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THE ROLE OF MARINE BACTERIA IN STAINLESS STEEL PITTING

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ABSTRACT

Flat plate and welded stainless steel coupons (316L, Nitronic 50 an AL6XN) were evaluated for potential microbiologically influenced corrosion in seawater. No pitting was observed in flat plate or welded AL6XN under the exposure condition after one year. Pits were located at welds of Nitronic 50 and 316L stainless steels after six- and eight-week exposures. In all cases, large numbers of bacteria were associated with the corrosion products. No corrosion was located on flat plate coupons of 316L or Nitronic 50.

INTRODUCTION

Microbiologically influenced corrosion (MIC) is used to designate corrosion due to the presence and activities of microorganisms. The spatial relationship between bacterial cells and pitting of weldments in austenitic stainless steels exposed in fresh water is well documented. [1-11] However, the reason for preferential microbial colonization at weldments has not been satisfactorily explained. Several case histories document selective attack at 316L stainless steel weldments exposed in marine environments.[12-14] It is generally accepted that the weld material is less resistant to pitting than the base metal because of differences in composition and structure resulting from heating and cooling. Welds typically contain ferrite, not found in the base metal. Little et al.[15] demonstrated that marine bacteria are co-located with iron corrosion product even when the bacteria were not responsible for the corrosion. Experiments in this paper were

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designed to determine the potential for MIC in stainless steel weldments and to document the electrochemical impact of marine organisms on welded austenitic stainless steels.

MATERIALS AND METHODS

EXPOSURE CONDITIONS

Flat coupons (10 cm x 10 cm x 3.2 mm) were prepared of three stainless steels (316L, Nitronic 50 and AL6XN). Coupons were also prepared with a tungsten inert gas butt weld across the width in the center of the coupon. The welds on the coupons were not burnished and no attempt was made to remove surface oxides. 316L and Nitronic® coupons were welded with matching fillers. AL6XN was welded with Inconel 625 and Hastelloy C-276. See Table 1 for USN numbers and alloy compositions. Samples were cleaned and degreased by rinsing consecutively in isopropyl alcohol, acetone, and blown dry with nitrogen gas. Experiments were conducted in natural seawater in Key West, Florida and in abiotic artificial seawater with a salinity of 35 ppm. Two coupons of each material were exposed to flowing seawater for one year. Serial dilutions of the natural seawaters were tested with MICkit V® (BioIndustrial Technologies, Georgetown, TX) to quantify aerobic bacteria (AERO), acid-producing bacteria (APB), sulfate-reducing bacteria (SRB), iron-related bacteria (IRB), and low-nutrient bacteria (LNB). Coupons were examined monthly until the end of the test period (one year). Location and general description of corrosion was noted.

TABLE 1.

USN Numbers and Alloy Compositions

Name	USN #	Nominal Concentration (wt%)
316L	S31603	Cr(16.0-18.0), Mo(2.0-3.0), Ni(10.0-14.0), C(0.035 max), Fe(bal)
AL6XN	N08367	Cr(20-22), Mo(6-7), Ni(23.5-25.5), Cu(0.75 max), N(0.18-0.25), C(0.03 max), Fe(bal)
Nitronic 50	520910	Cr(22), Mo(2.25), Ni(12.5), Mn(5), Si(1 max), N(0.3), Fe(bal)
Inconel	N06625	Cr(21.5), Mo(9.0), Nb + Ta (3.6), Ni(bal) (61.0)
Hastelloy	N10276	Cr(15.5), Mo(16.5), W(3.8), Fe(5.5), Ni(bal) (57.0)

MICROSCOPY.

At the end of the exposure periods, surface topography and chemistry (i.e., corrosion products, biological deposits, and inorganic deposits) were documented using an ElectroScan® Model E-3 environmental scanning electron microscope (ESEM). Stainless steel samples were removed from the exposure medium, fixed in 4% glutaraldehyde in abiotic seawater, carried through a series of water washes with a final distilled water wash and examined directly from distilled water. Samples were attached to a Peltier® stage, maintained at 4 °C and imaged in a water vapor environment at 2-5 torr to maintain samples in a hydrated state. Coupons were x-rayed for 20 minutes at 100 kV/3 mAmps.

ELECTROCHEMISTRY.

Anodic polarization scans were performed on 316L samples using a PAR horizontal flat cell with a defined working electrode area of 1 cm^2 with a knife-edge crevice-free gasket. Duplicate scans were performed at sites along the weld and approximately 2.5 cm away from the weld on the flat plate. A Pt-Nb mesh (2.5 cm^2) and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The open-circuit potential (OCP) was recorded for 10 minutes before scans were initiated. Scan range was from OCP to 0.7 V vs. SCE at a scan rate of 1 mV/sec.

Corrosion of the weld area was initiated by polarizing to 200 mV above OCP for 20 minutes in a Princeton Applied Research (PAR) Tait corrosion cell where the 316L coupon was at the bottom of the cell facing up. A glass tube (6.25 cm diameter) was placed on top of the sample with a rubber gasket seal. The top was sealed and the entire cell was clamped together using exterior bolts. Significant tightening was required to seal the bottom of the cell due to the height difference of the weld and the rest of the sample. The cell was filled with 200 mL of artificial seawater. The value of 200mV was chosen to drive active corrosion along the weld but not on the unwelded plate. Polarizations of welded and flat plate areas were conducted in duplicate. At the conclusion of the 20-minute polarization, OCP was monitored vs. SCE for two days. After two days, 20 mL of natural seawater were added to each system. Coupons were allowed to corrode freely for an additional four days.

RESULTS

EXPOSURE TESTING.

Key West natural seawater contained low levels (10 cells mL^{-1}) of AERO, APB, SRB, IRB, LNB. Flat coupons of Nitronic 50 and 316L exposed in natural seawater showed no signs of corrosion (Figure 1). Nitronic 50 and 316L showed visible corrosion in welds at six weeks in flowing seawater. Through-wall pitting was observed for 316L after an eight-week exposure (Figures 2a-c). In all cases corrosion was limited to weld areas. ESEM micrographs of the well-developed corrosion products demonstrated the presence of numerous microorganisms (Figure 3). There were no accumulations of bacteria on the unwelded plates or in areas away from the welds. Flat plate and welded AL6XN coupons did not show any visible corrosion after one-year exposures.

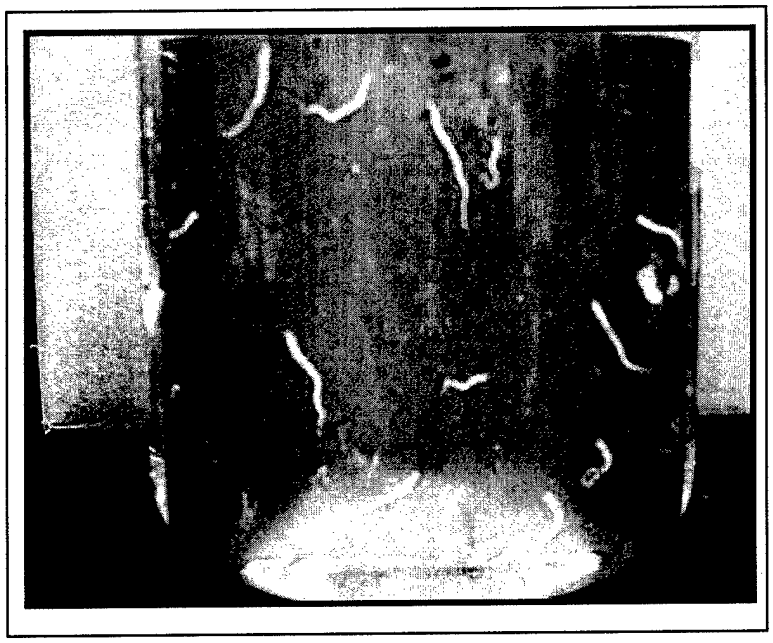

FIGURE 1. Nitronic 50 flat coupon exposed to flowing seawater.

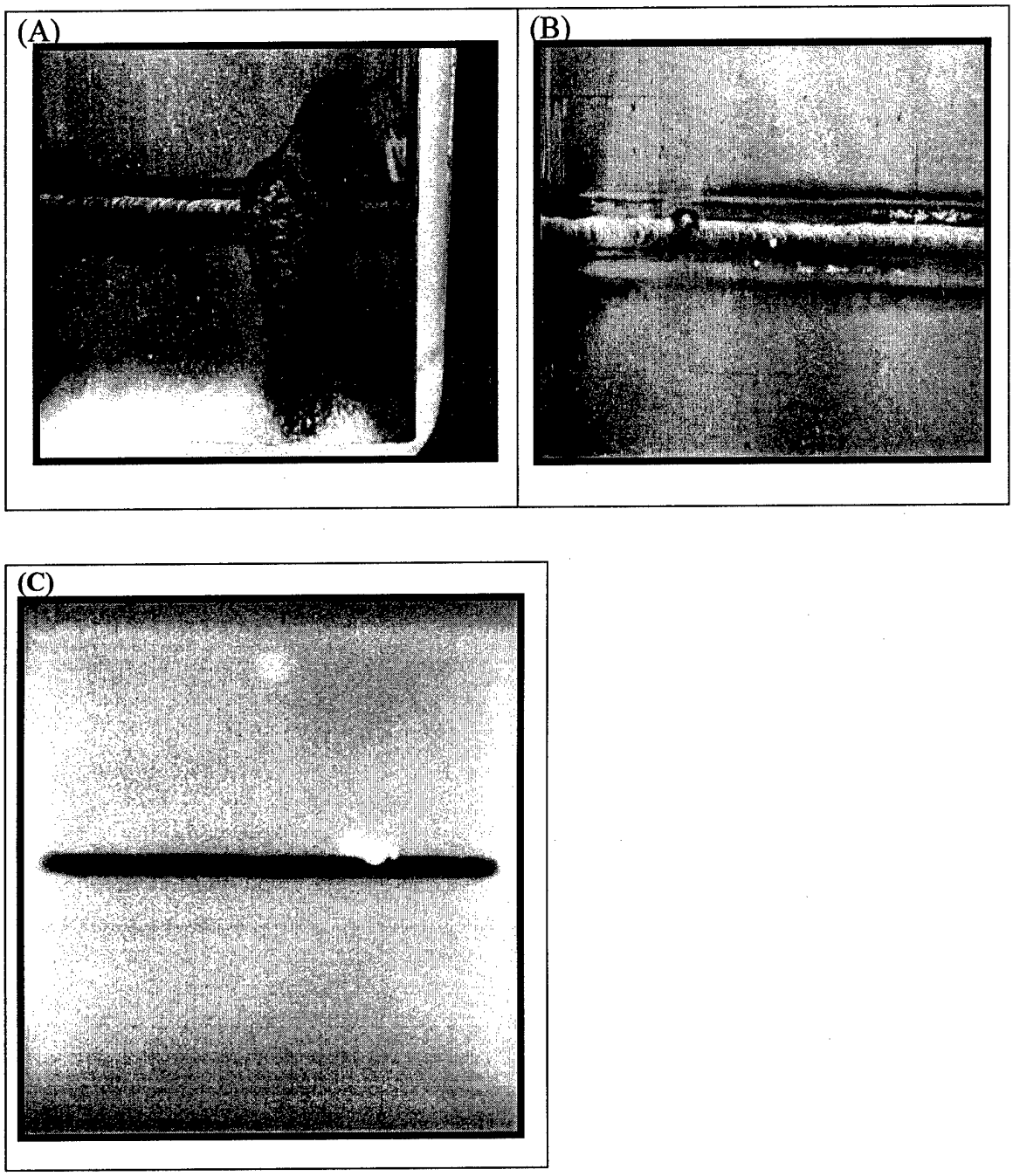

FIGURE 2. 316L stainless steel coupon with a center weld exposed to flowing seawater for 10 weeks:

(A) Pit with corrosion product

(B) Penetration through the wall

(C) X-ray of the weld after exposure

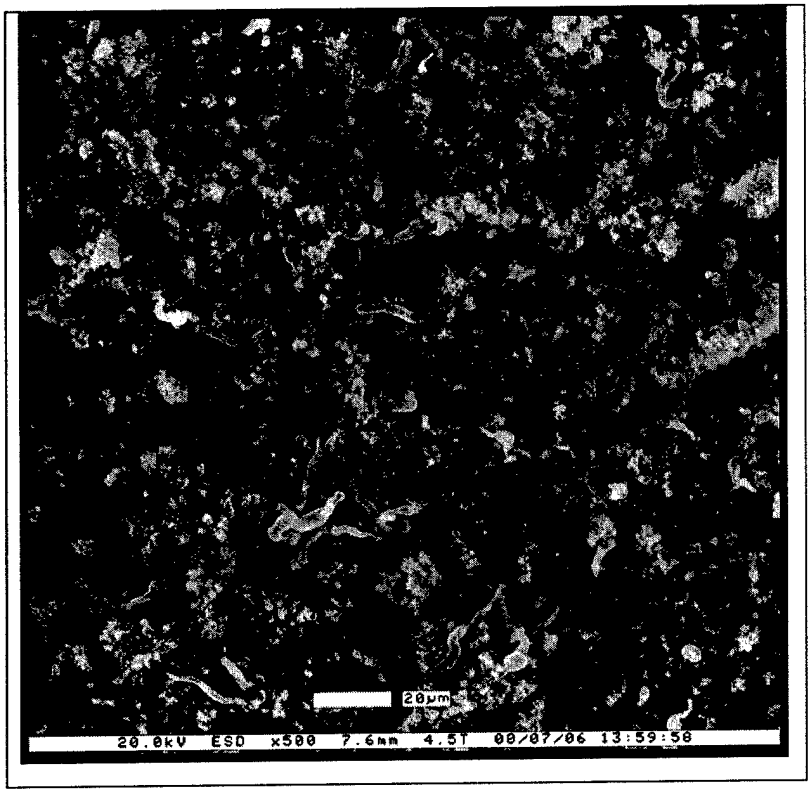

FIGURE 3. 316L welded coupon exposed to flowing seawater for 10 weeks.

OCP values for the welded 316L were ~70 mV lower than the ones recorded for the plate (Figure 4). The polarization scans of the welds indicate that there is a lack of passive behavior and that active corrosion initiated immediately above the OCP with a steady increase in current density with increasing potential. Anodic polarization scans of the flat plate indicated a distinct passive region between 0 and 450 mV where the maximum current density increased one order of magnitude with a maximum of 0.1 $\mu A/cm^2$. Current densities measured at the weld started at 0.1 $\mu A/cm^2$ and increased five orders of magnitude over the same range. Breakdown potentials were observed at 450 and 550 mV in scans for the two flat plate samples. No discernable breakdown potential was observed for the welded metal.

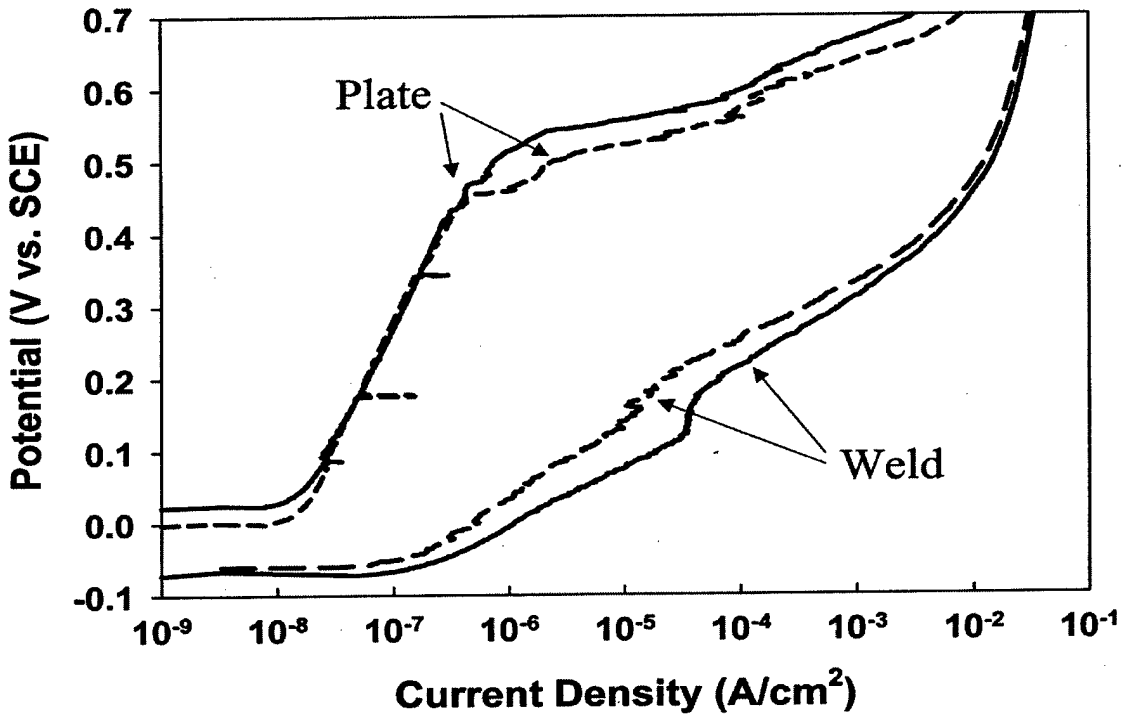

FIGURE 4. Anodic polarization scans of welded and as-received 316L plate.

Polarization at 200 mV produced varying amounts of corrosion on duplicate samples — heavy corrosion in one sample and less corrosion in a second sample as demonstrated in time transient OCP (vs. SCE) (Figure 5). OCP for the sample with less corrosion started at 155 mV and fluctuated in the initial 15 minutes of exposure with a minimum value of 60 mV. After 15 minutes, OCP returned to 155 mV and remained relatively stable over the next hour. During this hour, only a slight orange-red discoloration was observed at the weld indicating light corrosion. In contrast, the sample with more corrosion had an initial OCP of –50 mV. OCP dropped over the first 25 minutes of exposure with a minimum value of -90 mV. OCP returned to the initial value of –50 mV over the next hour. Over this period, significant orange-red discoloration was observed on the weld surface, indicating significant corrosion.

The time transient OCP for the two previously polarized samples (Figure 6) indicate two different responses after addition of natural seawater. The immediate impact of the additions can be seen on the figure as two small fluctuations in the first 0.25 hour. Over the next two days increases were observed in OCP for both samples. OCP for the lightly corroding sample increased from 150 mV to 210 mV, while the OCP for the sample with more corrosion increased from –50 mV to 0 mV. Addition of viable cells to the electrolyte of the sample with heavier corrosion had no influence on the OCP over 40 hours and OCP remained at 0 mV. In contrast the OCP for the sample with minor corrosion fluctuated over the next 40 hours with a minimum value of 160 mV. During this time, the weld continued to discolor. Over the next three days (six days after the initial anodic polarization) OCP increased for both samples — 250 mV and 160 mV for the lightly corroding and heavily corroding samples, respectively.

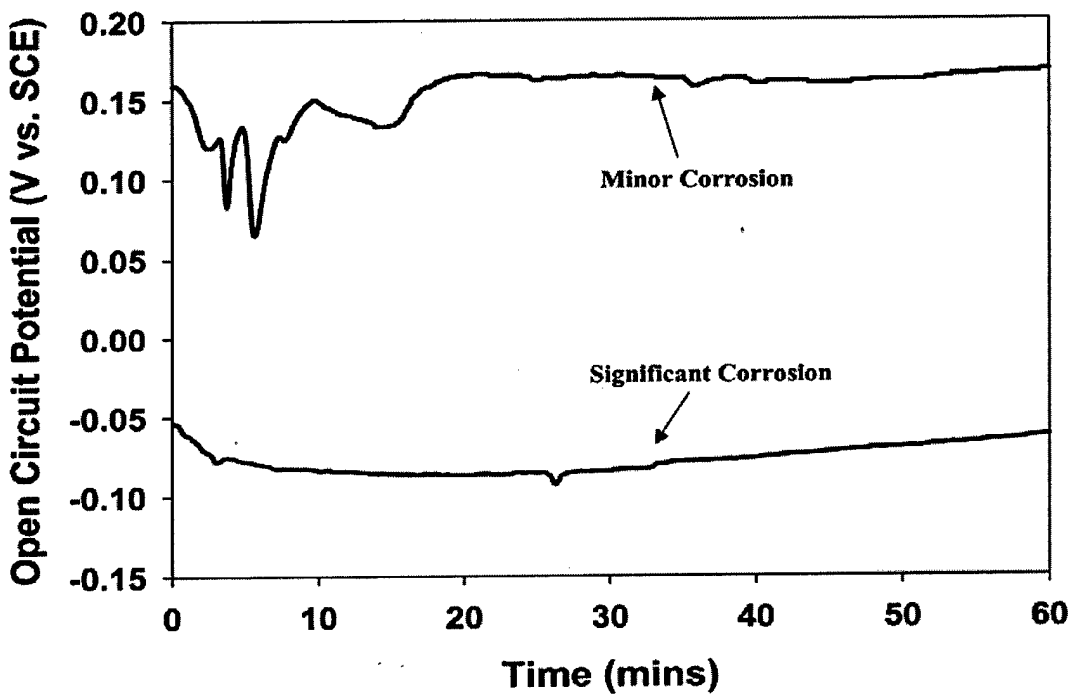

FIGURE 5. OCP measured after potential holds at 200 mV above the initial OCP.

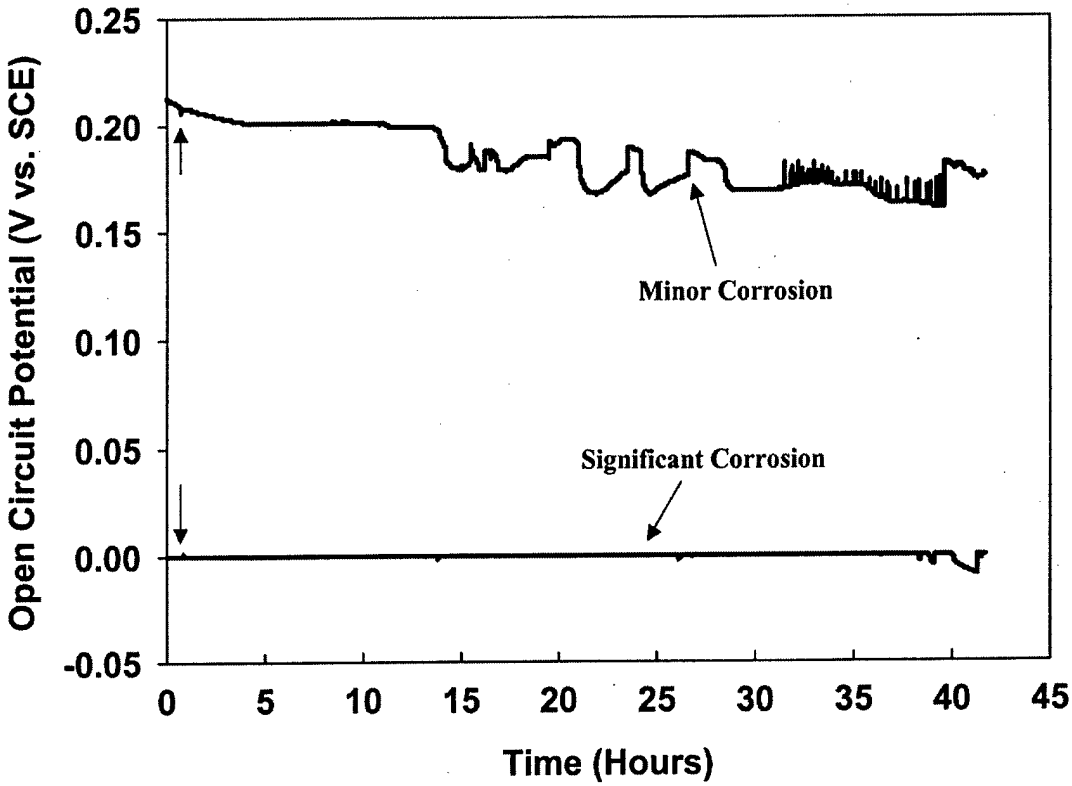

FIGURE 6. OCP measured two days after the anodic potential holds. Natural seawater was added at 0.25 hours as indicated by the vertical arrows.

There are many reports of MIC localized at welds in 300 series stainless steels exposed in fresh natural and chlorinated waters.[1-11] In these cases MIC is attributed to biomineralized deposits, resulting from oxidation of ferrous to ferric and accumulation of tubercle-like deposits of ferric hydroxide [$Fe(OH)_3$].[16] The oxidation can be carried out by a variety of organisms including bacteria, yeast, and fungi, but is particularly associated with genera of the so-called iron and manganese bacteria, *Siderocapsa, Gallionella, Leptothrix, Sphaerotilus, Crenothrix,* and *Clonothrix.* All are common in soil and groundwater. Deposits of cells and metal ions create oxygen concentration cells that effectively exclude oxygen from the area immediately under the deposit and initiate a series of events that are individually or collectively very corrosive. In an oxygenated environment, the area immediately under individual deposits becomes deprived of

oxygen. That area becomes a relatively small anode compared to the large surrounding oxygenated cathode. Cathodic reduction of oxygen may result in an increase in pH of the solution in the vicinity of the metal. Metal cations form at anodic sites. If the metal hydroxide is the thermodynamically stable phase in the solution, metal ions will be hydrolyzed by water with the formation of H^+ ions. If cathodic and anodic sites are separated from one another, the pH at the anode will decrease, and that at the cathode will increase. In addition, Cl^- ions from the electrolyte will migrate to the anode to neutralize any charge buildup, forming heavy metal chlorides that are extremely corrosive. Under these circumstances, pitting involves the conventional features of differential aeration, a large cathode to anode surface area, and the development of acidity and metallic chlorides.

This widely accepted mechanism does not account for the specificity of the attack at weldments. Several theories have been advanced, but none has been accepted. The two-phase weld metal appears to be the most susceptible, although the relative susceptibilities of ferrite and delta phases have not been clearly defined.[1] Garner[17] reported that the pitting potential and the critical pitting temperature were lower for welded than unwelded steel. Stein[2] determined that sensitization of the 300 series stainless steels does not affect susceptibility to MIC. The higher tendency for MIC of welds compared to unwelded material has been attributed to surface roughness or chemical composition that facilitates colonization. Pope et al.[18] speculated that more nutrients accumulated at roughened areas i.e., welds, causing increased biofilm formation. However, Holthe[19] showed that the increase in potential that accompanies biofilm development is just slightly more rapid on a rough surface than on a polished one. Eashwar and Dexter[20] published a paper entitled "Relation of Bacterial Settlement Patterns to Anodic Activity on Stainless Steel Weldments," but there are no data in the paper to support the title. Franklin et

al.,[21] working with a phosphate-buffered freshwater medium, demonstrated that an aerobic bacterium was attracted to anodic sites on flat plate carbon steel coupons and that pit propagation was related to microbial settlement.

Preferential attack at welds is common to both freshwater and marine exposures. However, there are fewer reports of MIC localized at welds in 300 series stainless steels exposed in seawater, possibly because there are fewer applications of 300 series stainless steels in chloride-rich media. Little et al.[12] reported MIC localized at weldments of 300 series stainless steel causing through wall pitting of .032 cm plate after six to eight weeks exposed to flowing or stagnant seawater. They further demonstrated that in the absence of microorganisms anodic sites initiated at welds but those sites were not sustained and did not develop into pits. In the presence of marine bacteria stable anodic sites formed within four weeks.

Despite the attraction of bacteria to anodic sites on steel substrata in both fresh and marine waters the mechanism for pit propagation may differ in the two environments. Freshwater contains a higher concentration of reduced iron, a lower concentration of chloride, and a different population of microorganisms. The concentration of total iron in open marine waters is in the nM range. The generally cited causative organisms are not prevalent in seawater environments. The chemical oxidation rate of iron in seawater at pH 8.2 is so high that microbial oxidation is not competitive. In the ocean, iron-oxidizing bacteria are found primarily in bottom waters and seeps, where ferrous iron is seeping into the ocean from anaerobic groundwater, or where it is being produced in the sediments by iron-reducing organisms.

CONCLUSIONS

Experiments presented in this paper demonstrate that welded 316L corrodes at a lower potential than does the unwelded plate, and that over short exposure times the electrochemical impact of marine bacteria varies between aggressively corroding sites and those that are producing lower current densities. It appears that under all circumstances marine bacteria are attracted to anodic sites that occur preferentially at welds. Under some circumstances the attraction produces an electrochemical impact and in other cases the cells have no impact.

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