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Short Communication

Influence of Pressure on Galvanic Corrosion of 907/921/B10 Couples in simulated deep-sea environment

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In this work, the galvanic corrosion rate, the electrochemical polarization curves and micro morphology of three-phase coupling composed by low alloy steel 907, 921 and copper-nickel alloy B10 under different pressure in simulated deep-sea environment were studied by means of the weight-loss method, the electrochemical method and the scanning electronic microscope (SEM), respectively. The results showed that pressure had little influence on the stable galvanic potential. When the pressure was less than 1000m, the corrosion of steel 907 was the most serious. While above 1000m the galvanic corrosion focused on steel 921.

Keywords: Deep-sea environment; Pressure; Three-phase coupling; Galvanic corrosion

1. INTRODUCTION

With the increasing demand for energy all over the world, much attention has been focused on the development of deep-sea resources. Thus a great number of deep-sea engineering equipments made of various metal materials have been applied[1-4]. In a deep-sea environment, it has much stricter requirements on the functions of materials and reliability of structure than that in the shallow sea or on the land. Corrosion and damage of any material may result in serious accidents. The marine engineering devices made of various metal materials serving in a harsh deep-sea environment for a long term will inevitably lead to galvanic corrosion problems and cause immeasurable loss to national economy and security. Therefore, it is of significance to lay theoretical foundation for protection of the

materials against galvanic corrosion, to provide theoretical basis for designing and choosing materials, and to improve the construction of the deep-sea engineering equipment.

The corrosion of deep-sea materials was studied in America, Japan and the former Soviet Union[5-9] as early as in 1960s. Given the harsh living environment in the deep-sea, simulated experiments were carried out in the labs. Many foreign institutions have made studies on corrosion resistance of metals including Ni by simulating the deep-sea environment[10-15]. In China, gradually, more and more studies have been focused on this field. For example, Liu[16] studied the influence of deep-sea pressure on the corrosion of two kinds of low carbon steel. Liu[17] made research on the impacts of sea water pressure on the passivation film properties of Ni in the greenhouse conditions. Tong[18] analyzed on the corrosion behavior of Ti-Al pseudo-alloy coating in a simulated deep-sea environment. As a result, the factors affecting corrosion of metal and alloy materials in the deep-sea environment become gradually clear [19-20].

Due to the requirements for structure and performance in marine environment, the parts of the equipment with different electrochemical properties have to make inevitable connection. Galvanic corrosion will significantly be accelerated in such a harsh environment. Therefore, it is necessary to study the corrosion behavior of a variety of metal coupling under deep-sea conditions. By weight loss, electrochemical and scanning electronic microscope (SEM) method, this study focused on the corrosion behavior of three-phase coupling 907/921/B10 influenced by the pressure in a simulated deep-sea environment using a self-designed device.

2. EXPERIMENTAL SECTION

2.1 Electrode preparation

Three kinds of metals, 907, 921, B10[21-22] commonly used for marine engineering were taken as the materials in the experiment, and the chemical compositions were shown in Table 1, 2 and 3. The specimens were processed into a size of 10mm×5mm×10mm, then assembled as shown in Fig.1. Specimen with higher potential was placed in the upper part of Fig.1. After being welded with wires respectively, the three kinds of specimens were sealed by epoxy resin together with the Ag/AgCl reference electrode.

Table 1.	Chemical	composition	of 907	low allo	y steel	(wt%)
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element	С	Si	Mn	S	Р	Ni	Cr	Cu	Nb	Ti	Fe
wt%	0.10	0.63	0.97	0.006	0.012	0.64	0.70	0.51	0.027	0.020	bal

 Table 2. Chemical composition of 921 low alloy steel (wt%)

element	С	Si	Mn	S	Р	Ni	Cr	V	Mo	Fe
wt%	0.06	0.17	0.30	0.010	0.015	2.5	0.90	0.04	0.20	bal

Before test, the working surfaces of the electrode were sanded with abrasive paper from 260# to 1500#, polished and cleaned ultrasonically in acetone and ethanol for 5~10 minutes. After that, the electrode was dried and ready for use.

eleme	nt Ni	Fe	Mn	Pb	S	С	Zn	Cu
wt%	10.13	1.71	0.834	< 0.01	< 0.005	0.0059	0.06	bal

Table 3. Chemical composition of B10 copper-nickel alloy (wt%)



Figure 1. Schematic diagram of a three-phase coupling electrode

2.2 Simulation of deep-sea environment

The simulated deep-sea environment was performed with a self-designed device, as shown in Fig.2. The environmental parameters selected in this experiment were as follows: temperature 8°C, pH 8.0~8.5, salinity 3.4%, DO 2.7~3ppm, main pressure 300m(3MPa), 500m(5MPa), 700m(7MPa), 1000m(10MPa).



Figure 2. Schematic diagram of the deep-sea simulation device

(1-acid solution, 2-alkali solution, 3-brine solution, 4-choke valve, 5-nitrogen vessel, 6-oxygen vessel, 7-storage tank, 8-condenser, 9-temperature controller, 10-high pressure pump, 11-temperature sensor,

12-pH sensor, 13- salinity sensor, 14- working electrode, 15-pressure vessel, 16- pressure meter, 17-Automatic elevator)

2.3 Galvanic potential and current test

Galvanic potential and current were measured by two National instrument (NI) PXI 4071 digital multi-meters simultaneously. PXI 4071 is a 7.5-digit digital multi-meter. In voltage measurement model, it can measure voltage in the range 10 nV-1000 V with more than 1010 Ω input resistance, while in current measurement model, it acts as a zero resistance meter and 1pA to 3A current can be measured. The schematic diagram is shown in Fig. 3. Measured galvanic potential and current data was automatically read and saved by NI Labview software every 60s.



Figure 3. Schematic diagram of galvanic potential and current test

2.4 Weight loss test

The weight loss test was carried out according to GB/T 15748-2013. Three parallel samples were set for each group. All the weight loss samples were processed into the size of 20mm×30mm×2mm. The different materials were tied with binding tapes in the form of coupling. For each sample, after 20mm×20mm of the working area had been reserved, the connected part in the middle was sealed with epoxy resin filler.

2.5 Surface morphology characterization

The surface morphology of the samples after removal of corrosion products was observed by the Ultra55 Zeiss field emission scanning electronic microscope (FE-SEM). And the chemical composition was analyzed by energy dispersive spectrometer (EDS).

3. RESULTS AND DISCUSSION

3.1 Electrochemical experiment analysis



Figure 4. Galvanic potential and current of 921/907/B10 GC under different pressures with time (aA: 300m, bB: 500m, cC: 700m, dD: 1000m)

The information on galvanic potential and galvanic current of each branch under different pressure was derived out and the curves were shown in Fig.4.

Under different pressures, the variations of galvanic potential of 907/921/B10 three-phase couplings with time were very similar. At the beginning of coupling, the mixed potential ranged between -620mV and -680mV. The potential difference with the open circuit potential of 907 and 921, about -740mV, was big, thus the galvanic driving force and the total galvanic current was large correspondingly. However, with the generation of oxide film on the surface of B10 copper alloy functioned as the cathode, the process of oxygen diffusion was hindered, while 907 and 921 functioned as the anode accelerated their dissolution speed under the pressure in the deep-sea environment. As the couplings were immersed in the sea water, corrosive factor such as Cl⁻ and O₂ directly contacted with a large part of the substrate and reaction occurred accordingly. The galvanic driving force changed much greater in a short time, so the galvanic potentials rapidly shifted negatively. About 24 hours later, the negative shift rate decreased. The diffusion and formation rate of anodic corrosion product film reached a balance with the dissolution and deposition process of cathodic passive film. The galvanic potentials gradually became stable. Forty hours later, the galvanic potentials under different pressure remained between -720mV and-730mV. Thus the changes of pressure had little effect on the galvanic potentials.

The galvanic current under the same pressure varying with time showed the similar trends. The initial galvanic driving force was big, but there was no products covered on the surface of the electrode. The reaction resistance was small while the instant galvanic current was large.

However, with the generation of anodic corrosion products and the integrity of the oxide film on the cathode surface, the diffusion of O_2 was hindered. As a result, the galvanic current decreased rapidly and gradually stabilized 24 hours later. According to the results, the current direction of steel 907 branch under the pressure of 300m, 500m, 700m was positive, while the current of steel 921 branch was weak, nearly zero. The current of Alloy B10 branch and that of steel 907 branch were equal in magnitude and opposite in direction. It showed that under those pressures, coupling circuit consisted of 907 and B10 was predominant among the three-phase couples composed by 907/921/B10. During corrosion reaction, steel 907 dissolved as the anode and oxygen depolarization reaction occurred with B10 as the cathode, and steel 921 as a branch in the couples was not involved in obvious galvanic corrosion. Under the pressure of 1000m, electrode coupling changed in the opposite manner. The galvanic corrosion composed of the coupling branch 921/B10 was serious, while steel 907 was not involved in the galvanic corrosion.

Fig.4 obviously showed that the galvanic current (accordingly, the corrosion rate) changed apparently with pressure. The branch current value of steel 907 was $10\mu A \cdot cm^{-2}$ under the pressure of 300m, reduced to $1\mu A \cdot cm^{-2}$ significantly under the pressure of 500m, and increased to about $7\mu A \cdot cm^{-2}$ under the pressure of 700m. Under the above three pressures, the current value of steel 921 was almost zero, indicating that the steel 921 was seldom involved in corrosion process. Under the pressure of 1000m, the polarity of the electric current of steel 907 and 921 changed reversely. The current value of steel 907 was approximately zero, while the stable current value of steel 921 was about $15\mu A \cdot cm^{-2}$. The coupling current of B10 changed in the opposite direction accordingly but with the same value.

The variation of coupling current under above pressures showed that when the pressure was less than 1000m, steel 907 among the three-phase galvanic couples served as the anode and anodic dissolution reaction occurred. Steel 921 and metal B10 were all being protected under the mixed potentials. As the corrosion potential of steel 921 was still lower than the galvanic potential, it was anodic. At the same time the mixed potential was close to the self-corrosion potential of steel 921, which was little involved in the reaction. However, when the pressure was 1000m, steel 921 mainly acted as anode with anodic dissolution. Compared with the current in metal B10 branch, the current directed to the opposite direction but with the same value.

3.2 Weight loss experiment analysis

		907		921				
	$W_{0}(g)$	W (g)	R _{gc} (mm/a)	$W_0(g)$	W (g)	R _{gc} (mm/a)		
	11.0021	10.9571	0.3542	11.3457	11.3295	0.0559		
200m	11.0633	11.0179	0.3593	11.3534	11.3364	0.0661		
50011	10.9978	10.9523	0.3605	11.3396	11.3206	0.0916		
	11.2335	11.1903	0.2749	11.0612	11.0208	0.1237		
500	11.3785	11.3428	0.2139	11.0182	10.9640	0.2992		
500m	11.2847	11.2404	0.3233	11.0553	10.9971	0.3500		
	10.5372	10.5163	0.1664	15.8712	15.8645	0.0101		
700	10.4227	10.4000	0.1893	15.9688	15.9605	0.0305		
700m	10.4273	10.4058	0.1740	15.9749	15.9667	0.0292		
	10.5361	10.4793	0.3228	10.7166	10.649	0.3296		
1000	10.5841	10.5403	0.1569	10.6891	10.6284	0.2418		
1000m	10.6283	10.5839	0.1904	10.6133	10.5551	0.2100		

Table 4. Weight loss results of 907/921/B10 GC under different pressures

According to the weight loss results, under the pressures of 300m, 500m and 700m, for the galvanic couples composed by 907/921/B10, the corrosion rate of steel 907 was significantly greater than that of steel 921. Under the pressure of 300m, the galvanic corrosion rate of steel 907 was 0.35mm/a while that of branch steel 921, 0.05mm/a. Therefore, in case of three-phase coupling, steel 907 acted as anode in the corrosion process and B10 as the cathode. It was the same under the pressures of 500m and 700m. However, under the pressure of 1000m, the corrosion rate of steel 907 was about 0.15mm/a, while that of steel 921 reached to 0.25 mm/a. It indicated that the corrosion of coupling focused on branch 921.

It revealed from Table 4 that in the conditions of 300m, 500m and 700m, the corrosion of 907/921/B10 GC followed the same rules: the corrosion of coupling focused on steel 907. However, in the case of 1000m, the weight loss results deviated from those of the electrochemical experiment.

According to the electrochemical experiment, the anode of galvanic corrosion completely shifted to steel 921, while steel 907 was under protection. The weight loss results showed that the corrosion rate of steel 921 was greater than that of steel 907, but an obvious corrosion also occurred on steel 907. The reason was as follows: firstly, the weight loss experiment was intended to measure the mass variation caused by the localized corrosion and grain-boundary corrosion on the surface in the corrosion process. The electrical current measured by the electrochemical method included the information concerning both the corrosion inside the grain cells and that on the surface of the metal. Secondly, the electrochemical parameters had been very weak, the instrument used in the electrochemical experiment would be inevitably interfered by the electrochemical noises from the high-powered inverter in the deep-sea equipment, resulting in unavoidable systemic deviation. However, the experimental results and those of the electrochemical experiment were generally consistent.

3.3 Morphological Characterization





Figure 5. Morphology of 907/921/B10 GC after corrosion under different pressures (abcd: 907, ABCD: 921; aA: 300m, bB: 500m, cC: 700m, dD: 1000m)

After removal of corrosion products, the SEM morphology showed that under the pressure of 300m, 700m and 1000m, the corrosion of 907 and 921 were typical general corrosion. Under the pressure of 300m, 700m the corrosion of steel 907 was more serious than that of steel 921. While under the pressure of 1000m, the corrosion of steel 921 increased obviously. It was consistent with the results of the electrochemical and weight loss experiment. In addition, under the pressure of 500m, there were some clear corrosion pits on the surface of steel 907 and steel 921. Relative research [23, 24] showed that under the deep-sea water pressure, the activeness of Cl⁻ ions in the seawater changed in the form of a parabolic curve. There might be an extremum of the activeness of Cl⁻ ions near 500m, resulting in serious pitting corrosion.

4. CONCLUSION

(1) At the beginning of coupling, the galvanic driving force and the total galvanic current of the three-phase couples composed by steel 907/921/B10 under different pressures was large. With the generation and integrity of oxide film on the surface of cathode and the formation of corrosion products on the surface of anode, the galvanic potentials shifted negatively and gradually became stable after forty hours. The final stabilized galvanic potential was hardly affected by pressure.

(2) When the simulated deep-sea pressure was less than 1000m, steel 907 dissolved as the anode in the galvanic corrosion of the three-phase couples composed by steel 907/921/B10. And steel 921 as another anode in the couples was not involved in obvious galvanic corrosion. Under the pressure of 1000m, the corrosion rate of steel 921 was greater than that of steel 907.

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