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Microbiologically Influenced Corrosion in Seawater and Corrosion Resistance of High Nitrogen Stainless Steel

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Type316L stainless steel specimens were exposed to natural seawater, and microorganisms in seawater created biofilms on the surfaces of the specimens. The concentration of H_2O_2 in biofilms was detected, and open circuit potentials (OCP) for the specimens were also measured. Then, H_2O_2 in biofilms was decomposed with Catalase or Peroxidase. The rise in OCP was offset by decomposing H_2O_2, and the value of OCP with H_2O_2-free biofilms was as low as that with no biofilm growth.

High nitrogen stainless steels (HNSS) were fabricated through pressurized electro-slag remelting (P-ESR), and their corrosion resistance was evaluated. Electrochemical measurements in a laboratory showed that crevice corrosion potentials were shifted in higher direction by adding N and that N could improve the corrosion resistance of stainless steels. Then, HNSS and commercial stainless steels (Type 316L and Type 329J4L) were exposed to natural seawater for 6 month or 1 year in a field sea area, where microorganisms have effects on corrosion. No corrosion was initiated on HNSS although both Type 316L and Type 329J4L were damaged with crevice corrosion.

Key words: Microorganism, Hydrogen peroxide, Open circuit potential, Pressurized electro-slag remelting, Crevice corrosion

1. Introduction

Microorganisms have a noticeable effect on surface conditions of materials that are placed in the natural environment. It is also recognized that microbiological effects can result in material degradation. For example, some stainless steels free from corrosion in synthetic seawater or filtered natural seawater can be damaged when placed in non-filtered natural seawater [1]. Open circuit potentials (OCP) for stainless steels that are exposed to natural seawater are raised [2-5]. OCP is a kind of index showing how corrosive the environment is for stainless steels, and OCP of high value may result in localized corrosion. Rise in OCP does not occur when steels are exposed to sterile seawater [6].

Marine microorganisms create biofilms on the surfaces exposed to natural water [7, 8]. The biofilms, which exhibit a shifting in the higher direction of OCP, are thought to play an important part in the microbiological corrosion of stainless steels [9]. Arguments have arisen concerning the effect of these biofilms on the rise in OCP and its mechanisms. A hypothesis is based on the presence of H_2O_2, generated by microorganisms in the biofilms [6, 10].

Also, prevention of bio-fouling such as biofilm formation and macro-fouling has been devised by means of toxicity. Injection of biocidal chemicals into water has been used widely. For the same purpose, toxic elements (Cu, Ag, Sn, *etc.*) have been added to metallic materials and paint coatings. However, it is desirable to reduce the use of such toxic elements and chemicals from a viewpoint of preserving the environment. To avoid degradation of a stainless steel without toxicity, its corrosion resistance has to be still higher than ordinary stainless steels. Although the contents of Cr and Mo are usually increased to improve corrosion resistance, there is a possibility of Cr ions or Mo ions having toxicity.

Levey and van Bennekom [11] showed that N in stainless steels had the property of improving their corrosion resistance and that the effect of N was grater than Cr and Mo. It is, therefore, expected that high nitrogen stainless steels (HNSS) would be not only resistant to corrosion but also resource-saving.

The present paper aims at explaining the mechanism of microbiological corrosion, fabricating HNSS through pressurized electro-slag remelting (P-ESR) and evaluating their corrosion resistance.

2. Experimental procedures

2.1 Decomposition of H_2O_2 and measurement of OCP

Commercial Type 316L stainless steel specimens were exposed to natural seawater in a field sea area for a month. After the exposure, the specimens, covered with biofilms formed by marine microorganisms, were brought into synthetic seawater adjusted to pH 8.2 and the tests were conducted at the laboratory. OCP for the specimens were measured and the concentration of H_2O_2 in the biofilms was gauged with analytical test strips (Merck, Merckoquant 1.10081.0001 and 1.10011.0001). Some parts of the biofilms were removed from the specimens and put on the reaction zones of the test strips. The H_2O_2 concentration was determined according to variations in the colors of the reaction zones.

Catalase and Peroxidase are typical enzymes, which have catalysis to disintegrate H_2O_2, and were used in the H_2O_2 disintegrating tests. 5mg of Catalase (specific activity : 1200units / mg) were dosed to 1dm^3 of the synthetic seawater and the water temperature was varied from 23ºC (room temperature) to 33ºC (suitable for the action of the enzymes). OCP for the specimens and the concentration of H_2O_2 in the biofilms were measured at each temperature. 30mg of Peroxidase (specific activity : 129units / mg) were dosed instead of Catalase. OCP and H_2O_2 concentration were measured on the same procedures as the decomposing tests with Catalase.

2.2 Fabrication of HNSS

HNSS were fabricated with a P-ESR furnace, whose major specifications are as follows: the maximum weight of ingot is 20kg, the maximum pressure of N_2 gas is 5 MPa. A copper crucible and materials were installed in a chamber of 50 dm^3 in inner volume. FeCrN powders, which were used as N source, were packed in stainless steel tubes and sintered. These tubes were spot-welded into a stainless steel rod, which was the main material. They were melted by joule heating with electric current in the chamber filled with N_2 gas. The pressure of N_2 gas was adjusted to a proper value ranging from 1 MPa to 4MPa. Mixtures of CaF_2, CaO and Al_2O_3 were used as fluxes, which were put into the crucible in advance. In the initial stage of the melting, the flux was melted to be a slag pool, in which the material electrode was able to be melted. The voltage was varied from 27 to 30 V for the purposes of adjusting the current to values between 2 and 3 kA and adjusting the melting rate to 0.5-0.7 kg/min. The ingots obtained through P-ESR were forged and rolled to plates. Solution treatments were conducted at 1200 ºC in order that HNSS can have a single austenitic phase.

2.3 Evaluation of corrosion resistance

Stainless steels form oxide films, which cover their surfaces and protect the matrix metals from corrosion. However, the protective oxide films can be destroyed partially under severe conditions such as seawater containing Cl^- and microorganisms. Localized corrosion of stainless steels is classified into 2 types. One is pitting corrosion, which is initiated and propagated on free surfaces. The other is crevice corrosion observed on surfaces facing crevices. Crevice corrosion can be initiated and propagated under comparatively mild conditions where pitting is not initiated. Therefore, crevice corrosion is more serious than pitting, and we evaluated crevice corrosion resistance of HNSS.

23%Cr-4%Ni-0%Mo-(0.8 or 1.0)%N stainless steels and 23%Cr-4%Ni-1%Mo-(0.7 - 1.1)%N stainless steels were used for the tests measuring crevice corrosion potentials. Crevice corrosion potentials are regarded as maximum values of potentials, at which stainless steels are free from crevice corrosion. When OCP are higher than crevice corrosion potentials, there is a possibility that crevice corrosion can be initiated. A couple of multi-crevice assemblies made of polysulfone resin was attached to a specimen from both sides. The specimens were exposed to synthetic seawater adjusted to pH 8.2 and 35 ºC. The potentials of the specimens were set at certain values with a potentiostat for 48 h. If no corrosion had been initiated at a set potential, the same test was conducted at 25 mV higher potential. These procedures were repeated, and the highest values of the set potentials with no corrosion were defined as crevice corrosion potentials.

Type 316L (16%Cr-13%Ni-2%Mo-1%Mn), Type 329J4L (25%Cr-7%Ni-3%Mo) commercial stainless steels and 23%Cr-4%Ni-2%Mo-(0.8 or 1)%N stainless steels fabricated through P-ESR were exposed to natural seawater in a field sea area for 6 month or 1 year. Multi-crevice assemblies were attached to these specimens on the same procedures as mentioned above to evaluate their crevice corrosion resistance.

3. Results and discussion

3.1 Effect of H_2O_2 on microbiological rise in OCP

Table I shows H_2O_2 concentration in the biofilms and OCP for the specimens, before and after decomposition of H_2O_2 by means of the enzyme. Before the elevation of the water temperature (23ºC), OCP for the specimens covered with biofilms reached approximately +0.6V vs. SHE both with and without Catalase, and H_2O_2 in the biofilms was detected in concentration ranging from 10 to 30ppm. At the elevated water temperature in the Catalase-dosed water (33ºC), OCP for the specimen covered with the biofilms fell to values equal to OCP for the specimen without biofilms (+0.2V vs. SHE), and H_2O_2 was not detected in the biofilms (< 0.5ppm). In the case of no Catalase, OCP for the specimen with the biofilms remained higher than +0.5V vs. SHE, and H_2O_2 concentration in the biofilms was ranging from 10 to 30ppm at 33ºC. After the water temperature was lowered to 23ºC, the values of OCP and H_2O_2 concentration were as high as those values that were measured before the elevation of the water temperature.

The results of the decomposing tests with Peroxidase were also shown in Table I. OCP and H_2O_2 concentration behaved in the same way as the experiment with Catalase.

These results reveal that H_2O_2 was one of necessary conditions of the rise in OCP induced by marine microorganisms in biofilms. OCP for Type 316L covered with native biofilms in enzyme-dosed water were ennobled again according to the drop in water temperature. This result suggests that the experimental procedures had influence on neither the activity of microorganisms nor the structure of native biofilms, and that the microorganisms in native biofilms continued to produce H_2O_2.

Table I Effect of enzyme and water temperature on OCP and H_2O_2 concentration in biofilms

Temp. (ºC)	Enzyme	[H_2O_2] (ppm)	OCP (Vvs. SHE)
23	-	10 – 30	0.6 – 0.7
	Catalase	10 – 30	0.6 – 0.7
	Peroxidase	10 – 30	0.6 – 0.7
33	-	10 – 30	0.5 – 0.6
	Catalase	< 0.5	0.2 – 0.25
	Peroxidase	< 0.5	0.2 – 0.25
23	-	10 – 30	0.6 – 0.7
	Catalase	10 – 30	0.6 – 0.7
	Peroxidase	10 – 30	0.6 – 0.7

3.2 Crevice corrosion resistance of HNSS

Fig.1 shows a relationship between N contents in stainless steels and their crevice corrosion potentials in synthetic seawater at 35 ºC. There was a positive correlation between N contents and crevice corrosion potentials in the both cases of 23%Cr-4%Ni-0%Mo and 23%Cr-4%Ni-1%Mo. This result reveals that N in stainless steels has an improving effect on their crevice corrosion resistance. Fig.1 also shows that the addition of N could shift the crevice corrosion potentials to values higher than 0.7 V vs. SHE. OCP for stainless steels in natural seawater were raised by biological effects. However, their maximum value was approximately 0.7 V vs. SHE as shown above. Crevice corrosion does not occur if the value of OCP is lower than the crevice corrosion potential. It was, therefore, expected that microbiologically influenced corrosion could be avoided by alloying stainless steels with N. For the purpose of proving this expectation, exposure tests were conducted in a field sea area.

Fig.2 shows the results of crevice corrosion tests in a field sea area. All specimens of Type 316L and Type 329J4L were damaged with crevice corrosion after both 6 month exposure and 1 year exposure. On the other hand, neither HNSS was degraded after 6 month or 1year exposure to natural seawater under crevice conditions. The contents of Cr, Ni and Mo in HNSS used for the tests were less than those in Type 329J4L. Nevertheless, HNSS had an excellent property of resisting crevice corrosion. Therefore, it can be regarded that HNSS would be a sound material free from corrosion in natural seawater and a resource-saving stainless steel.

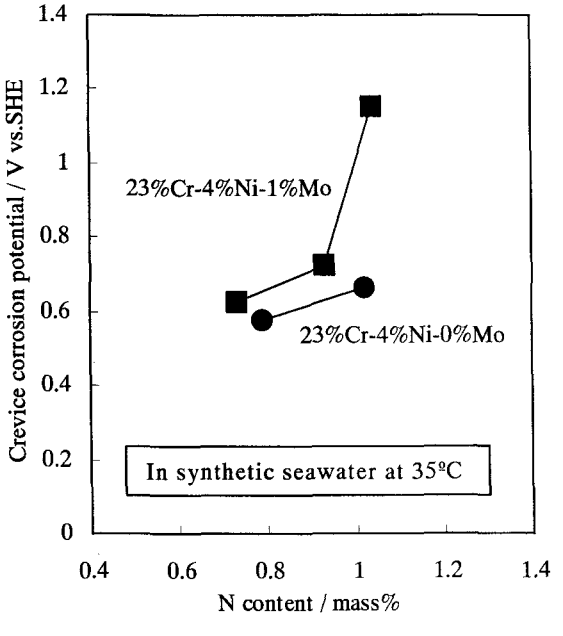

Fig.1 Effect of N on crevice corrosion potentials.

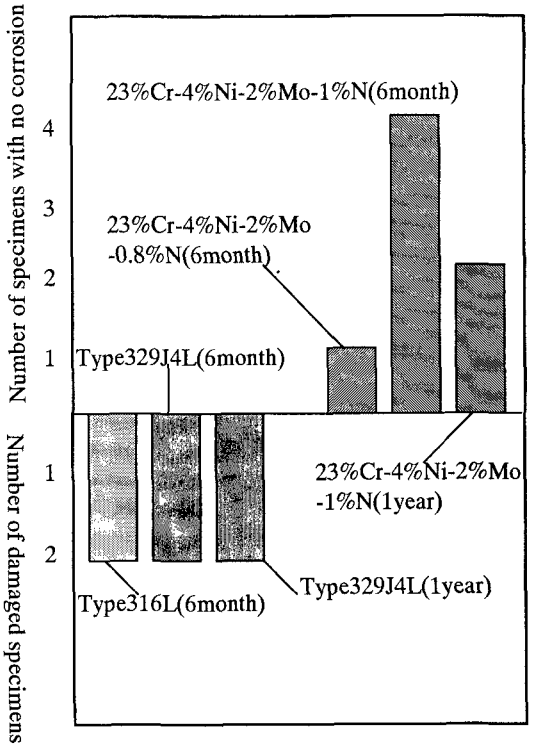

Fig.2 Number of specimens with and without crevice corrosion in natural seawater.

4. Conclusion

(1) Marine microorganisms produce H_2O_2 that are enriched in biofilms on material surfaces exposed to natural seawater.

(2) H_2O_2 in biofilms is an essential factor in OCP rise, which is a major cause of corrosion initiation of stainless steels.

(3) N in 23%Cr-4%Ni-(0 or 1)%Mo stainless steels raises crevice corrosion potentials, which leads to higher corrosion resistance.

(4) 23%Cr-4%Ni-2%Mo-(0.8 or 1)%N stainless steels are not degraded under crevice-attached conditions in natural seawater, where Type 329J4L is damaged as well as Type 316L.

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