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CORROSION2003

CORROSION MECHANISMS OF UNS N04400 IN SEA WATER

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ABSTRACT

Pitting and dealloying were observed when 70Ni/30Cu (UNS N04400) welded plates were exposed to artificial seawater containing sulfate-reducing bacteria. Attempts were made to differentiate biotic and abiotic corrosion mechanisms. Experiments were conducted in alternating aerobic/anaerobic conditions in the presence of inorganic sulfide and sulfate-reducing bacteria over the course of five months.

Keywords: Nickel-copper alloys, microbiologically influenced corrosion, weld, seawater, sulfate-reducing bacteria, sulfide

INTRODUCTION

Most of the literature on sulfide induced corrosion of copper and nickel alloys does not differentiate between corrosion due to waterborne sulfides and sulfides produced by sulfate-reducing bacteria (SRB) within biofilms. The problem of accelerated corrosion of copper/nickel and nickel/copper alloys by waterborne sulfides was identified in the 1970's and early 1980's[1-4]. In most cases, investigators used laboratory experiments in which 90/10 or 70/30 copper/nickel alloys were exposed to artificial or natural seawater with sodium sulfide. Others designed experiments in which sulfides, produced by putrification of marine plants and animals, were pumped into artificial seawater. Those investigators demonstrated that corrosion attack was related to the conversion of oxide surface films to sulfides. Gudas and Hack[5] demonstrated that inorganic sulfide films enhanced galvanic corrosion under some circumstances. In the 1980's, Syrett[6-8] demonstrated that deaerated seawater containing dissolved inorganic sulfides did not immediately lead to accelerated corrosion. Instead, a porous sulfide corrosion product interfered with the formation of an oxide film on subsequent exposures to oxygenated seawater. Others demonstrated the poor mechanical properties of copper sulfide surface films that were easily removed by flow[5, 9]. In the mid 1980's investigators recognized that most failures of copper and nickel alloys in actual seawater service were related to *in situ* sulfide production by SRB in biofilms. Maxwell[10] was the first to demonstrate the presence of SRB in anaerobic niches of a biofilms exposed to aerobic seawater.

Nickel/copper alloy N04400 is used for seawater and brackish water handling because of its resistance to chloride-ion stress corrosion cracking and erosion corrosion. The nominal composition in wt% is as follows[11]: Ni, 66.5; Cu, 31.5; Fe, 1.25; Mn, 1.0; Si, 0.25 and carbon, 0.15. Friend[12] established that nickel/copper alloys containing more than 30% nickel formed a passive film similar in structure to that formed on pure nickel. Localized corrosion of N04400 in seawater service is related to stagnation and/or intermittent flow[13, 14]. N04400 is susceptible to pitting and crevice corrosion when chlorides penetrate the passive film, underdeposit corrosion, intergranular corrosion, sulfide derivitization and dealloying (denickelfication).

Blundy and Pryor[15] worked with alloys containing 10-40% nickel and demonstrated that the % nickel in total reaction products (dissolved, precipitated and reaction product film) was a function of potential. At more active potentials there was preferential corrosion of nickel from the alloys. Early investigators using waterborne or inorganic sulfides did not report dealloying as a contributing mechanism for the accelerated corrosion of copper/nickel or nickel/copper alloys. Gouda et al.[16] working with Arabian seawater demonstrated intergranular corrosion and selective dealloying of iron and nickel from N04400 in the presence of SRB. Little et al.[14] made similar observations using Gulf of Mexico water. Investigators working with SRB and natural seawaters consistently have reported dealloying of nickel from both copper/nickel and nickel/copper alloys. Dealloying has also been reported in extreme conditions, including elevated temperature in combination with a galvanic couple[17]. It is generally recognized that biofilms can maintain conditions at the biofilm/metal interface that are different from conditions in the bulk medium or that cannot be predicted based on thermodynamic arguments. McNeil et al.[18] demonstrated that copper sulfides produced as a result of SRB in biofilms were unique and could be used as mineralogical fingerprints for SRB influenced corrosion. Experiments were designed to evaluate corrosion mechanisms of N04400 in seawater, especially the role of SRB in denickelfication.

MATERIALS AND METHODS

Materials
Butt-welded N04400 coupons (10 x 10 x 0.3 cm) were purchased with an as-milled finish. The weld ran the entire length of the coupon along the midline. N04400 filler metal 60 (UNS N04060) was used for the weld. Table 1 lists the chemical composition of each alloy as supplied by the manufacturer. Each coupon was cut into four 2.54 x 10 cm samples with the weld across the 2.54 cm width and centered along its length. A 0.475 cm hole was drilled through one end. As-received sample finishes were left intact. No attempt was made to polish the surface or remove heat tint. Prior to cleaning, samples were X-rayed for voids. Samples were sonicated in acetone for 15 minutes, rinsed with isopropyl alcohol, and dried with nitrogen gas. A loop of monofilament line was strung through the drilled hole to allow the sample to be hung vertically.

Description of microbial cultures
SRB used in the current study have been described previously[14, 19, 20]. They include:

P10 - isolated from a 4140 steel coupon with a 5 step iron phosphate primer (no topcoat) in a constant immersion flume tank (marine water) at the Naval Surface Warfare Center (NSWC)/Ft. Lauderdale, FL.

P14 - isolated from a 4140 steel coupon with a 5 step iron phosphate primer + an epoxy topcoat in a constant immersion flume tank (marine water) at NSWC/Ft. Lauderdale, FL.

49Z - isolated from a 4140 steel coupon with a zinc primer (no topcoat) in a constant immersion flume tank (marine water) at NSWC/Ft. Lauderdale, FL.

CG59 - isolated from the seawater piping system of a surface ship at Long Beach Naval Station, Long Beach, CA (marine water).

C130 - isolated from aluminum alloy with an epoxy primer + polyurethane topcoat from moisture trapped under the cargo ramp of a C-130 transport plane at the Naval Air Depot (Cherry Point, NC).

All isolates are positive for desulfoviridin (characteristic of *Desulfovibrio sp.*). 100-ml stock cultures of SRB were maintained in liquid growth medium (Postgate's B)[21] supplemented with NaCl (3% w/v). Cultures were kept in glass bottles fitted with rubber septa and aluminum crimped tops and were placed in glass canisters with an anaerobic gas generating system (BBL™ Gas Pak Plus™; Becton Dickinson Co., Sparks, MD) at 24°C until use.

Reactors

Three 3.5 L glass vessels were used as the experimental reactors (Figure 1). Artificial seawater (ASW) was used throughout the experiment with a salinity of 35 parts-per-thousand (ppt) and pH = 8.2. Vessels were labeled 'A - SRB', 'B - 1 ppm S^{2-}, and 'C - ASW Only'. Ten N04400 samples were hung vertically inside each reactor using plastic hooks attached to the inner rim with waterproof epoxy. A spigot at the bottom of each vessel facilitated removal of solution. Nitrogen gas was used to purge each system of oxygen and an injection port was used to add bacteria and sulfide. Samples 2A - 11A were hung inside vessel 'A'; samples 'B' and 'C' were hung within their respective vessels.

Aerobic/anaerobic cycling

At the start of the experiment, vessel 'A' was filled with 2.945 L of ASW. Vessels 'B' and 'C' were filled with 3 L of ASW. All three were purged with N_2 for 1 hour. N_2 flow was decreased to 2 bubbles per second to maintain positive pressure within the vessels. 5 ml aliquots from each SRB stock culture were aseptically withdrawn with a syringe and used to inoculate vessel 'A'. 30 ml of Postgate's B medium (1% final concentration) was added to the vessel to provide a low concentration of nutrients. An additional 650 ppm lactate (6.5 ppm final concentration) was added after 8 weeks exposure to increase SRB growth. 10 ml from vessel 'A' was drawn using the spigot for determination of SRB cell count. 5 ml of 1000 ppm S^{2-} was made from Na_2S dissolved in deionized water. 3 ml was added to vessel 'B' for a final concentration of 1 ppm. 2 ml was used to determine the actual dissolved sulfide concentration using the methods described below. After two weeks 30 ml of the solutions from vessels 'A' and 'B' were drawn separately using the spigots. Solution sample from 'A' was used to determine SRB cell count and dissolved sulfide concentration. The subsample from 'B' was used to determine dissolved sulfide concentration. Oxygen was introduced freely by removing the vessel tops and draining all 3 vessels using the spigots. Samples 2A, 2B, and 2C were removed from their respective vessels and fixed in 4% glutaraldehyde in ASW buffered with 21.4 g/L cacodylic acid. Corrosion products, morphology and biofilm structure were examined using an ElectroScan model E3 environmental scanning electron microscope (ESEM) equipped with a Noran energy dispersive spectrometer (EDS) system. After 15 minutes exposure to air, vessels were filled again with their respective solutions. Air was bubbled through each vessel for 45 minutes, followed by 1 hour of purging by N_2 gas. Sulfide and

SRB were again added to vessels 'A' and 'B' respectively. This cycle was repeated another 8 times (total experimental time = 20 weeks) until all 10 samples from each vessel were removed.

Most probable numbers (MPN)

1 ml samples from the artificial seawater vessel were inoculated into vials containing 9 ml of Postgate's B medium for enumeration of SRB. The initial dilution was serially diluted by 10X in sterile media. Each dilution series consisted of 10 vials (10^{-1} to 10^{-10}) and was performed in triplicate. The vials were placed in glass canisters with an anaerobic gas generating system at 24°C. Anaerobic dilution vials were scored for SRB by noting the presence of a black FeS precipitate in the vial after 28 days at 24°C. MPN were determined using a commercial computer program[*] with a 90% confidence level.

Sulfide Concentration Measurements

Dissolved sulfide (S^{2-}) was determined by the methylene blue method[22]. Briefly, 0.5 ml of an amine-sulfuric acid solution and 0.15 ml of concentrated $FeCl_3$ solution was added to 7.5 ml of fresh sample in a clean cuvette. The mixture was capped and inverted one time. After 3 minutes, 1.6 ml of 50% $(NH_4)_2HPO_4$ was added and the mixture inverted one time. After 5 minutes, the cuvette was placed in a Hach Model DR/2500 spectrophotometer (Hach Co., Loveland, CO) and the absorbance read at 664 nm. S^{2-} concentrations were estimated from plotted absorbance values on standard curves. In addition, the spectrophotometer had a factory-installed program (# 690) for sulfide determination. The S^{2-} concentration was estimated by both A_{664} and Hach Program #690; in general, the two methods showed good agreement. For S^{2-} concentrations greater than the high concentration limit for the spectrophotometer (800 ppb), the samples were diluted (10-1000X) and then measured. All measurements were performed in triplicate and averaged.

RESULTS

The as-received surface of the N04400 alloy was rough and irregular (Figure 2a). EDS spectrum indicated the approximate weight % concentrations of nickel (64%), copper (32%), iron (2%) and lesser amounts of manganese, silicon, and magnesium (Figure 2b). The butt weld surface was characterized with ridges (Figure 2c) that contained localized concentrations of titanium (Figure 2d). MPN estimates of planktonic SRB (Table 2) determined at the beginning and end of each anaerobic period indicated a range of 10^{-2} to 10^{-10} cells ml^{-1}. In the beginning stages of the experiment, planktonic MPN decreased significantly from inoculation to time of sample collection. During the first 2 anaerobic periods (May 1, 2002 – May 15, 2002 and May 15, 2002 – May 29, 2002), population size decreased by two orders of magnitude. Thereafter, SRB populations decreased typically by one order of magnitude. Decrease in the planktonic SRB may have been due to bacteria adhering to the surface of the metal coupons (biofilm formation), cell death or an inability to grow specific organisms in the consortium.

Initial dissolved S^{2-} measurements for the biotic (SRB) and abiotic (Na_2S) culture vessels were similar, 0.3 ppm and 0.5 ppm, respectively, at the onset of anaerobic conditions (Table 3). After the 2-week anaerobic incubations, dissolved S^{2-} levels in abiotic ASW decreased by approximately 90% (average 0.04 ppm) as S^{2-} reacted with alloy. In contrast, dissolved S^{2-} levels in the ASW with SRB decreased less than 50% (average 0.18 ppm). In two instances (July 24, 2002 - August 7, 2002 and September 4, 2002 - September 18, 2002) dissolved S^{2-} increased from initial values in biotic cultures.

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[*] Most Probable Number Calculator© Version 4.04, A. J. Klee (1996) Cincinnati, OH: Environmental Protection Agency.

After 20 weeks exposure to alternating aerated/deaerated stagnant, uninoculated ASW, there was no pitting on either base metal N04400 or weld. Similarly, there was no localized corrosion on coupons exposed to ASW + inorganic sulfides. Surfaces exposed to ASW + SRB remained free of localized corrosion for 11 weeks. At 12 weeks, SRB were associated with localized corrosion away from the weld in the base metal (Figure 3a-b). After acid cleaning (ASTM G1, C.6.1)[23], pitting was identified in the base metal. The pitting was intergranular but there was no dealloying (Figure 3c-d). Also at 12 weeks, SRB were associated with pitting, as well as dealloying in the weld (Figure 4a-d). At 14 weeks pitting was detected in association with SRB at the base metal of the weld (Figure 5a-d). The weld had also been dealloyed and undercut at the weld/heat-affected-zone (HAZ) interface (Figure 6a-c). The pitting in the HAZ was intergranular, (Figure 6d) but no dealloying was observed. After 16 weeks the appearance of the SRB changed from curved rods (Figure 4b) to elongated stalks encrusted with sulfides on both the weld (Figure 7a-b) and base metal (Figure 7c-d).

After 20 weeks exposure to ASW + SRB, base metal and weld filler were completely covered by a dark film (Figure 8a). Sulfide encrusted SRB were detected in association with the film and EDS indicated a high concentration of sulfur (16%) (Figure 8c-d). Acid cleaning only partially removed the dark film from both base metal and weld filler (Figure 8b). After 20 weeks exposure to ASW + abiotic sulfides, base metal and weld filler were slightly discolored and had small, localized black deposits on the surface containing 3% sulfur (Figure 9a,c-d). Acid cleaning completely removed surface discoloration and the small deposits from both base metal and weld filler (Figure 8b).

DISCUSSION

Despite similar dissolved S^{-2} concentrations in the biotic and abiotic ASW exposures of alloy N04400, the observed corrosion varied between the exposure conditions. Corrosion resulting from exposure to abiotic conditions was uniform. Localized corrosion, including pitting, intergranular corrosion and dealloying were observed in exposures containing SRB. Several investigators have demonstrated that waterborne sulfides will derivatize copper or nickel in alloys. They have further demonstrated that flow (mechanical stress) or introduction of oxygen is required to cause localized corrosion. Apparently the introduction of oxygen under the circumstances in this laboratory experiment was not aggressive enough to cause the sulfide to spall from the surface or to convert the oxide to sulfide. Localized corrosion was only observed in the presence of SRB.

It is well established that N04400 is susceptible to SRB influenced corrosion[13, 16, 24]. The process is as follows: as a result of microbial respiration, SRB within a biofilm reduce the sulfate in seawater (2 gm L^{-1}) to sulfide. The sulfides react with the copper/nickel oxides to produce a sulfide-rich layer. In addition to sulfides SRB with biofilms produce extracellular polymeric substances (EPS). The role of EPS in corrosion has been investigated[25]. The role in increasing the tenacity of the sulfide layer on copper/nickel alloys has not been investigated.

Sulfide layers on N04400 form rapidly, causing acceleration in the corrosion rate during its formation. Gouda et al[24] studied the electrochemical behavior of copper-containing alloys in seawater exposed to sulfides and SRB. Using polarization resistance (R_p) and anodic polarization scans, they demonstrated that passivation of the metal surface occurred upon initial exposure of N04400 to an SRB environment. After 6 h. of exposure, a distinct active peak in the anodic scan had developed, resulting in a decrease of the passive region of the curve. After 7 and 26 days of exposure the metal indicated an active behavior with no passive region and a Tafel slope of 120 mV. Two anodic Tafel slopes were derived from the Gouda data - one for the initial active/passive condition (60 mV) and one for later

developed active condition (120 mV). The cathodic Tafel slope was not taken into account in the above reaction because the cathodic oxygen reduction reaction is diffusion limited[26]. Mansfeld *et al.*[27] examined the polarization behavior of copper alloys in flowing and stagnant natural and artificial seawater. They determined that Tafel slope values for stagnant conditions were similar for all exposure times and conditions. An initial anodic Tafel slope of 70/30 Cu-Ni was found to be 60 mV, increasing to 120 mV after prolonged exposures, values similar to those derived from the Gouda data for N04400.

Another observation related to the SRB on the surface of N04400 was that cells were encrusted in copper/nickel sulfides. Bacteria require Cu and Ni as trace inorganic nutrients but excessive quantities are inhibitory or lethal. Microorganisms immobilize, mobilize or transform metals by extracellular precipitation reactions, intracellular accumulation, oxidation and reduction reactions, methylation and demethylation, and extracellular binding[28]. These mechanisms impede toxic metals from entering and killing the cell. Bacteria can react with soluble metals by binding and precipitating metal ions on their surface, producing minerals. Precipitation reactions can be divided into two general categories: passive and active mineralization[29]. Passive mineralization, or surface catalysis, is caused by the net negative charge on most bacterial cell surfaces which nucleates the precipitation of metallic cations from solution. In many bacteria, capsules or slime, consisting of extracellular polymers, represent the outermost layer of the cell surface. Capsules consist of linear polymers of polysaccharides or repeating amino acid units and contain over 90% water. They may contain anionic moieties such as carboxyl groups, and occasionally phosphate and sulfate groups, which enable them to bind metals[30, 31]. Bacterial extracellular polymers have been proposed as carriers for metals in aquatic environments[32]. Binding sites for metals are also found in proteins, nucleic acids and specialized[33]. Complexing ligands may be necessary for binding of specific metals; in aqueous solutions, metals ions are often hydrated and can be attracted to a number of dissolved, colloidal or solid organic or inorganic substances[30]. Metal binding to cell surfaces is pH and temperature dependent due to their influence on metal and cell wall chemistry[34-36]. Passive metal binding by bacterial surfaces represents an electrostatic interaction; consequently, it is not necessary that the cells be viable, only that their surfaces remain intact[30].

Differences in sulfides produced by bacteria within biofilms and waterborne inorganic sulfides were identified. Sulfide layers formed in biofilms during exposure to ASW + SRB covered the entire surface of the sample. In contrast, exposure to ASW + abiotic sulfides resulted in only localized sulfide deposits covering a fraction of the metal surface. Sulfide layers formed in biofilms were also more tenacious towards removal by acid cleaning than those formed abiotically. Chemical composition of biotic and abiotic sulfide layers also differed. Biotic layers had a high sulfur concentration of 16%, while abiotic layers were composed of only 3% sulfur. The sulfur concentration in the biotic layer is especially high considering the bulk solution had a sulfide concentration of less than 1 ppm. These findings indicate a connection between bacterial activities and the resulting surface morphology found in this system. Active bacterial surface-mediated mineralization occurs either by the direct transformation of metals (i.e., methylation, redox reactions) or by the formation of metal-reactive by-products (i.e., sulfate reduction producing sulfide). Experimental work with cultures of SRB has shown that metal ions sorbed to bacterial cells tend to be more chemically active than when they are in solution[37] and reduced iron and other base metals are commonly precipitated on dissimilatory SRB cell surfaces as sulfides[29].

The morphology of SRB observed in samples after 14 weeks (9A-11A) was filamentous. Cells were unusually elongated suggesting that cell division had been inhibited. A number of physical and chemical agents are known to cause elongation in bacteria, that is, inhibit cell division but not growth. Rod shaped bacteria form long filaments when cell division is blocked with certain antibiotics, such as penicillin[38]. Transition metals, dyes, osmotic pressure changes, temperature changes, magnesium deficiency or UV radiation can cause cell elongation[39, 40]. Cell elongation can be a response to DNA

damage[41]. It also occurs when cultures are grown for extended periods[42] or grown in the presence of toxins[43]. In most instances, when the causative agent is removed or when conditions become more favorable, normal cell growth and division resumes[39]; however, in some cases the cell may grow past a threshold length in which recovery is not possible[40]. In terms of our experiment, cell elongation after 16 weeks appeared to be the result of prolonged growth (i.e., old cultures).

The poor performance of N04400 in stagnant artificial and natural seawater has been previously documented[9, 11, 13, 16, 24]. In a three-year study at the Inco Test Facility (Harbor Island, NC)[11], the maximum pit depth measured in stagnant natural seawater for N04400 was 42 mil or 1.067 mm deep. N04400 ranked after N06625, N08825 and N05500 in terms of corrosion resistance to stagnant natural seawater. No pitting was observed in N06625. The natural seawater contained a population of SRB and sulfate, however the study was not designed to evaluate SRB specifically or the impact of stagnation followed by flow.

Gouda et al.[13, 16] examined the susceptibility of N04400 towards microbial attack in Arabian Gulf seawater. Results indicated that SRB attack is initiated beneath black sulfur-rich deposits. The deposits were found to be mostly iron nickel sulfides. No corrosion was detected after 3 weeks of exposure under anaerobic SRB conditions, but upon addition of aerated solution, the corrosion rate increased significantly. The authors stated that failure of N04400 heat exchanger tubes could take place if SRB are present irrespective of their concentration. Also, their results indicated that N04400 is highly susceptible to SRB attack when compared to 70/30 Cu-Ni alloy, brass or N08825 under the same conditions. The mode of SRB attack was intergranular corrosion that was accompanied by selective dealloying of nickel and iron. Using EDS they found that under black iron and nickel sulfides severe intergranular corrosion had taken place. The attacked regions were copper-rich while the regions around the active sites had higher Ni concentrations. Black deposits were also found to be devoid of appreciable copper compounds which indicated preferential attack of nickel and iron. However, a green corrosion layer, found on top of these black deposits, was composed of mainly copper chloride indicating that copper corrosion took place after the initial sulfide attack. Another interesting finding was that SRB growth on N04400 was optimum at 30°C as compared to 19°C and 50°C and the SRB attack was intensified when the bulk liquid phase was aerobic.

Popplewell et al.[9] examined a variety of copper alloys with varying concentrations of zinc and nickel in 3.4 wt% salt water (artificial seawater) and low sulfide concentrations. They showed that copper alloys with 10% nickel or 20% zinc had the lowest corrosion rates. N04400 performed only slightly better than C12200 (99% Cu). The effects of sulfide, dealloying or chloride attack were not evaluated individually.

Preferential corrosion attack of welds in stainless steels has received considerable attention by the research community[44-49]. Fewer studies have evaluated corrosion in welds of copper and nickel alloys. Little et al.[50] studied the impact of SRB on welded copper-nickel alloys in seawater. They found that upon addition of 50 ppm aerated sulfide, the weld root and adjacent flow zone became coated with a highly adherent black Cu_2S layer. EDS analysis indicated that these zones were copper-rich while adjacent zones were nickel-rich. The nickel-rich zones also blackened but upon exposure to fresh artificial seawater under flowing conditions, the black layer was spalled down to fresh metal. Therefore, with each repetition of sulfide addition, the surface blackened, followed by the removal of the corrosion products in the nickel rich zones away from the weld. The authors suggested that accelerated sulfide-induced corrosion should occur near to, but not at, the weld itself, predominantly on the downstream side of the weld in the heat-affected zone. Amaya et al.[49] studied the effect of the shape of the weld on bacterial adhesion and microbiologically influenced corrosion in type 304 stainless steel. In their six studies, bacterial adhesion and pitting were observed at the toe region of the weld and the heat-affected zone of the as-weld surfaces.

CONCLUSIONS

Distribution, tenacity and chemical composition of sulfides produced by bacteria within biofilms are different from those produced by waterborne inorganic sulfides. The resulting potential and corrosion mechanisms would be expected to be different. SRB within biofilms can produce sulfides locally, creating the conditions for galvanic interactions between sulfide and oxide covered areas whereas inorganic sulfides react uniformly over a surface. Because bacteria enmeshed in biofilms produce extracellular polymeric materials the tenacity of sulfide layers produced by bacteria may differ from those produced abiotically. In the experiments described, localized corrosion in the presence of SRB, including pitting, intergranular corrosion, and dealloying, were observed.

ACKNOWLEDGEMENTS

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Table 1. Chemical composition of N04400 and N04400 weld filler 60 (N04060).

	Ni	Cu	Fe	Mn	Si	S	Ti	C	P	Al
UNS N04400	63.76	31.95	2.25	1.11	0.14	0.003	0.2 max	0.132	0.002	0.03
UNS N04060	65.57	27.48	0.11	3.54	0.98	0.005	2.21	0.03	0.007	0.04

Table 2. Planktonic SRB populations measured by MPN analysis. Estimates were made at the onset (initial) of anaerobic conditions and after 2 weeks (final).

Anaerobic Period	INITIAL MPN (cells ml^{-1})	FINAL MPN (cells ml^{-1})
5/1/02 - 5/15/02	2.40E+02	0.00E+00
5/15/02 - 5/29/02	2.40E+04	2.40E+02
5/29/02 – 6/13/02	4.27E+04	1.47E+03
6/13/02 - 6/26/02	9.33E+04	4.94E+04
6/26/02 - 7/10/02	1.00E+10	1.47E+04
7/10/02 - 7/24/02	2.40E+05	9.33E+03
7/24/02 - 8/7/02	4.27E+04	2.40E+03
8/7/02 - 8/21/02	7.41E+04	2.40E+03
8/21/02 - 9/4/02	9.33E+04	2.40E+03
9/4/02 - 9/18/02	2.40E+05	2.40E+04

Table 3. Dissolved inorganic S^{2-} in ASW with and without SRB. Estimates were made at the onset (initial) and after 2 weeks (final) by two methods.

Anaerobic Period	SRB/ASW Initial (A_{664}) ppm[a]	SRB/ASW Final (A_{664}) ppm[a]	SRB/ASW Initial (Hach) ppm[b]	SRB/ASW Final (Hach) ppm[b]	ASW Initial (A_{664}) ppm[a]	ASW Final (A_{664}) ppm[a]	ASW Initial (Hach) ppm[b]	ASW Final (Hach) ppm[b]
5/1/02 – 5/15/02	ND	0.093 ± 0.015	ND	0.068 ± 0.014	ND	0.064 ± 0.009	ND	0.059 ± 0.006
5/15/02 – 5/29/02	ND	0.048 ± 0.002	ND	0.046 ± 0.005	ND	0.021 ± 0.002	ND	0.023 ± 0.004
5/29/02 – 6/13/02	0.214 ± 0.041	0.034 ± 0.007	0.196 ± 0.014	0.044 ± 0.001	0.466 ± 0.006	0.013 ± 0.001	0.427 ± 0.014	0.031 ± 0.001
6/13/02 – 6/26/02	0.181 ± 0.058	0.041 ± 0.002	0.166 ± 0.057	0.041 ± 0.002	0.483 ± 0.006	ND	0.441 ± 0.014	ND
6/26/02 – 7/10/02	0.533 ± 0.003	0.048 ± 0.007	0.480 ± 0.013	0.050 ± 0.001	0.630 ± 0.009	0.024 ± 0.006	0.562 ± 0.020	0.032 ± 0.001
7/10/02 – 7/24/02	0.242 ± 0.044	0.124 ± 0.035	0.232 ± 0.046	0.115 ± 0.012	0.520 ± 0.008	0.017 ± 0.002	0.476 ± 0.015	0.031 ± 0.006
7/24/02 – 8/7/02	0.300 ± 0.009	0.613 ± 0.021	0.279 ± 0.013	0.561 ± 0.032	0.520 ± 0.004	0.040 ± 0.006	0.476 ± 0.009	0.047 ± 0.001
8/7/02 – 8/21/02	0.269 ± 0.004	0.049 ± 0.006	0.249 ± 0.008	0.044 ± 0.003	0.487 ± 0.004	0.074 ± 0.005	0.446 ± 0.008	0.078 ± 0.01
8/21/02 – 9/4/02	0.403 ± 0.010	0.049 ± 0.002	0.395 ± 0.030	0.052 ± 0.006	0.481 ± 0.004	0.032 ± 0.007	0.426 ± 0.004	0.040 ± 0.001
9/4/02 – 9/18/02	0.581 ± 0.072	0.809 ± 0.040	0.532 ± 0.068	0.730 ± 0.037	0.486 ± 0.009	0.048 ± 0.006	0.432 ± 0.099	0.046 ± 0.002

[a]Dissolved S^{2-} measured by methylene blue formation at 664 nm
[b]Dissolved S^{2-} measured by factory-installed program (Hach)
ND, not determined
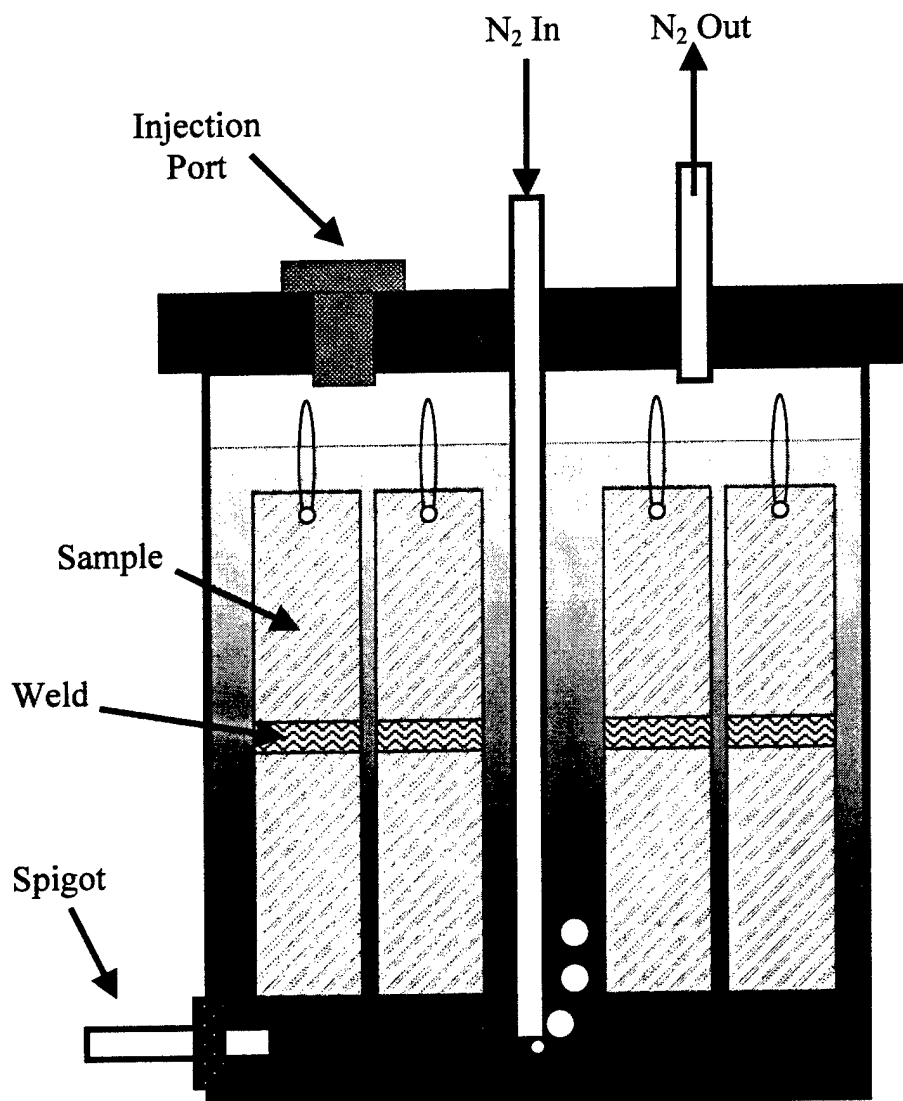
Figure 1: Schematic of reactor with welded coupons.
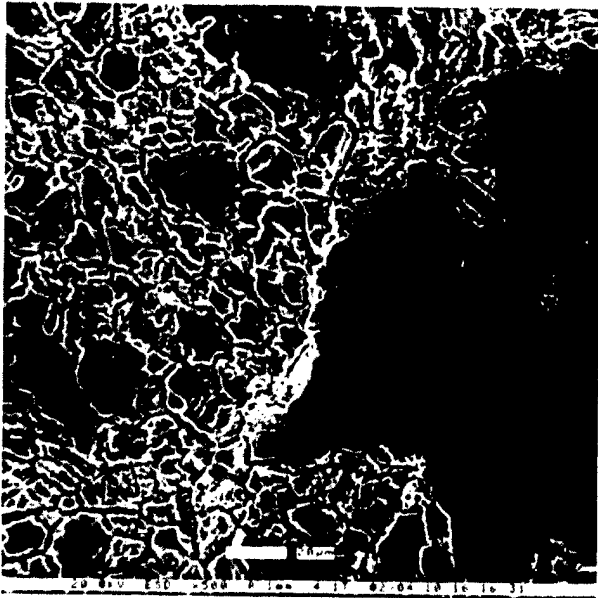
Figure 2a: As-received N04400 base metal with mill finish.

64% Ni
32% Cu
2% Fe
2% Mn, Si, Mg
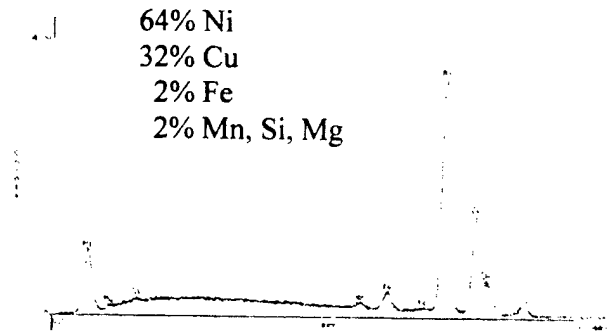
Figure 2b: EDS of as-received N04400 base metal with mill finish.
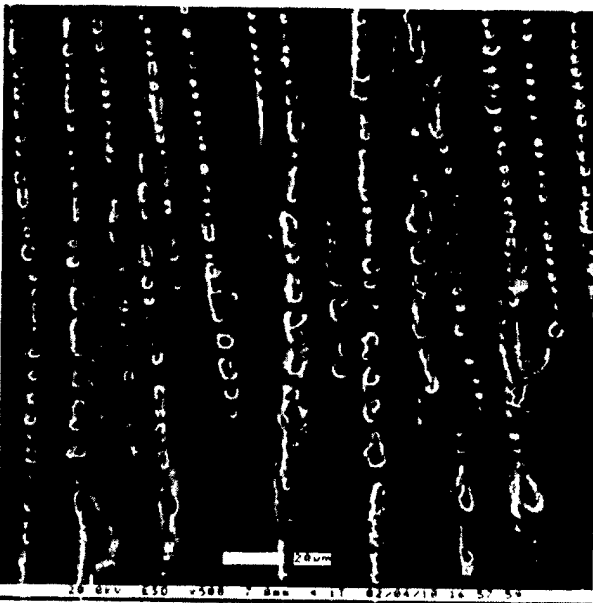
Figure 2c: As-received N04060 weld filler with titanium localized in ridges.

62% Ni
32% Cu
2% Fe
2% Mn, Si
2% Ti
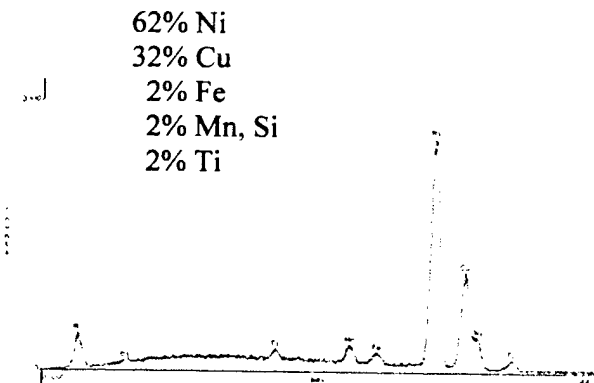
Figure 2d: EDS of as-received N04060 weld filler with titanium localized in ridges.

43% Ni
39% Cu
10% S
3% Fe
2% Mn
3% Ti, Ca, P, Si
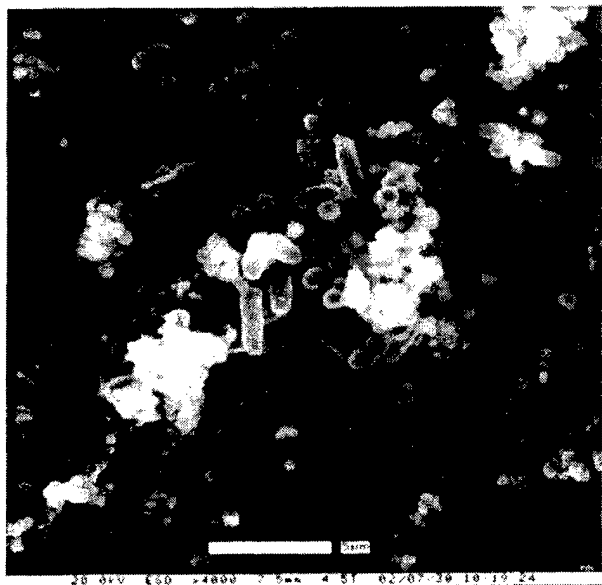
Figure 3a: Base metal with patchy distribution of SRB after 12 weeks exposure to ASW + SRB.
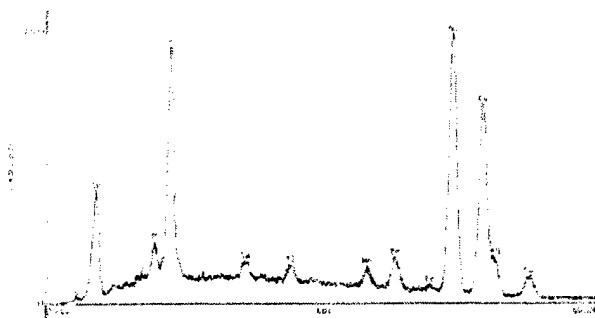
Figure 3b: EDS of base metal with patchy distribution of SRB after 12 weeks exposure to ASW + SRB.
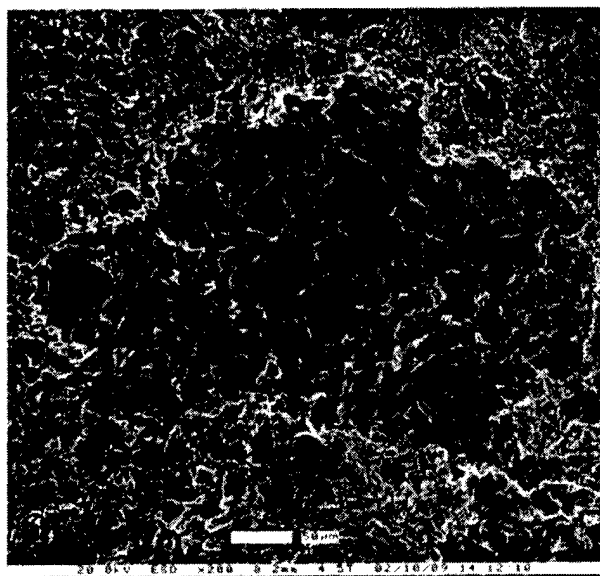
65% Ni
32% Cu
2% Fe
1% Mn

Figure 3c: Pit in base metal revealed after acid cleaning and 12 weeks exposure to ASW + SRB.
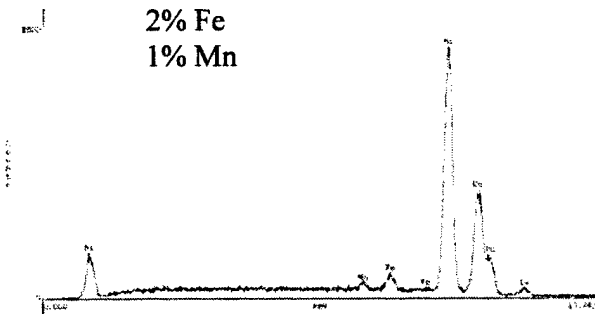
Figure 3d: EDS of pit in base metal revealed after acid cleaning and 12 weeks exposure to ASW + SRB.

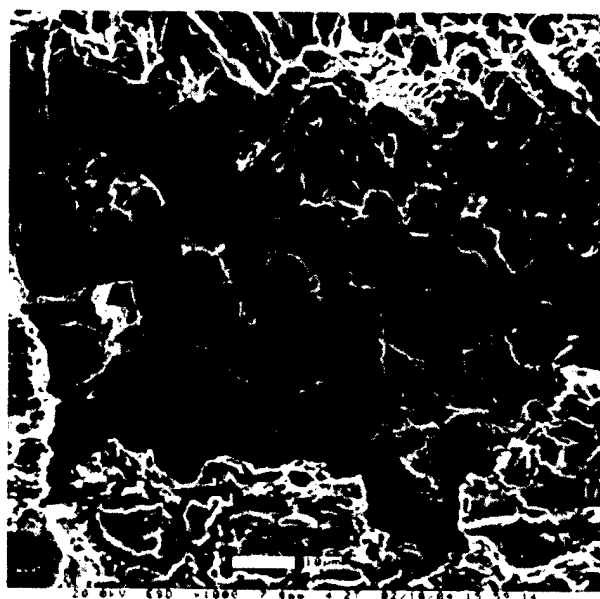**Figure 4a:** Weld filler with SRB and corrosion layer after 12 weeks exposure to ASW + SRB.

Figure 4b: Weld filler with SRB and corrosion layer after 12 weeks exposure to ASW + SRB.

Figure 4c: Weld filler with dealloying under layer after 12 weeks exposure to ASW + SRB.

50% Ni
15% Cu
13% Ti
7% Si
6% Fe
4% Cl
2% Mg
1% Mn
1% Al
1% S, P
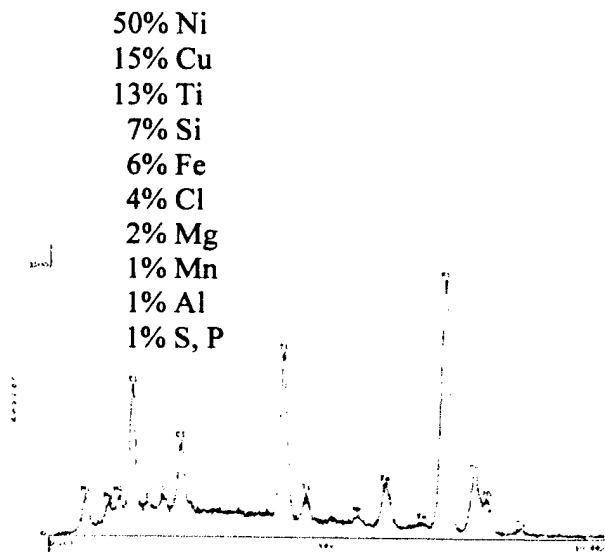
Figure 4d: EDS of weld filler with dealloying under layer after 12 weeks exposure to ASW + SRB.

Figure 5a: SRB and corrosion layer covering base metal after 14 weeks exposure to ASW + SRB.

49% Ni
35% Cu
8% S
4% Fe
2% Mn
1% Ti
1% Si, P, Ca
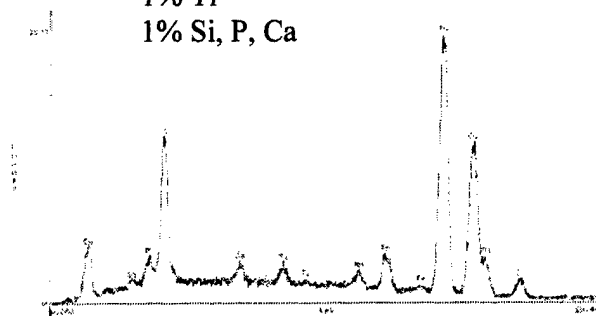
Figure 5b: EDS of SRB and corrosion layer covering base metal after 14 weeks exposure to ASW + SRB.

Figure 5c: Pit in base metal revealed after acid cleaning and 14 weeks exposure to ASW + SRB.

63% Ni
29% Cu
3% Mn
2% Ti
1% Fe
1% S
1% Al, Si, P
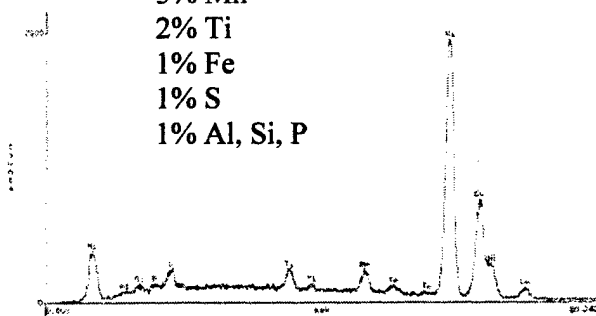
Figure 5d: EDS of pit in base metal revealed after acid cleaning and 14 weeks exposure to ASW + SRB.
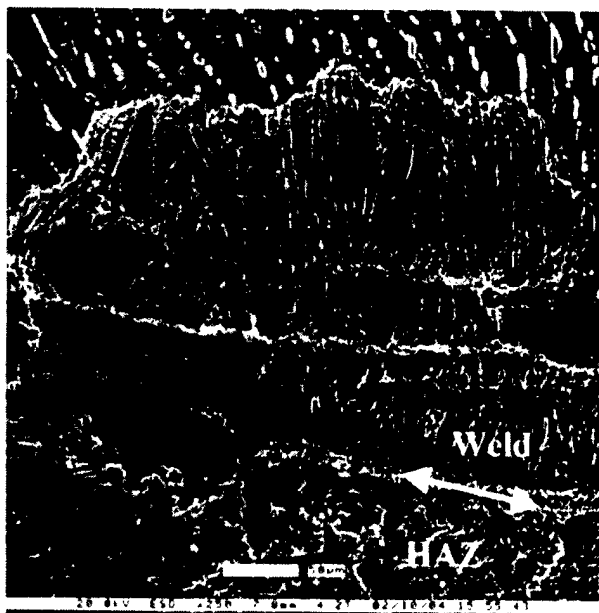
Figure 6a: Pitting and undercutting at weld filler/HAZ interface revealed after acid cleaning and 14 weeks exposure to ASW + SRB.

Figure 6b: Pitting and undercutting at weld filler/HAZ interface revealed after acid cleaning and 14 weeks exposure to ASW + SRB.
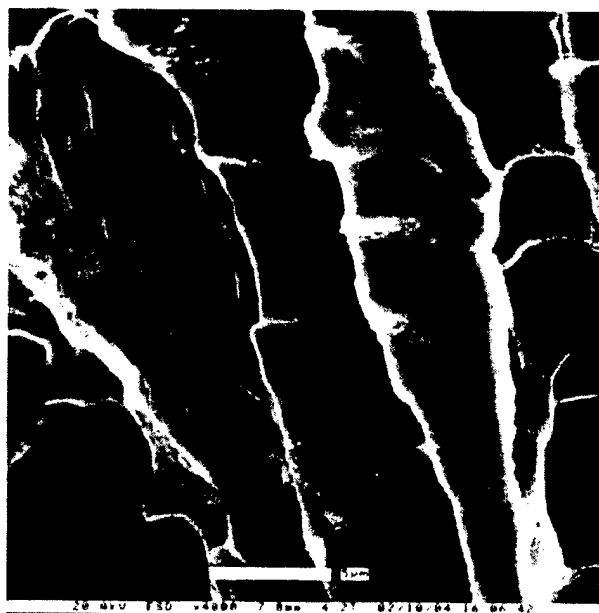
Figure 6c: Dealloying in weld filler revealed after acid cleaning and 14 weeks exposure to ASW + SRB.

Figure 6d: Intergranular corrosion in HAZ revealed after acid cleaning and 14 weeks exposure to ASW + SRB.
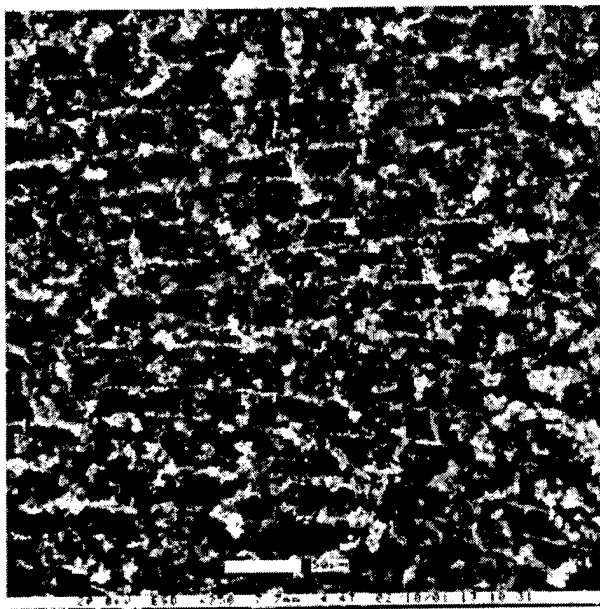
Figure 7a: Weld filler with sulfide encrusted SRB after 16 weeks exposure to ASW + SRB.

Figure 7b: Weld filler with sulfide encrusted SRB after 16 weeks exposure to ASW + SRB.
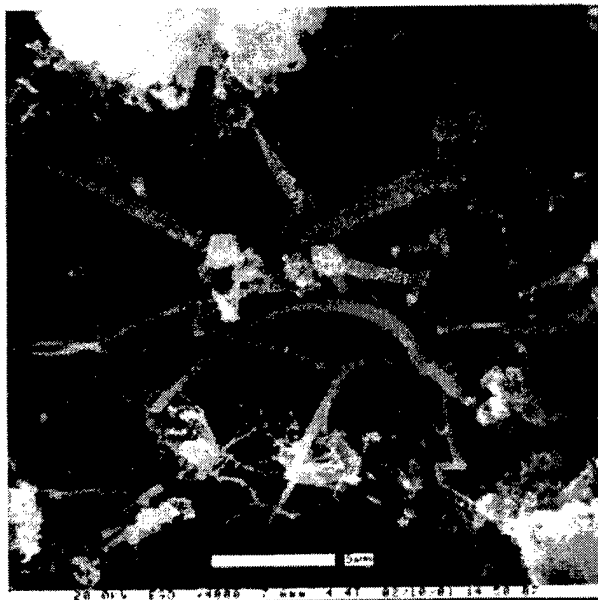
Figure 7c: Base metal with sulfide encrusted SRB after 16 weeks exposure to ASW + SRB.

Figure 7d: Base metal with sulfide encrusted SRB after 16 weeks exposure to ASW + SRB.
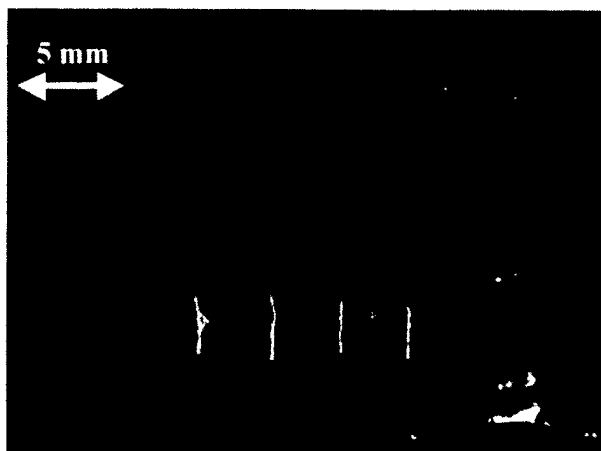
Figure 8a: Black sulfide-rich layer after 20 weeks exposure to ASW + SRB completely covering both base metal and weld filler (before cleaning).

Figure 8b: Acid cleaning only removed patches of black sulfide-rich layer from base metal and weld filler (20 weeks exposure to ASW + SRB).
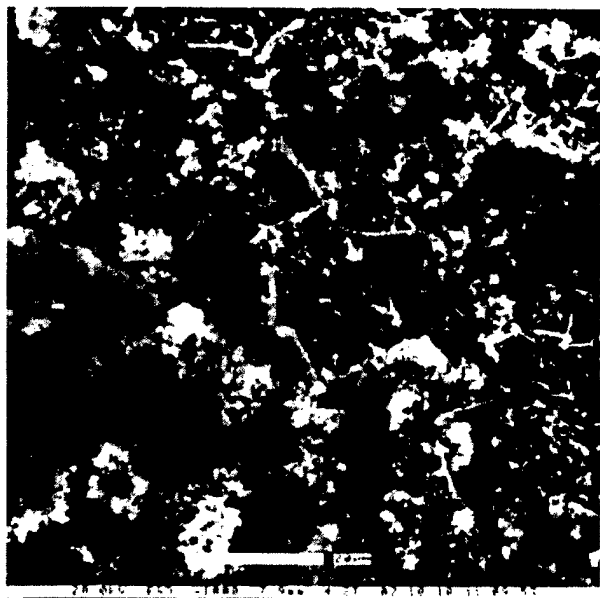
Figure 8c: Base metal covered with sulfide encrusted SRB and associated with black sulfur-rich layer after 20 weeks exposure to ASW + SRB (before cleaning).
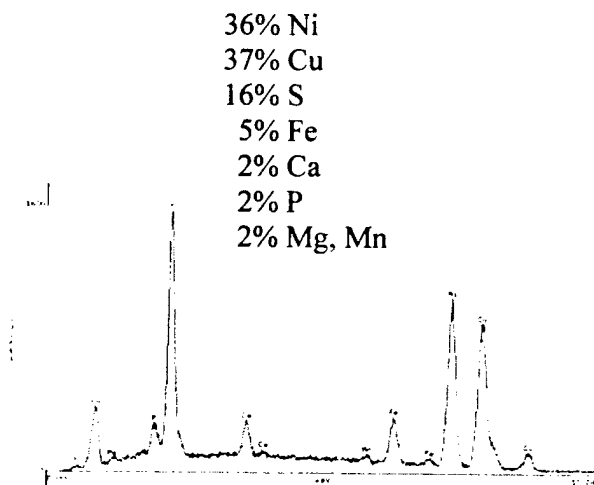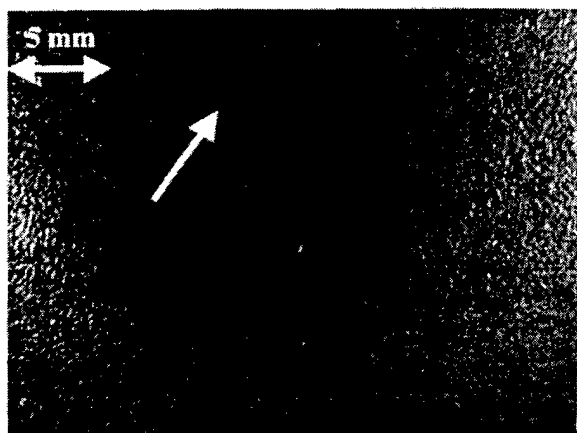

36% Ni
37% Cu
16% S
5% Fe
2% Ca
2% P
2% Mg, Mn

Figure 8d: EDS of base metal covered with sulfide encrusted SRB and associated with black sulfur-rich layer after 20 weeks exposure to ASW + SRB (before cleaning).

Figure 9a: Base metal with localized black deposits after 20 weeks exposure to ASW + abiotic sulfides (before cleaning).
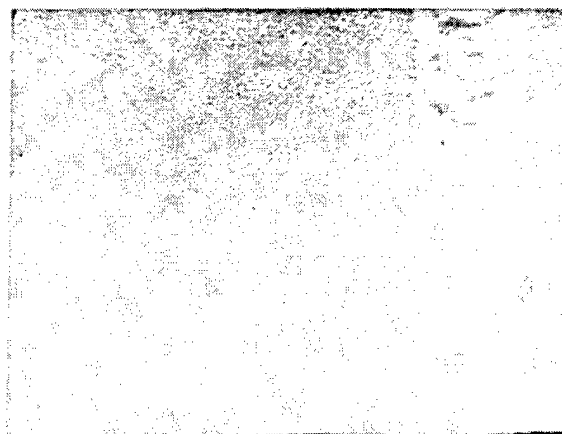

Figure 9b: Acid cleaning completely removed all deposits from base metal and weld filler (20 weeks exposure to ASW + abiotic sulfides).
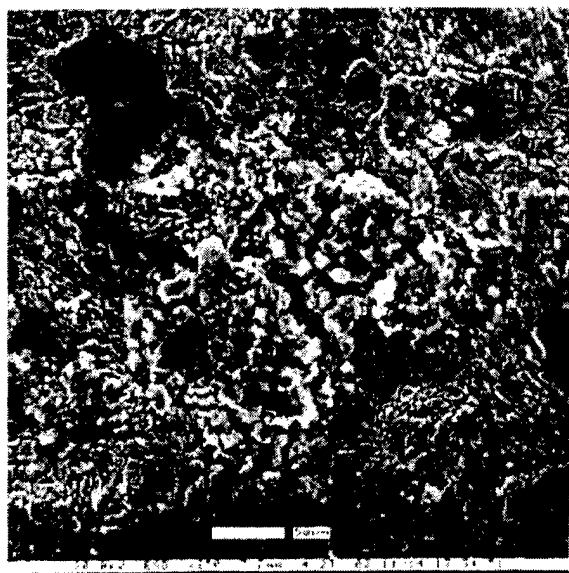

Figure 9c: Black deposit on base metal after 20 weeks exposure to ASW + abiotic sulfides (before cleaning).

51% Ni
25% Cu
7% Mg
5% Si
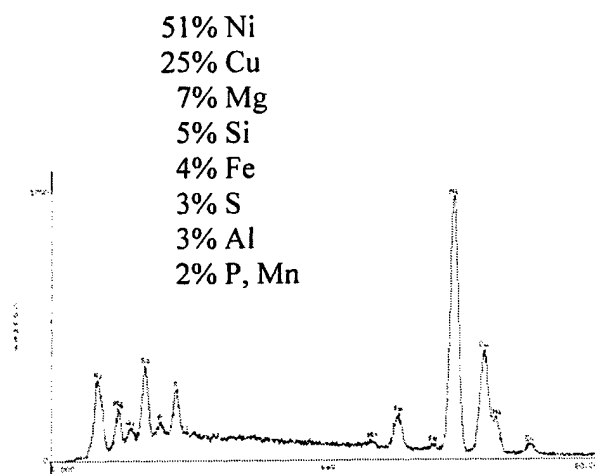4% Fe
3% S
3% Al
2% P, Mn

Figure 9d: EDS of black deposit on base metal after 20 weeks exposure to ASW + abiotic sulfides (before cleaning).