ethanol. The samples were kept in a silica gel desiccator before use. Before the experiment test, the samples would be sterilised by ultraviolet irradiation for 30 min. *2.4*

The seawater used in this test was obtained from Huiquan Bay, Qingdao. Then it was filtrated preliminarily by the sea water purification system and autoclaved at the temperature of 121 °C.

2.4 Electrochemical procedure

Electrochemical experiments were carried out by using Shanghai ChenHua CHI 760C. All the tests were carried out in a three-electrode system consisting of a saturated calomel electrode (SCE) as the reference electrode, a Pt plate as the counter electrode and Zn-Al-Cd samples as the working electrode. 40 ml of amphora was added into 400 ml sterile f/2 medium and mixed uniformly, which used as biotic system. Another 440 ml sterile f/2 medium without amphora was chosen as the blank system. Measurements were performed at 28±2 °C. Open circuit potential (E_{ocp}) and EIS measurements were performed during the circle of 10 d without another addition of medium. EIS was performed using 10 mV amplitude sinusoidal voltage signals over the frequencies ranging from100 kHz to 10 mHz. The polarization curve was measured at a potential scanning rate of 0.5 mV/s from E_{ocp} −250 mV to E_{ocp} + 250 mV.,. Data were collected using Zplot software and analysed by ZSimpWin software.

2.5. The Surface Analysis Experiment

Two 500 mL jars were chosen after sterilization at 121℃ high temperature and high pressure treatment. 440 mL sterilized culture medium was added into one jar in the ultra-clean workbench as blank system. Another jar was inoculated with 40mL overnight algae-containing culture solution and added 400 mL sterilized culture medium as the Amphora-containing system.Three samples were immersed in sterilize and biotic jars respectively and sealed by silicon rubber, then placed at room temperature. Samples without Amphora were removed quickly after 10 d in clean workbench and then treated. Alcohol with gradients of 50%, 70%, and 100% were used to dewater, and the dewatering time was 15 min for every gradient. Samples with Amphora were soaked in the PBS solution containing 5 % glutaraldehyde for 2 h, and then dewatered just as the sterilized samples above. Finally, the electrode was sent to the testing room, supercritically dried with CO_2, observed with SEM by using S-3400N.

3. RESULTS AND DISCUSSION

3.1 The Identification and Growth Curve of Amphora

The phylogenetic tree was constructed by MEGA5 software after analyzing the 18s rRNA sequences and compered with the phylogenetic tree of Amphora (Figure 2)， from which we could see that the sequence of our sample was the same as that of bacillariophyta sp.bMBIC10809.

The growth curve of Amphora in f/2 culture solutions during one growth cycle was shown in Figure 3. Figure 3 shows that the quantity changes of Amphora in culture solutions can be divided into three phases: 1-4 day as the adjustment phase, 4-7 day as the exponential growth phase, and 7-10 day as the decline phase. The maximum number of amphora was gotten in the 7^{th} day because of a lot of

nutrients, and then the reproduction of Amphora gotten slower and slower, the number of living cells declined rapidly because of depletion of limited nutrient [13].

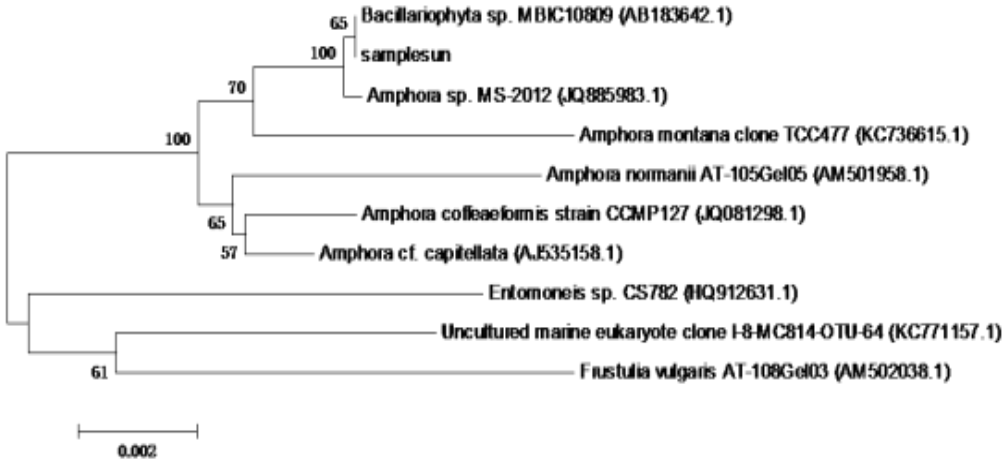

Figure 2. The phylogenetic tree of Amphora

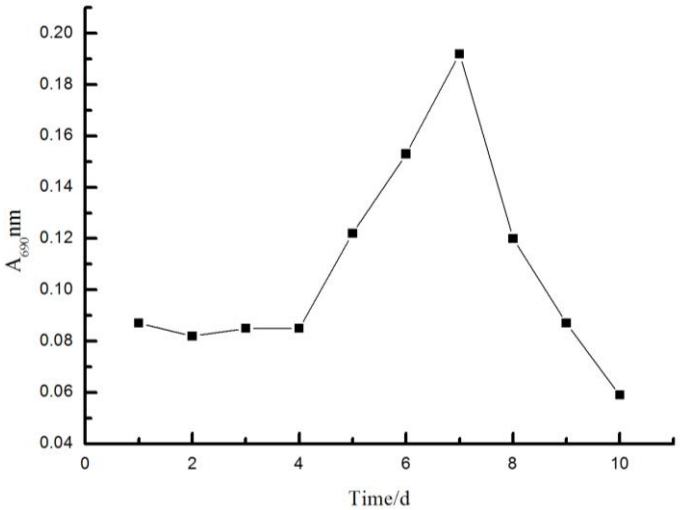

Figure 3. Growth curve of Amprhora

3.2 The Analysis of Electrochemical Impedance Spectroscopy

Figure 4 shows the AC impedance Nyquist spectroscopy of Zn-Al-Cd alloy in the f/2 culture medium without and with Amphora. The EIS data of the samples could be fitted on the basis of equivalent circuit (Figure 5) according to the characteristics of experimental system by using Zsimpwin software[14-15]. In Figure 5, R_s is the solution resistance, Q_f is the capacitance of the surface film, R_{ct} is the charge transfer resistance, and Q_{dl} is the capacitance of the double layer. The constant phase angle element Q was described as follows: $Z_{CPE}=Y_0^{-1}(j\omega)^{-n}$ (0< n <1), where Y_0 was a

constant phase element and n was an empirical exponent that can reflect the degree of heterogeneity on the sample surface [14].

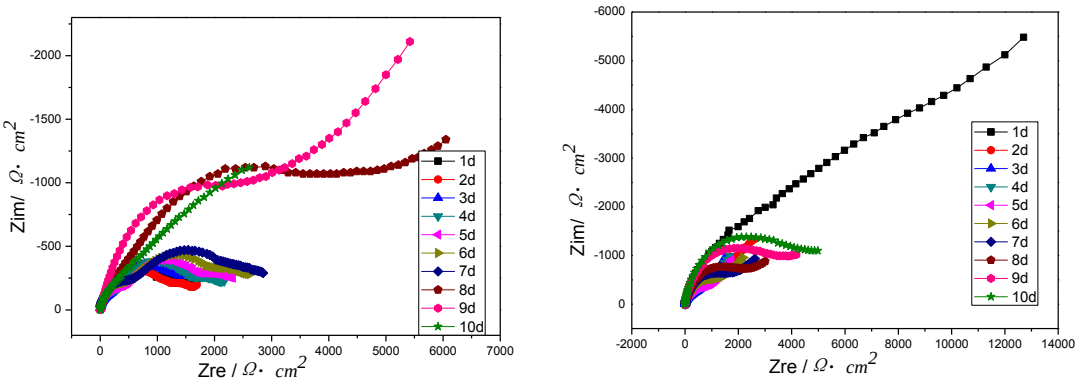

Figure 4. EIS results of Zn-Al-Cd alloy immersed in f/2 culture medium without (a) and with (b) Amprhora

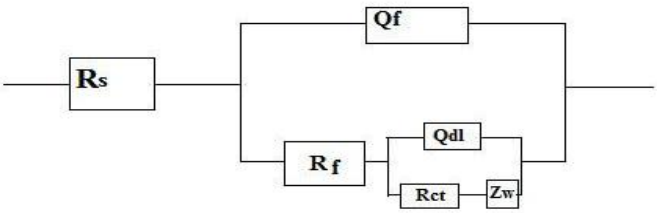

Figure 5. The equivalent circuit model for Zn-Al-Cd alloy immersed in f/2 culture medium without and with Amprhora

Changes in the electrochemical parameters of the samples without and with Amprhora over time were shown in Tables 1 and 2. Table 1 shows that the value of R_{ct} of Zn-Al-Cd alloy immersed in the culture medium without Amphora increased with the immersion time until the 9th day. The maximum value of R_{ct} was 4762 $\Omega \cdot cm^2$ on the 8th day. The value of R_f changed relatively obvious with the immersion time in the culture medium without Amphora, the maximum value of R_f was 3260 $\Omega \cdot cm^2$ on the 9th day, which was considered as the corrosion products constantly compacted on the surface of alloy and shown a better barrier action [16].

Table 2 shows that for the Zn-Al-Cd alloy immersed in the culture medium with Amphora, the value of R_{ct} decreased gradually, and the minimum value was 519.9 $\Omega \cdot cm^2$ on the 4rd day, then the value of R_{ct} increased slowly, until the 8th day, reached the maximum value of 2049 $\Omega \cdot cm^2$. The membrane resistance R_f had the same trends as R_{ct}. During the adjustment period of Amphora, with the slow growth of Amphora, the value of R_{ct} decreased slowly. From the 4th day, the value of R_{ct} began to rapidly increase, the corrosion rate decreased. The reason was considered as that the mixed complex membrane of Amphora and corrosion products was formed, which slowed the damage of Cl^- to the metals [17]. Though the concentration of oxygen was increased because of the metabolism of

Amphora, which could increase the corrosion of the samples, the effect of metabolism oxygen was smaller than that of the protection of biofilm, so the whole corrosion rate was decreased. on the 9-10 days, with the decline of Amphora and the fall-off of corrosion products, the corrosion rate increased gradually [18]. The value of R_f for Zn-Al-Cd alloy immersed in the culture medium with Amphora was varied from 337.6 $\Omega \cdot cm^2$ to 1121 $\Omega \cdot cm^2$, which indicated that the Amphora adhesion on the metal surface was relatively stable. The minimum value of R_f was reached on the 3rd day, and the reason was considered as that the oxide film of the metal surface was destroyed, and the adhesive ability of Amphora was not strong in this adjustment phase.

Compared Table 1 and 2, we could find that during the whole the experimental time, the value of R_{ct} for Zn-Al-Cd sample without Amphora was significantly greater than that of samples with Amphora, which showed that the metabolism of Amphora and the generation of oxygen were contributed to the corrosion of the Zn-Al-Cd alloy. Little et.al. indicated that the biofilm formation of microalgae changed the dissolved oxygen and pH, which affected the corrosion performance of material [19]. Maruthamuthu et.al. found that the attached microalgae could change the pH value of biofilm.[20] However, the accumulation of corrosion products occurred easily on the surface of sample, which easily hindered further corrosion [21]..

Table 1. Electrochemical parameters obtained from EIS of Zn-Al-Cd sample immersed in f/2 culture medium without Amprhora

Time/d	R_s $\Omega \cdot cm^2$	Q_f*10^{-6} Ω^{-1} cm^{-2}	R_f $\Omega \cdot cm^2$	$Q_{dl}*10^{-5}$ Ω^{-1} cm^{-2}	R_{ct} $\Omega \cdot cm^2$	Z_w $\Omega \cdot cm^2$
1	2.056	23.81	928.1	65.78	793.6	0.01205
2	1.507	1.285	94.76	6.74	1359	0.009495
3	0.096	1.209	177.5	7.753	1543	0.007315
4	9.015	0.826	232.7	8.232	2321	0.00023
5	0.1175	1.394	372.2	8.681	1715	0.00822
6	7.196	0.6468	344.4	10.1	2156	0.009587
7	1.002	0.609	382	10.24	2445	0.01095
8	1.002	0.7879	468.8	5.117	4762	0.001902
9	3.036	46.8	3260	60.86	1923.6	0.000187
10	3.074	18.38	1636	47.23	1436.7	0.000097

Table 2. Electrochemical parameters obtained form EIS of Zn-Al-Cd sample immersed in f/2 culture medium with Amprhora

Time/d	R_s $\Omega \cdot cm^2$	Q_f*10^{-5} Ω^{-1} cm^{-2}	R_f $\Omega \cdot cm^2$	$Q_{dl}*10^{-5}$ Ω^{-1} cm^{-2}	R_{ct} $\Omega \cdot cm^2$	Z_w $\Omega \cdot cm^2$
1	6.8	1.072	828.5	11.41	775.2	$4.353*10^{-5}$
2	6.814	4.585	551	54.27	1915	0.0001407
3	6.31	12.65	337.6	58.33	530.6	0.002518

4	5.945	13.89	401.3	39.18	519.9	0.002526
5	5.947	11.84	436.5	38.18	603.2	0.002727
6	5.887	10.46	439.5	95.7	1000	$1.7*10^{-9}$
7	6	8.277	646.6	30.1	1515	0.002823
8	5.713	7.146	737.8	28.34	2049	0.003331
9	5.556	5.966	1121	22.93	1112	0.000216
10	7.359	2.845	1158	6.801	1320	$3.258*10^{-5}$

3.3 Analysis of Polarization Curve Characteristics

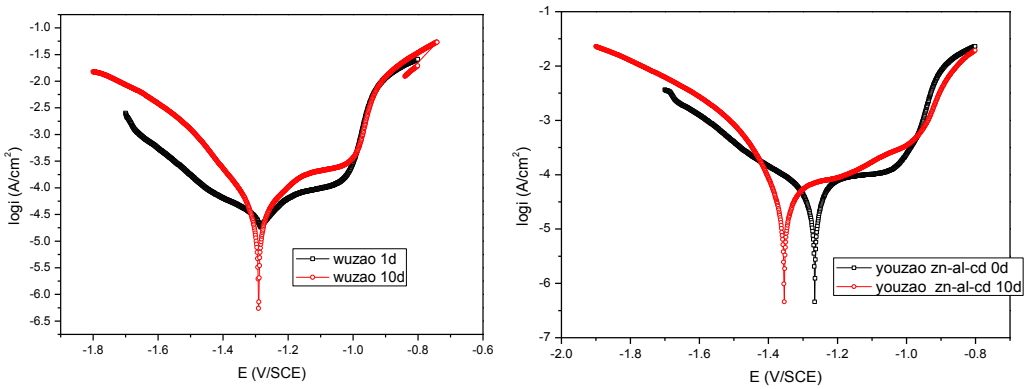

Figure 7. Polarization curves of Zn-Al-Cd sample immersed in f/2 culture medium for 1d , 10d without and with Amprhora

Fig. 7 illustrated the polarisation characteristics of Zn-Al-Cd sample exposed to f/2 culture medium without and with Amprhora for 1d and 10d respectively. The electrochemical parameters (anodic Tafel slope (*ba*), cathodic Tafel slope (*bc*), corrosion potential (E_{corr}), corrosion current density (i_{corr}), and polarization resistance (R_p)) were tabulated in Table 3.

From Table 3 we could find that the corrosion potential of Zn-Al-Cd sample in the culture medium for 10 d without Amphora was positive shift than that for 1d (from -1.261 V to -1.241 V), the corrosion current density decreased sharply (from 108.7 μA/cm^2 to 27.64 μA/cm^2), which may be due to the formation of a protective film of corrosion products on the surface of Zn-Al-Cd alloy sample that would inhibit the aggressive media erosion [22]. For the Zn-Al-Cd sample with Amphora, the corrosion current density decreased sharply (from 108.5 μA/cm^2 to 47.09 μA/cm^2), which may be considered as the formation of mixed microalgae film and corrosion products on the surface of sample, showing an effectively protective action.

In the immersion for 1 d, the current corrosion potential and corrosion current density of Zn-Al-Cd sample without and with Amphora were the basically same. While after 10 d, the corrosion potential of the sample with Amphora was significant negative than that of sample without Amphora, and the corrosion current density was greater than that of sample without Amphora. The reason was that Amphora photosynthesis produced a large amount of oxygen, and the dissolved oxygen concentration on the surface of the sample with Amphora was higher than that without Amphora, so Amphora attachment can accelerate the corrosion rate of alloy [23].

Table 3. Electrochemical parameters obtained form polarization curves of Zn-Al-Cd sample immersed in f/2 culture medium witiout and with Amprhora

Sample	without Amprhora		with Amprhora	
time	1d	10d	1d	10d
E_{corr} (V, vs.SCE)	-1.261	-1.241	-1.266	-1.354
i_{corr} (uA/cm^2)	108.7	27.64	108.5	47.09
b_c (mV/dec)	-3.205	-6.426	-4.183	-9.942
b_a (mV/dec)	0.645	6.213	1.704	2.225
R_p ($\Omega \cdot$cm^2)	1039	1245	681	759

3.4 The Sample Surface Analysis

Figure. 8 shows the metallographic micrographs of Zn-Al-Cd sample without Amphora (A) and with Amphora (B) after immersion for 10 d. From this figure, we could see that the corrosion of sample with Amphora was more serious than that of sample without Amphora, and corrosion holes can be seen on the surface of sample with Amphora. White corrosion products could be seen on the surface of sample without Amphora. Comparing these two kinds of samples, we can find that the sample with Amphora occurred local corrosion and show more serious corrosion.

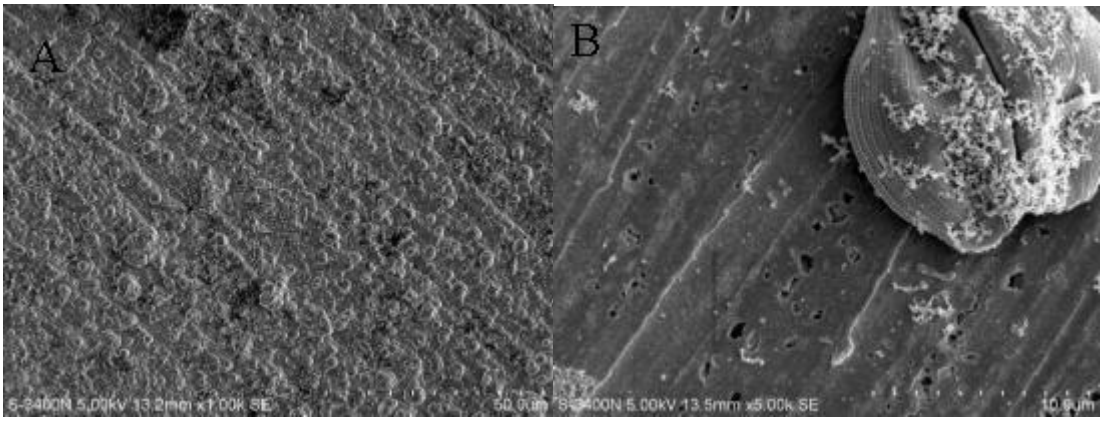

Figure 8. SEM images of of Zn-Al -Cd sample immersed in f/2 culture medium witiout (A) and with(B)Amprhora for 10 days

EDS analysis results of Zn-Al-Cd sample without Amphora and with Amphora after immersion for 10 d were shown in Table 4. From Table 4, we could find that the concentrations of C in the surface of samples immersed in Amphora-containing conditions are higher than those of samples without Amphora. The reason was thought as follows: One hand, vitamin B12 ($C_{63}H_{88}CoN_{14}O_{14}P$) and biotin ($C_{10}H_{15}N_2O_3S$) were used in the culture medium, which were more easily adsorbed to the

material surface, and formed a layer of film on the surface; on the other hand, Amphora adhered on the specimen surface, the main metabolites components were organic, which also made carbon percentage increasing. In addition, compared with the blank culture medium, Magnesium was detected on the surface of Zn-Al-Cd specimen in the culture medium with Amphora. Magnesium was the central atom of the pyrrole ring of chlorophyll (including chlorophyll a, chlorophyll b and chlorophyll c). The emergence of magnesium indicated that Amphora adhering on the material surface had partly decayed, so a large amount of pigment contained in the cells was released [24].

Table 4. The EDS element analysis results

without Amprhora	Intensity(c/s)	Atomic%	with Amprhora	Intensity(c/s)	Atomic%
C	12.83	6.552	C	24.64	24.404
O	489.15	55.504	O	38.60	8.818
Al	4.73	0.232	Mg	4.39	0.540
Si	207.28	8.221	Al	19.37	1.687
P	5.99	0.214	Si	17.11	1.191
S	11.04	0.347	P	210.34	12.503
Cl	30.00	0.873	S	17.53	0.956
Mn	1.51	0.057	Mn	2.56	0.156
Fe	2.13	0.089	Fe	2.19	0.148
Zn	257.64	27.910	Zn	285.17	49.554
		100.000	Tc	1.36	0.042
					100.000

4. CONCLUSIONS

(1) The corrosion rate of Zn-Al-Cd alloy in Amphora-containing culture medium is greater than that of alloy in sterilized culture medium.

(2) SEM micrographs prove that more corrosion pits appears on the surface of the alloy with Amphora than without Amphora.

(3) Amphora attachment improves the corrosion rate of the alloy because of the production of oxygen and metabolites by Amphora.

ACKNOWLEDGEMENTS
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