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Crevice Corrosion Resistance of Stainless Steels in Natural Sea Water with different Post Welding Treatment

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Crevice corrosion of stainless steels in natural seawater was investigated for several post weld treatments; as-annealed, as-welded, pickled, and ground. The results confirmed the effect of the biofilm on the cathodic reaction leading to an ennoblement of the rest potential. The degree of ennoblement of corrosion potential depends on the surface finish. As-annealed and pickled samples show stable corrosion potential approaching to 200 ~ 300 mV (SCE) while as-welded and ground samples show the fluctuating corrosion potential. This points to a situation where there are conflicting effects determining the trend in free corrosion potential. Crevice corrosion initiation will tend to pull the free corrosion potential in the active direction, whereas the presence of biofilm will tend to ennoble corrosion potential. There was no visible attack on UNS S31803, S32550, and 2205W. Therefore, those stainless steel grades appeared to be resistant to crevice corrosion in natural seawater on condition of weld metal.

Keywords : *surface finish, ennoblement, cyclic potentiokinetic polarization.*

1. Introduction

Although numerous corrosion investigations of stainless steels had been conducted on non-welded specimens in marine environments,[1)~4)] more information has been needed on corrosion behaviors of welded materials. Since the weld-modified material might differ from the base material with respect to chemical composition, chemical composition uniformity, microstructure, or surface condition, it was reasonable to expect that the weld-modified material might respond differently than the base material with regard to corrosion resistance associated with a natural marine environment. To get a better understanding of corrosion resistance of weld metal in seawater, untreated, pickled and ground specimens of welded joints were exposed to natural seawater. Resultant corrosion rates and corrosion behaviors were evaluated and compared.

2. Experimental

2.1 Materials

Table 1 shows the weldments selected for evaluation, including welding condition, base metals, and surface treatments. They include five stainless steels (SS) with base metals of UNS S30400, UNS S31603, UNS S31803, UNS S32550, and W-containing duplex alloy. Experimental welding has been performed applying automated TIG welding process. Following the welding procedures, plates were cut into coupons measuring 25 mm by 50 mm, with the weld region centered on, and perpendicular to, the length of the coupon. Weldments were prepared to match surface conditions normally used in service. Surface conditions of weldments are summarized in Table 2.

2.2 Exposure conditions

All test were performed at the seawater facility located at Youngdo-gu, Busan-shi. The seawater was pumped from the Young-do coast into the reservoir. There is no access of light to the seawater between pumping system in the sea and the exposed coupons. The seawater is completely renewed: It is a single pass loop and there is no recirculation of the seawater. The seawater flows at 0.01 ms^{-1} inside the reservoir.

Table 1. Chemical composition of tested stainless steels (wt%)

Alloy	C	Ni	Cr	Mo	W	N
UNS S30400	<0.05	8.2	18.5	-	-	-
UNS S31803	<0.03	5.5	17.9	3	-	-
2205W	<0.03	5.8	22	1.8	-	0.17
	<0.03		24.7		-	0.23
	<0.03		22.2		2.2	0.17

Table 2. Post weld treatment of weldments

As-welded	• Weldments were left in basically an untreated condition • This involved filing off the shear edges that had formedduring the cutting process
Ground with wire wheel	• Weldments were briefly brushed with a UNS S30400 wire brush to remove the bits of slag that remained from the welding process
Pickled (1)	• Weldments were ground with wire wheel and subsequently pickled in mixed acid including Nitric acid and Hydrofluoric acid at 50℃
Pickled (2)	• Weldments were pickled in mixed acid including Nitric acid and Hydrofluoric acid at 50℃
Polished	• Weldments were ground with a emery paper (#320)

Table 3. Seawater compositions during the tests (μg/Kg)

Salinity	pH	Temp. (℃)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	Br^-	F^-	HCO_3^-	SO_4^{2-}	$B(OH)_3$
32.5	7.3	16~25	10.09	0.384	1.218	0.387	0.007	19.35	0	<0.001	0.12	2.65	0.024

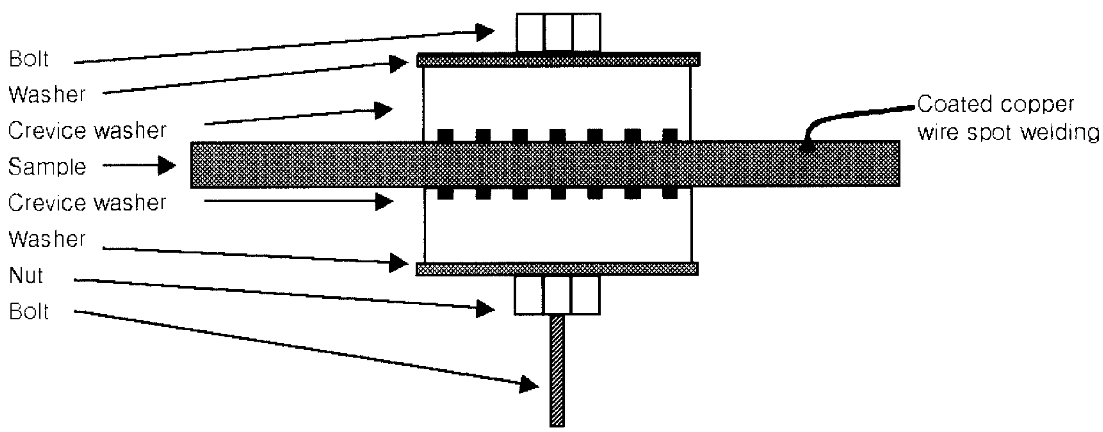

Fig. 1. Crevice corrosion test assembly

2.3 Measurements

The free corrosion potentials of plates were measured vs saturated calomel electrode (SCE) every hour. Seawater temperatures were also measured every day. Chemical analyses of the seawater were conducted during the tests and included analyses of the main cations and anions. Mean values obtained during the tests are shown in Table 3. No major variations were observed except the ambient temperatures of seawater that varied from 16℃ to up to 25℃.

For electrochemical measurements, electrical connections were made to each coupon. For the initial exposure, coated copper wires were spot-welded to the stainless steels and wire/coupon connections were coated prior to testing to reduce the possibility of galvanic effects due to composition differences between the wire and stainless steels. For exposures involving the creviced condition, the assembly (Fig. 1) was employed. Bolts, washers, and nuts were fabricated from alloy C-276 while the crevice washer was fabricated from PFTE. The samples were mounted on a isolated alloy C-276 bolt. Alloy C-276 nuts were tightened with a torque force of 2Nm using a 6Nm torque wrench. The crevice former gives a crevice area 0.6 cm^2 on each side of sample.

Steady state E_{corr} and cyclic potentiodynamic polarization (CPP) were performed on the flat specimens in 1-L cell Electrochemical instrumentation consisted of EG&G Princeton Applied Research Model 273A. The Potentiostat was controlled using EG&G 352 software running on a personnel computer. CPP test were conducted using ASTM G61-86 as a guide, with modifications. Scans of specimens were performed at a rate of 1.2V/h. Parameters of the CPP began with the initial potential at 0 V vs the open circuit corrosion potential (OCP). It was assumed that the reference of crevice corrosion initiation is the potential at which the current density begins to increase drastically in the passive range in natural seawater. Therefore, the point at which the CPP curve reversed direction was controlled with a threshold current of 500 $\mu A/cm^2$ to maintain consistent test parameters for all tests. The current density of base metals in natural seawater does not exceed 100 $\mu A/cm^2$ on condition of no abrupt crevice corrosion initiation while that of weldments exceeds 100 $\mu A/cm^2$ in seawater

3. Results

3.1 Free corrosion potential evolution

Experiments were conducted with three plates made of UNS S30400, S31603, S31803. Free corrosion potential evolutions are illustrated in Fig. 2 for these plates.

Corrosion potential reached its maximum value between 15 and 20 days after the start of the exposure depending on its alloys. Alloys that contain Mo show a rapid increase of the corrosion potentials compared to UNS S30400. A shift of the corrosion potential up to 350 mV(SCE) was observed, perhaps a little faster, in UNS S31803. Corroded specimens had lower corrosion potentials and fluctuated as illustrated by the 304 and 316L potential behavior in Fig. 2. UNS S31803, excluding the 304 and 316 grade, showed a very good behavior: depassivation was observed under the crevice washers but without weight loss or depth of penetration. Fig. 3. shows the potential evolutions of creviced weldments. Conversely, on inspection of Fig. 3, ennoblement did not occur. Crevice corrosion initiation

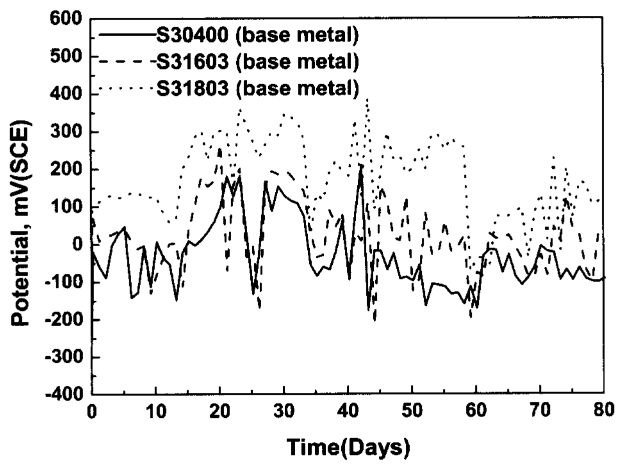

Fig. 2. Potential evolution of crevice coupons exposed to flowing seawater.

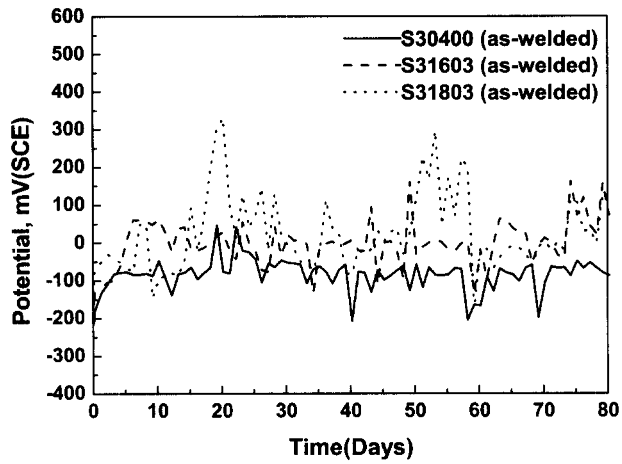

Fig. 3. Potential evolution of crevice coupons exposed to flowing seawater.

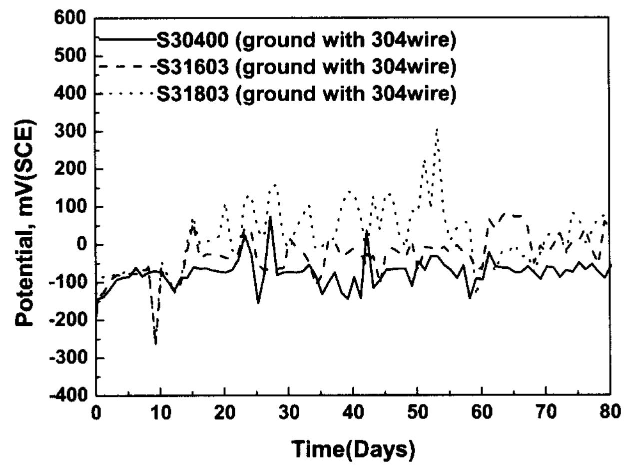

Fig. 4. Potential evolution of crevice coupons exposed to flowing seawater.

tends to decreas the free corrosion potential in the active direction, whereas the presence of biofilm will tend to ennoble corrosion potential.

Fig. 4 shows the potential evolution of specimens ground with 304 wire brush. Like the potential evolution of as-welded specimens, there is no sharp potential increase during the seawater exposure periods. It is well known that the disadvantages of mechanical descaling are the fact that the surface defect may be obscured, making them difficult to detect. Such defects may be operated as a source of crevice. Secondly, corrosion resistance of 304 wire brush is inferior to the materials being worked on, making the small anode and large cathode susceptible to localized corrosion.

Acid pickling removes the surface contaminants such as embedded 304 particles and imparts passivity to

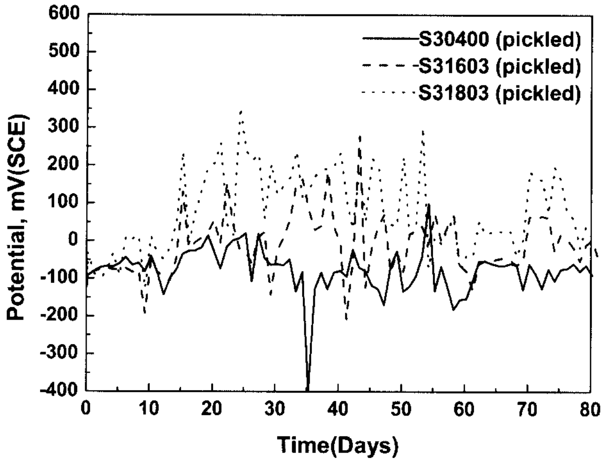

Fig. 5. Potential evolution of crevice coupons exposed to flowing seawater.

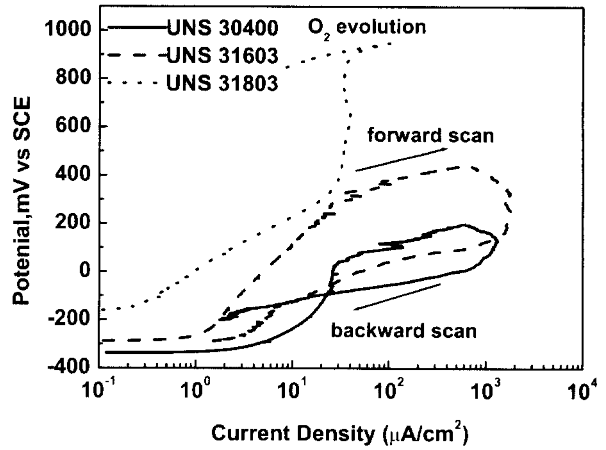

Fig. 6. CPP curves for creviced base metals in natural seawater (polished)

Table 4. Maximum crevice corrosion rates (mm) of SS's exposed to natural seawater for 10 months

Conditions / Steel Grades	as-annealed	as-welded	ground with 304 wire	pickled after grinding with 304 wire
UNS S30400	1.51	0.90	1.70	1.63
UNS S31603	0.33	0.36	<0.30	<0.30
UNS S31803	0	<0.30	<0.30	<0.30
UNS S32550	0	<0.30	<0.30	<0.30
2205W	0	<0.30	<0.30	<0.30

stainless steel surface. Compared to potential evolution of base metals, it was believed that some 304 particles were present (Fig. 5.) after wire brush accompanied by acid pickling. Therefore, wire brushes should be of a stainless steel that is equal in corrosion resistance to the materials being worked on.

3.2 Crevice corrosion

Crevice corrosion test with artificial crevice former were carried out on five stainless steel grades exposed in natural seawater in a single pass loop using a reservoir located outdoors. Results for specimens exposed to natural seawater after 10 months are given in Table 4. Crevice is found on UNS S30400 of 0.9 ~ 1.7 mm in depth and crevice depths of all other grades of stainless steel are around 0.3 mm in depth. The most severe corrosion of UNS S30400 occurs on the crevice area formed by artificial crevice former after grinding with a maximum crevice depth of up to 1.7 mm. UNS S31803, S32550 and W-containing duplex SS evaluated in this project exhibited excellent resistance to corrosion over the 10 month exposure in seawater.

CPP experiments were performed on five polished base metals in natural seawater. Results for three base metals are shown in Fig. 6. The natural seawater CPP for UNS S30400 and S31603 showed a large hysteresis loop. The large hysteresis area in natural seawater was typical of CPP data for UNS S30400 and S31603 and explains the deep crevice depth. There was a large variation of the crevice initiation potential between UNS S30400 and S31603. Therefore, based upon visual examination and measuring of the maximum crevice depth, there was correlation between the crevice initiation potential and the occurrence of crevice corrosion. This explains why UNS S31603 is more resistant to natural seawater compared to UNS S30400. The maximum crevice depth of UNS S31603 was 0.33mm. CPP experiments performed on UNS S31803, S32550, and 2205W showed distinct difference compared to low alloyed stainless steels. As shown in Fig. 5 the curve contained a full passive range. The reverse curves followed the oxygen evolution curve. The lack of significant hysteresis and the position of crevice initiation potential indicated resistance to localized crevice corrosion. Visual inspection of the CPP samples revealed no crevice corrosion on the surface. These CPP results are well in accordance with the data obtained in the exposure test. Though some slight depassivation processes were observed under the crevice washers on a lot of coupons, there was no visible attack on UNS S31803, S32550, and 2205W. Therefore, those stainless steel grades appeared to be resistant to crevice corrosion in natural seawater on condition of base metal.

On the contrary to the curves consisted of full passive range found in polished base metals of S31803, S32550, and 2205w, welding removes the passivity of stainless steels as shown in Fig. 7. Crevice liability of welded specimens without further treatment is high irrespective of stainless steel grades. The results from Fig. 7 obviously prove that the crevice corrosion resistance depends on the post weld treatment.

CPP experiments were performed on five polished weld metals in natural seawater. Results for five weld metals are shown in Fig. 8. The CPP for UNS S30400 and S31603 showed large hysteresis loop. Once crevice corrosion initiated on UNS S30400 and S31603, it continues to corrode. The crevice corrosion resistance decreases in the following sequence, 2205W > UNS S31803 = UNS S32550 > UNS S31603 > UNS S30400. The results from Fig. 8 obviously prove that the crevice corrosion resistance depends on the post weld treatment and mechanical polishing has a significant favorable effect.

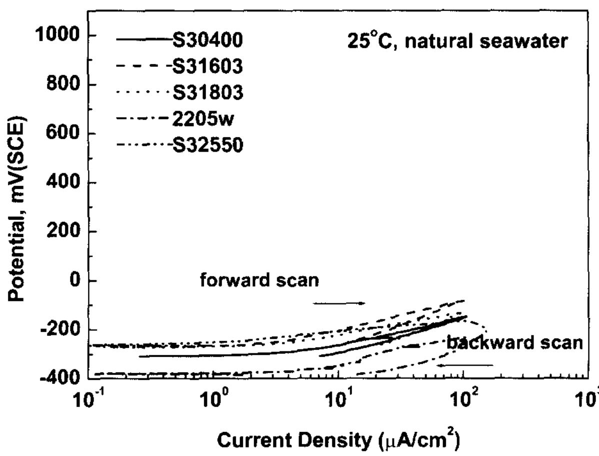

Fig. 7. Cyclic polarization curves for creviced weld metals in natural seawater

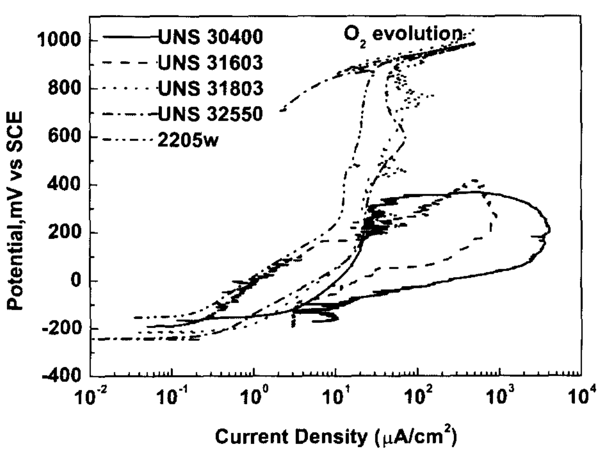

Fig. 8. Cyclic polarization curves for creviced weld metals in natural seawater (polished)

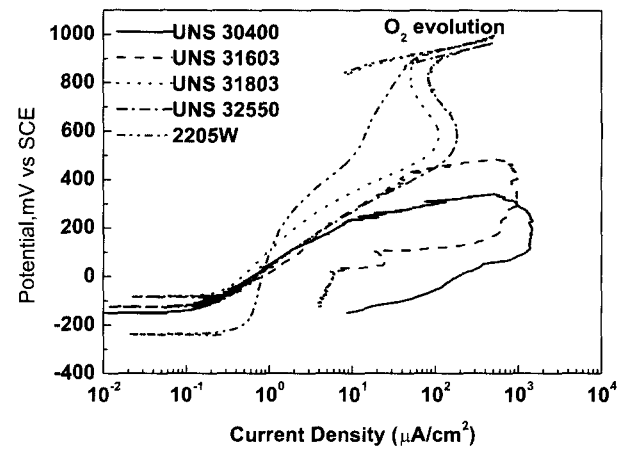

Fig. 9. Cyclic polarization curves for creviced weld metals in natural seawater (pickled)

CPP experiments were performed on five pickled weld metals in natural seawater. Results for five weld metals are shown in Fig. 9. The natural seawater CPP for UNS S30400 and S31603 showed large hysteresis loop. Once crevice corrosion initiated on UNS S30400 and S31603, it continues to corrode. The crevice corrosion resistance decreases in the following sequence, 2205W > UNS S31803 = UNS S32550 > UNS S31603 > UNS S30400. Scale formed on stainless steels during welding has a disadvantage with respective to corrosion. Its porous morphology and Cr-depleted layer beneath the scale accelerated the crevice corrosion. Pickling and polishing restored the corrosion resistance to that of its base metal. But the use of wire brush, having inferior corrosion resistance compared to materials being worked on, must be avoided. At least, wire brushes should be of a stainless steel that is equal in corrosion resistance to the materials being worked on.

4. Conclusions

1) An increase of the free corrosion potential of stainless steels in natural seawater occurred, rising from about 100 mV to some 350 mV(SCE) depending on the post weld treatment.

2) Crevice liability of welded specimens without further treatment was high irrespective of stainless steel grades. Mechanical polishing and pickling restored the degraded corrosion resistance of weld metals

3) CPP results were in accordance with the maximum crevice depth of stainless steels exposed to natural seawater. Crevice corrosion occurred on UNS S30400 and S31603 specimens, while depassivation was observed on

UNS S31803, S32550, and 2205W on condition of base metal, polished, and pickled weldment.

References

1. A. Mollica an A. Trevis, Proc. 4th Int. Congress, on Marine Corrosion and Fouling, Juan Les Pins, *France*, 351 (1976).
2. R. Johnson and E. Bardal, *Corrosion*, **41**(5), 296 (1985).
3. V. Scott, R. D. Di Cientio and Marcenaro, *Corros. Sci.*, **25**(3), 185-194 (1985).
4. S. C. Dexter and G. Y. Gao, *Corrosion*, **44**(10), 717 (1988).