

CORROSION INHIBITION BY FRESHWATER BIOFILM ON 316 STAINLESS STEEL

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Studies on corrosion and microfouling on 316-stainless steel were carried out in natural pond water. The effect of freshwater biofilm on corrosion of 316 stainless steel in natural environment has been found out by various methods like potential measurement, polarization and impedance measurements for an exposure period of 100 days. Fresh water biofilm was able to ennoble the corrosion potential of 316 stainless steel. Less corrosion current and high resistance values were observed for 316 stainless steel in presence of pond water biofilm. The broad phase angle obtained from impedance measurements indicates the presence of intact passive film on 316- stainless steel in the presence of natural biofilm.

Keywords: 316-stainless steel, biofilm, corrosion inhibition and passivation.

INTRODUCTION

Stainless steels are alloys of iron containing 12-30% chromium to provide corrosion resistance. Although they are not usually resistant to reducing environments, they are quite corrosion resistant under oxidizing conditions. Areas depleted of oxygen, such as crevices or under slime deposits are there fore susceptible to corrosion. Very few studies on the Biorrosion mechanisms of these alloys have been carried out. Microbiologically influenced corrosion of stainless steel particularly of 300 series was reported by a number of authors [1-2]. However, several investigations reveal that little or no attack was found on stainless steel [3]. Many workers have attributed ennoblement to the catalysis of the oxygen reduction reaction through microbial enzymes [4], organometallic complexes [5] and extra cellular chemicals [6-7]. Chandra sekaran and Dexter [8] have suggested that peroxide generated from bacterial activity could be an added contributor to ennoblement at low pH conditions. The biofilms enhanced the passivity of stainless steel alloys by increasing both the passive region and the critical breakdown potential. On the basis of photoelectrochemical studies, [9-10] alloys having an overlayer of n-type semi conducting oxide film only exhibited a substantial positive shift of corrosion potential, but, whether the biofilm improves passivity is not known.

In the present study, the behaviour of 316-stainless steel during the formation of natural biofilm in fresh water has been examined to find out the role of bacteria.

EXPERIMENTAL

316-stainless steel specimens were polished with 240 grit paper, degreased, weighed and exposed to natural pond water system and abiotic system for a period of 100 days. Specimens of 1 cm² area were used for the electrochemical studies. Natural pond water was changed at every 24 hours intervals in order to make the biofilm alive. The same water was sterilized by autoclaving at 423 K for 15 to 20 minutes. This sterilized water was used as the control system (without bacteria).

Isolation and characterization of the microorganisms in the biofilm samples were done in the laboratory. The metallic coupons of 316-stainless steel of 10.5 cm x 5.5 cm were used. Morphologically dissimilar well isolated colonies were randomly selected and streaked on nutrient agar plates to obtain pure culture. After noting the colony morphology and pigmentation of the colony, the pure cultures were streaked on nutrient agar slant and stored below 277 K to keep the bacterial strains viable. Periodic subculture was done once in a month. The characterization of bacteria upto generic level was done according to the key

described in the Bergeys manual of systematic bacteriology.

Periodical potentials were measured by using a multimeter. Tafel polarization measurements were carried out potentiodynamically using potentiostat (PAR Model 173) in conjunction with a potentiocan generator (PAR 175) and an XY recorder employing a stationary electrode. The electrode potential was fixed at 200mV cathodic to open circuit potential and allowed to attain a steady state value. The steady state polarization was carried out from - 200 mV to +200 mV with reference to the OCP at a scan rate of 0.5 mV/Sec. The icorr values were obtained from the plots of E vs logi curves. The impedance studies were carried out using computer controlled EG & G electrochemical impedance analyzer (model M6310) with software M398. After attainment of a steady state potential AC signal of 10 mV amplitude was applied and impedance values were measured for frequencies ranging from 0.01 Hz to 100 KHz. The values of R_p were obtained from the Nyquist plots.

RESULTS AND DISCUSSION

The biological characteristics of the pond water system are given in Table I. The bacterial counts of heterotrophic bacteria in natural pond water were in the range of 4.3×10^5 to 7.06×10^7 CFU/cm². It shows that the attachment of stainless steel loving bacteria takes place on 316-stainless steel. The pH and dissolved oxygen concentration of the pond water were in the range of 7.1 to 7.3 and 4.87 ppm to 5.01 ppm.

Table II gives the test results of the bacterial strains, isolated and identified from the biofilm samples collected from 316 stainless steel coupons on exposure to natural pondwater for 100 days. The organisms were belonging to different genera such as Xanthomonas sp., Staphylococcus sp., Micrococcus sp., Bacillus sp., Pseudomonas sp., Vibrio sp. and Achromobacter sp. There was no significant weight loss in 316 stainless steel during their immersion period in the natural pond water system

Microbiologically Influenced Corrosion (MIC) on stainless steel has been observed by many workers that biofouling has produced ennoblement of sea-immersed stainless alloys. While it is generally

TABLE I: Biological characteristics of biofilm, pH and dissolved oxygen values of natural pond water system

No of days	Bacterial count attachment in pond water (CFU/cm ²)	pH	Dissolved oxygen (ppm)
10	4.30×10^5	7.2	4.99
20	6.15×10^6	7.3	4.89
40	7.06×10^7	7.1	4.87
60	8.56×10^6	7.3	5.01
80	7.43×10^6	7.3	5.00
100	6.85×10^6	7.1	4.98

agreed that marine biofilms affect electrochemical reactions at the metal surface, the major mechanism of a positive shift in corrosion potential by several hundred mV still remains debatable. Fig. 1 shows the open circuit potential (OCP) variation for stainless steel exposed to natural pond water system and its control. The results clearly indicated that the OCP of 316 stainless steel increased with time to positive values. In natural pondwater system the positive shift was about 380 mV but in control system of pondwater slight positive shift of about 150mV was observed. These results clearly show that a large ennoblement is contributed by the bacteriologically produced biofilm.

There are many theories proposed by many research groups on ennoblement of organometallic complexes [5]. Low pH theory by Chandrasekar and Dexter [8], Neutral pH theory with anodic passivation by Eashwar *et al.* [11], Adsorption theory by Maruthamuthu *et al.* [12]. The remarkable protective effect of the biofilm cannot be due solely to a reduction of the oxygen concentration on the stainless steel surface in the presence of the biofilm. The present work confirms

TABLE II: Name of the bacterial genera present on 316 stainless syteel in pond water

1. Xanthomonas sp
2. Pseudomonas sp
3. Achromobacter sp
4. Bacillus sp
5. Micrococcus sp
6. Vibrio sp
7. Staphylococcus sp

The earlier observation by Dexter and Zhang [13] that biofilm from fresh pond water are able to enoble the corrosion potential of alloys as happens in seawater. This observation is in agreement with that of Dexter [14], Maruthamuthu *et al.* [10], Eashwar *et al.* [11]. On the contrary, ennoblement has been noted by Little *et al.* [14] in Gulf of Mexico waters. In the present investigation, the OCP values gradually increased with time in presence of natural biofilm. However Little *et al.* [14] have performed oxygen measurements through microprobe to show that the biofilm substratum interface remained virtually oxygen free. Further, the sharp influence in corrosion potential was found to coincide with an increase in the number of *Desulfovibrio* and *Desulphotomaculum* species. It may be a reason for the fast/slow ennoblement in the present study. Because the slow adsorption of bacteria on SS-316 in natural biofilm. The anodic polarization clearly reveal that the ennoblement process involves a reduction of the passive current (I_p) at the same time the biofilm increases the pitting probability by shifting the potential nearer to the breakdown potential [15-16].

Table III show the polarization behaviour of 316 stainless steel in natural pond water and its control system. The corrosion rates were less in the natural pond water biofilm in the range of 0.022-0.074 $\mu\text{A}/\text{cm}^2$ during 100 days immersion

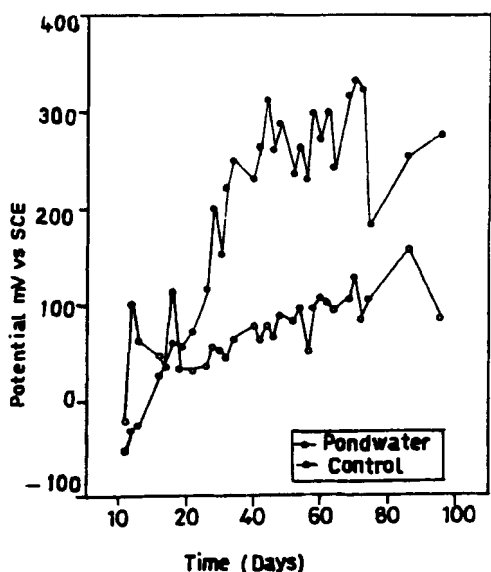


Fig. 1: Potential time behaviour of 316 stainless steel in natural pond water system and sterile control system

TABLE III: Corrosion rates of stainless steel-316 in natural pond water system and abiotic system by polarisation technique

No of days	Natural pond water		Control system	
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	mmpy	I_{corr} ($\mu\text{A}/\text{cm}^2$)	mmpy
10	0.022	2.4506×10^{-4}	0.024	2.6734×10^{-4}
20	0.045	5.0126×10^{-4}	0.100	1.139×10^{-3}
40	0.030	3.3417×10^{-4}	0.045	5.0126×10^{-4}
60	0.054	6.0151×10^{-4}	0.100	1.1139×10^{-3}
80	0.074	8.2430×10^{-5}	0.010	1.1139×10^{-4}
100	0.012	1.3367×10^{-4}	0.065	7.2404×10^{-4}

period. But in the control system the corrosion rates were high in the range of 0.022-0.10 $\mu\text{A}/\text{cm}^2$. The corrosion rates were less in the natural pond water biofilm when compared to control system. Polarisation figures also explain that the influence of natural pond water biofilm in anodic reaction with 100 days' time. The corrosion rates were less in the natural pond water biofilm when compared to control system. Table IV show the impedance parameters for 316 stainless steel in natural pond water and its control system. The high R_t values in presence of natural pond water biofilm obtained in impedance studies suggest that the high resistance film was developed on stainless steel by natural biofilm which supports the results of polarization studies. The impedance spectrum contains contributions from the corrosion reaction and their film performance. The broad phase angle with wide frequency indicates that the presence of intact passive film on 316-stainless steel. The fluctuation of phase angle in presence of biofilm also indicates the improvement of passivity in presence of natural biofilm.

TABLE IV: Impedance parameters for stainless steel-316 in natural pond water system and abiotic system

No of days	Natural pond water		Control system	
	R_t ($\text{K}.\text{ohm}.\text{cm}^2$)	mmpy	R_t ($\text{K}.\text{ohm}.\text{cm}^2$)	mmpy
10	1085	3.26×10^{-6}	2143	1.93×10^{-6}
30	565	1.15×10^{-5}	339	1.92×10^{-5}
60	195	2.00×10^{-5}	35	7.35×10^{-5}
100	191	2.00×10^{-5}	35	7.35×10^{-5}

CONCLUSION

- The present work confirms that the biofilm from fresh water is able to ennoble the corrosion potential of 316-stainless steel.
- Polarisation studies also confirm that the influence of natural biofilm reduces the corrosion rate of stainless steel specimens.
- The high R_t values in the presence of pond water biofilm indicate the improved passivity due to the biofilm. The broad phase angle with wide frequency indicates the presence of intact passive film on 316-stainless steel in the presence of biofilm.

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