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**MICROBially INFLUENCED CORROSION
OF AUSTENITIC STAINLESS STEEL WELDMENTS**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Ping Li

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ABSTRACT

This dissertation investigated microbially influenced corrosion of austenitic stainless steel weldments in fresh water systems. The corrosion studies were carried out in the laboratory using a simulated Tennessee River water and in the field using a ground water which contained a high chloride concentration and a low dissolved oxygen content. The weldments used in the studies were Type 304L and 316L base materials, and 308L and 316L filler materials, in which a variety of welds was produced using gas tungsten arc welding. The corrosion behavior of the weldments was studied using electrochemical techniques and visual surface examinations in the fresh waters. Crevice and pitting corrosion resistance of the 304L/308L weldments was evaluated in the fresh water and a ferric chloride solution. The oxides produced on the 304L/308L weldments during welding and on 304L plates using the Gleeble simulation technique were examined by x-ray photoelectron spectroscopy, Auger electron spectroscopy, and scanning electron microscopy techniques. It was found that when the weld oxide was removed chemically or electrochemically, the weldment specimen was corrosion resistant regardless of the presence of an imposed crevice and bacteria. When the weld-oxide was not removed, and the bacteria were not present, the weldment specimens showed corrosion resistance in the absence of an imposed crevice. However, if a crevice was present in the weld oxide area, crevice corrosion developed in the form of corrosion nodules. When the weld oxide was not removed, and the bacteria were present, the weldment specimen showed reduced corrosion resistance. Anodic polarization tests revealed that the weldment specimens

were not passivated under these conditions, which indicates that both the as-welded surface and the bacteria simultaneously contributed to the enhanced corrosion. It also was found that the low temperature oxide remote from the weld bead was susceptible to pitting corrosion in a ferric chloride solution whereas the high temperature oxide adjacent to the weld bead was not susceptible. Explanations for the various corrosion behavior of the stainless steel weldments are presented based on corrosion potential, oxide characteristics, aspect ratio of oxide defects, IR drop, and the presence or absence of imposed crevices.

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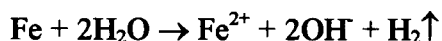
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INTRODUCTION

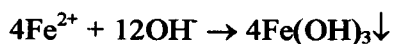
There exist serious and widespread corrosion problems of steel and stainless steel in fresh water systems. The steel or stainless steel, designed for many years of service, fails in a short period of exposure time because of corrosion. From a corrosion engineering point of view, the problems are associated with predominant iron acting as the anodic reaction and dissolved oxygen and/or water supporting the corrosion through cathodic reactions. When iron corrodes in the presence of dissolved oxygen in fresh water, the iron reacts with water owing to the low corrosion potential (and the high exchange current density) and enters into the water in the form of ferrous ions:



In the strongly aerated condition (water saturated with dissolved oxygen), ferrous ions are oxidized to ferric ions by the dissolved oxygen:



These ferric ions react with hydroxyl ions to form a brown deposit of ferric hydroxide according to the reaction:



In a less aerated condition, the ferrous ions react with oxygen to form magnetite (Fe_3O_4).

In general, corrosion is governed by the reduction of dissolved oxygen in a neutral solution. In a deaerated condition, corrosion is controlled by the rate of water reduction, which is much slower and depends on the rate of hydrogen evolution at the iron surface.

Although the iron does not corrode appreciably in the deaerated water, the corrosion rate in some natural environments is found to be abnormally high in localized regions. The high rate of localized corrosion has been traced to the presence of sulfate-reducing bacteria. Stainless steel is considered to be corrosion resistant in natural environments because of the formation of a passive film in which chromium is mainly responsible for the corrosion resistance. However, the passive film can be degraded when the solution contains chloride ions. Localized corrosion problems are serious issues for stainless steel in many applications. Many localized corrosion problems have been associated with iron-oxidizing bacteria. These microbially influenced corrosion (MIC) problems have distinct corrosion characteristics as compared to classic corrosion problems. An acceptance of the roles of bacteria in corrosion is important for understanding the corrosion mechanisms of MIC and ultimately resolving the problems in natural water systems.

Welding of stainless steels is inevitable in practical applications and may adversely affect corrosion resistance. Among various welding processes, gas tungsten arc welding (GTAW) is widely used on stainless steels because it is capable of producing clean and sound welds. However, incomplete inert gas shielding causes material degradation by forming an oxide layer on the surface at and adjacent to the fusion zone. Removing the shielding gas after the root pass produces the heat tint on the down side plate due to the subsequent passes (for instance, by shielded metal arc welding). This heat tint region is sometimes subject to pitting or crevice corrosion when the base metal is not.

The overall objective of this research was to study microbially influenced corrosion of austenitic stainless steel weldments in fresh water system. The project was triggered by

an idea that a real situation (a piping system following a hydrostatic test or a piping system with a constant water flow) was simulated to induce microbially influenced corrosion in laboratory and field. The specimens used in the tests were from industry-fabricated 12 inch diameter stainless steel pipes, each of which contained a circumferential weld with different welding procedures or post-welding treatments. The bacteria applied in the laboratory tests were cultured from fields where microbially influenced corrosion had occurred. The field site was selected on the basis of previous occurrences of microbially influenced corrosion. Corrosion tests were conducted in the laboratory and the field. Microscopic analyses on welding oxide which closely associated with corrosion behavior of the weldments were performed.

CHAPTER 1

LITERATURE REVIEW

1.1. Case Histories

Microbiologically influenced corrosion (MIC) is a relatively new term as far as corrosion control technology is concerned. Before about 1980, MIC was not widely accepted as a real problem to be managed in industrial corrosion control. As more damage has been diagnosed as bacteria related, people gradually have recognized the significance of controlling MIC in industrial fresh water systems.¹

MIC problems most often occur in new systems when they are first wetted. When the problem occurs in older systems, it is almost always a result of changes in the system, such as new sources or quality of water, new materials of construction, new operating procedures, or new operating conditions. Numerous case studies indicate that MIC is most likely to occur in water piping systems following hydrostatic tests or outages in operation.²⁻⁵ A stagnant condition or operation with low or intermittent flow is also amenable to microbial growth.⁶ Most microbial attack observed on carbon steel is highly localized with formation of nodules under which pitting occurs. Iron sulfide is normally found inside the nodule such that sulfate reducing bacteria (SRB) are believed to have a major role in the corrosion process. Almost all MIC in stainless steel occurs at welds or

crevice locations forming tubercles within which iron-oxidizing bacteria (IOB) are readily found. It is concluded that two parameters are of major concern in MIC of carbon steel and stainless steel: (1) an appropriate environment suitable for bacterial growth and (2) the presence of SRB, IOB, and other bacterial communities to form an aggressive consortium.⁷

In the 1970's, industries began to give attention to corrosion problems in relation to MIC. Case studies of corrosion failures that could not be explained by normal corrosion mechanisms on carbon steel and stainless steel were reported.¹⁻¹⁴ These reports involved various piping and tankage systems in the chemical industry, the power industry, the pulp and paper industry, the metal working industry, the oil industry, and the marine industry. The materials having MIC problems included the carbon steels, stainless steels, aluminum alloys, nickel-based alloys and copper alloys. The only material with no reported case histories of MIC was titanium. The wide range of bacteria involved in MIC included sulfate-reducing bacteria, iron oxidizing bacteria, sulfur oxidizing bacteria, organic acid producing bacteria and pseudomonous bacteria. Although MIC has occurred over various circumstances, some common trends can be generalized from these case histories. The following reviews will be focused on MIC problems of carbon steel and stainless steel in fresh water systems. Some typical case studies of MIC will be described in detail in order to better understand MIC characteristics.

The Electric Power Research Institute published a sourcebook for microbiologically influenced corrosion in nuclear power plants in 1988.⁸ Seven MIC cases on carbon steel pipes were listed and four of them were associated with SRB. The other

three were not diagnosed by microbiological means but were suspected to be caused by SRB. Corrosion nodules were formed inside pipes and had a black-brown soft crust; with a black paste inside when hydrated. Pitting corrosion at a very high corrosion rate was found underneath the nodules. One of the case studies indicated that failure was due to crevice corrosion under a backing ring, exacerbated by SRB activity deep in the crevice. Five cases involving failure of welds on stainless steel were reported, all of which were associated with iron oxidizing bacteria. Tubercles were formed at the locations of attack and they were described as black, reddish-brown in color, with soft slimy outer layers and hard tenacious inner layers. Three out of the five cases indicated higher chloride content in the tubercles. In two of the case studies, metallurgical examination revealed preferential attack of the weld metal: in one study, the attacked phase was delta ferrite; in the other, it was austenite. Four of the cases involved corrosion attack after the systems had changes in operating histories.

The first complete case study on MIC damage of 304L and 316L stainless steels was reported by Kobrin.² In this report, it was found that many pipes and tanks made from austenitic stainless steels developed leaks in one to four months after the system had undergone a hydrostatic water test. The water used for the hydrostatic test was a well water containing approximately 200 ppm chloride. To minimize crevice corrosion and gasket leaks, nearly all of the piping was fabricated by butt welding. The leaks were found on butt welds in several long horizontal runs of 304L piping. Inspection revealed perforation of the 1/8 inch (nominal) thick pipe walls by pits adjacent to butt welds. Large, reddish-brown deposits covered the pits. Nearly all pits were found at the edges

of, or very close to, weld seams. The pits were characterized by a minute mouth at the metal surface, and a thin shell of metal covering a bottle-shaped pit, which had consumed both weld and base metal. There was no evidence of intergranular or interdendritic attack of base or weld metal. Microbiological analysis of the well water showed high iron and manganese bacterial counts. Active colonies of these bacteria were also found in mound-like deposits. No other corrosive microbes were found. Chemical analysis of typical deposits showed high concentrations (several thousand ppm) of iron, manganese, and chloride.

Crevice corrosion of stainless steel in recirculating cooling water was reported by Tatnall.³ Severe crevice corrosion was found in and around gasketed joints. The corrosion sites typically showed localized soft deposits, either directly over or adjacent to, the corrosion at the edge of the crevice in the gasketed joint. The bulk deposits were usually light to medium brown and slimy to the touch. Corrosion sites directly underneath deposits appeared bright and active when the deposits were washed away. The adjacent corroded areas underneath the gaskets typically contained black corrosion products that gave off hydrogen sulfide when treated with hydrochloric acid. Chemical analysis of the brown deposits showed high levels of iron and silt, but little or no chloride, manganese, or sulfur. Bacteria analysis showed the bulky deposits having high counts of *Pseudomonas* (slime forming bacteria) and a few *Sphaerotillus* filamentous iron bacteria. *Desulfovibrio* sulfate-reducing bacteria were confirmed in the black underlayer. This case indicated SRB attack of the stainless steel by crevice corrosion.

Another typical MIC attack on stainless steel was reported in 1978. A 304 stainless steel piping system was completed and hydrostatically tested with potable well water.¹¹ After testing, the lines were drained and steam traced. The system sat idle for about five months. When the system was placed in service, leaks were noticed in the piping butt welds. Spot radiography indicated that 80% of all welds contained large, subsurface cavities. Gallionella iron oxidizing bacteria were confirmed to have caused the corrosion. The deposits were found to be high in iron and manganese, apparently concentrated by Gallionella. The deposits also contained high chloride concentrations. Preferential corrosion of the delta ferrite structure in the weld metal also was observed. It was reported that this preferential attack of the ferrite phase was typical of corrosion by ferric chloride and dilute HCl.

Felder and Stein have conducted a four-year field MIC test on stainless steel, titanium, copper-nickel, and carbon steel pipes containing seam and girth welds.⁶ The water for testing, which operated under continuous, intermittent and stagnant conditions, was raw water with 500 to 1000 ppm chlorides. Throughout the four years of testing, no bacteria colonization occurred on the titanium. However, large, bulbous, adherent nodules with predominantly black interiors were observed on the stainless steel pipes in all flow loops. Three morphologies of the pits were noticed: pits with extensive tunneling beneath pinhole openings, shallow surface attack, and open pits. The deep tunneling morphology with pinhole openings was caused by Gallionella iron oxidizing bacteria while the open pits and shallow surface attack were typical of attack caused by sulfate reducing bacteria on the stainless steel. The chloride concentration was very high inside the

nodules. It was found that the Type 304/308 weldment was more susceptible to MIC than the Type 316/316L weldment. The attack in the Type 308 weld metal was found to be preferential to the ferrite phase and the attack in the Type 316 weld metal was found to be preferential to the austenite phase. It also was reported that the low susceptibility to MIC for the titanium alloys and the 6% Mo stainless steel alloys was expected due to the greater corrosion resistance of these alloys; however, the low occurrence of colonization on these alloys was unexpected. These results suggested that there was a difference in susceptibility to colonization.

As evident from the case studies just discussed, microbially influenced corrosion is a very complicated problem. Every case is more or less unique, involving such variables as the material used, the water applied, the type of bacteria involved, the temperature adopted, the operation procedure experienced, and other variables. However, as more MIC case studies are reported, some common factors contributing to the MIC corrosion process become evident. People summarize these factors in terms of the "MIC fingerprint" described in the following paragraphs:¹⁴

In carbon steels, black-brown nodules with black paste inside are formed on the metal surface and underneath the nodules exist cup-shaped, hemispherical pits. SRBs are readily found at the corrosion sites. Chloride may or may not play a significant role.

In stainless steels, reddish-brown nodules are formed on the metal surface. Deep tunneling pits with small openings are discovered when the nodules are removed. Iron-oxidizing bacteria may be found inside the nodules. Chloride plays an important role in the corrosion.

1.2. Biofilms*

Microbial cells attach firmly to almost any surface submerged in an aquatic environment. The immobilized cells grow, multiply, and produce extracellular polymers that frequently extend from the cell forming a tangled matrix of fibers. These fibers provide structure to the assemblage, which has been termed a biofilm. In the simplest case, biofilms are composed of the microbial cells and their products. Biofilms can consist of less than a monolayer of cells or can be as thick as 30-40 mm, as in algal mats. Such a biofilm generally is a very adsorptive and porous (more than 95% water) structure. The microbial species and their morphology, as well as the extracellular polymer composition, largely determine the physical properties of the biofilm. Biofilms contain at least two phases: (1) a continuous liquid (water) phase, which fills a connected fraction of the biofilm volume and contains different dissolved and suspended particulate materials and (2) a series of solid compartments each composed of specific particulate material, such as a species of microorganism, extracellular material, or inorganic particles.

In aquatic environments, microorganisms may be suspended freely in the bulk water (planktonic existence) or attached to an immobile substratum or surface (sessile existence). The environmental conditions largely dictate whether the microorganisms will exist in a planktonic or sessile state. Sessile microorganisms do not attach directly to the substratum surface but rather to a thin layer of organic matter (conditioning film) adsorbed on the surface. As microbes attach to, replicate, and excrete exopolymer material on the

*from William G. Characklis and Kevin C. Marshall (Ref. 15)

substratum, a biofilm is formed over the surface. Over time, species of planktonic bacteria and nonliving particles become entrained in the biofilm and contribute to a growing community of increasing complexity. As the biofilm increases in thickness, diffusion of dissolved gases and other nutrients from the bulk liquid to the substratum becomes impeded. Conditions become inhospitable to some of the microorganisms at the base of the biofilm, and eventually many of these cells die. As the foundation of the biofilm weakens, shear stress from the flowing liquid causes sloughing of cell aggregations, and localized areas of bare surface are exposed to the bulk liquid. The exposed areas are subsequently recolonized, and new microorganisms and their exopolymers are woven into the fabric of the existing biofilm. This phenomenon of biofilm instability occurs even when the physical conditions in the bulk liquid remain constant.

1.3. Bacteria

1.3.1. Characterization

Bacteria are small, their size on the order of a micrometer. They can produce an enormous number of cells in a short time, thus allowing them to bloom and quickly take over an environment. They have specific receptors for certain chemicals, which allow them to seek out higher concentrations of these substances. Generally, most aquatic environments are short of nutrients, especially organic nutrients, but metal surfaces adsorb these materials and create areas of relative plenty. Bacteria can withstand a wide range of temperatures (-10 to 99°C), pH (about 0 to 10.5), and oxygen concentrations (0 to almost

100% O₂). They can form synergistic communities with other bacteria, fungi, algae, plants, and animals. Such communities can accomplish things that the individuals alone can not perform.¹⁶

Bacteria have a large surface-to-volume ratio which leads to extensive interactions with the environment. Heterotrophic bacteria use organic carbon compounds as an energy source. During the metabolic process of fermentation, the bacteria produce a wide variety of organic acids. Autotrophic bacteria use oxygen, nitrate, sulfate, carbon dioxide, and other inorganic compounds as the final electron acceptor in their respiratory metabolism. The result is that the oxygen concentration is altered and various mineral acids are produced by the metabolic processes. Some bacteria can oxidize or reduce metals or metallic ions directly. Many organisms produce enzymes such as hydrogenase, which may be excreted outside the cell and act on substances outside the cells. As a result, cathodic depolarization may occur.¹⁷

1.3.2. Sulfate Reducing Bacteria

Sulfate-reducing bacteria (SRB) are the microorganisms most widely implicated in cases of biocorrosion arising in a wide range of natural and industrial environments. SRB are obligate anaerobes that use sulfate as the terminal electron acceptor for their respiratory metabolism, therefore producing significant amounts of sulfide. This kind of sulfate reduction is formally similar to respiration with oxygen so that it is also called

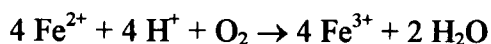
sulfate respiration or dissimilatory sulfate reduction. The main product of this reduction is hydrogen sulfide:¹⁷



Most of the hydrogen sulfide produced in nature is due to this reaction. SRB occur predominantly in decomposing sediments and black mud where organic materials undergo anaerobic degradation. SRB seem to be especially adapted to the products of incomplete carbohydrate metabolism, i.e., fatty acids, oxyacids, alcohols, and hydrogen from fermentations. The mass of hydrogen sulfide occurring in nature can be regarded as the end-product of sulfate respiration. Contaminated water often contains 10^4 to 10^6 , and black mud 10^7 , sulfate reducing organisms/ml. For an enriched culture of SRB, the nutrient medium must contain a suitable hydrogen donor, assimilable substrate, mineral salts, and sulfate; anaerobic conditions and a sufficiently low redox potential (-200 mV vs SHE) are also required.¹⁷

1.3.3. Iron Oxidizing Bacteria

Iron oxidizing bacteria oxidize ferrous iron to ferric iron:



Gallionella ferruginea and *Leptothrix ochracea* are two of the most well-known and easily recognized species of the iron bacteria. They are found in drain pipes and mountain streams associated with flakes and thick coverings of iron oxides. Apart from iron, this group of bacteria also can oxidize manganese from Mn^{2+} to Mn^{4+} . There is no doubt that

the bacteria are associated with oxidized iron and that their cellular structures become encrusted with Fe^{3+} , which often occurs on such a scale that the product is easily visible to the naked eye. Gallionella are kidney-shaped or rounded cells, 2 to 3 μm long, producing a stalk (0.4 to 1.0 μm wide, but of variable length) at right angles to the long axis of the cell. There is heavy Fe^{3+} deposition on stalks, which may account for up to 90% of the weight of the cell mass. These sites, at which Fe^{3+} is deposited on outer cell surfaces, are usually anionic in charge.¹⁸

1.4. Microbially Influenced Corrosion (MIC) Mechanisms

Regarding the mechanisms of microbially influenced corrosion, there is a lack of consistency in the interpretation of biocorrosion. A few years ago, MIC drew tremendous amounts of attention both by microbiologists and corrosion engineers. From a corrosion point of view, anything altering the corrosion variables such as pH, dissolved oxygen concentration, chloride concentration, and concentration of other aggressive species will lead to an increase or decrease in the corrosion rate of materials. Bacteria are able to manipulate these variables very well. As a result, extensive research on MIC has been conducted using the resources of microbiology, metallurgy, and electrochemistry. In general, laboratory research is carried out in such a way that a specimen is immersed in a medium and inoculated with specific types of bacteria and then corrosion measurements are made. In order to define basic mechanisms of attack, a large amount of work involving interactions between bacteria, biofilms, and metal surfaces has been performed.

However, there exists confusion in identifying the dominating variables related to MIC.

Consequently, formulating a general and a conclusive mechanism has proven difficult.

The symposium on Microbiologically Influenced Corrosion Testing, sponsored by ASTM Committee G-1 on Corrosion of Metals (1994), gave in its overview an explicit description of the current dilemma of MIC:¹⁹

“There were several challenges. The first was to organize an interdisciplinary task group with expertise in the use of electrochemical, metallurgical, surface analytical, microbiological, and biotechnological techniques. This was a particularly difficult problem because of limited communication between the different disciplines. Microbiologists had the skills necessary to manipulate and characterize microbial behavior and, consequently, their contributions tended to dominate the field. In addition, many practicing corrosion engineers were skeptical of claims made about the unique characteristics of MIC, since most of the observed corrosion could be accounted for by traditional concepts of localized and underdeposit corrosion. The second challenge in developing standardized MIC tests was that much of the information on the performance and testing of materials in microbiologically active environments consisted of anecdotal evidence and descriptive case histories. There was virtually no consensus on how to conduct corrosion tests in microbiologically active environments or how to interpret test results. Exaggerated claims about the possible corrosive effects of microbial activity alarmed many people, but the lack of reliable, quantitative test data prevented the inclusion of microbiological factors in engineering designs.”

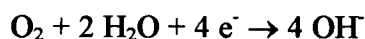
Although these controversies exist in understanding MIC mechanisms, some general trends associated with MIC mechanisms have been recognized through the extensive research studies.

1.4.1. Anaerobic Corrosion

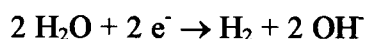
When a metal such as iron is placed in an aqueous environment, the metal goes into solution as a metallic ion at the anodic site:



In a neutral aerobic environment, the electrons are consumed at a nearby cathodic site where oxygen is reduced:

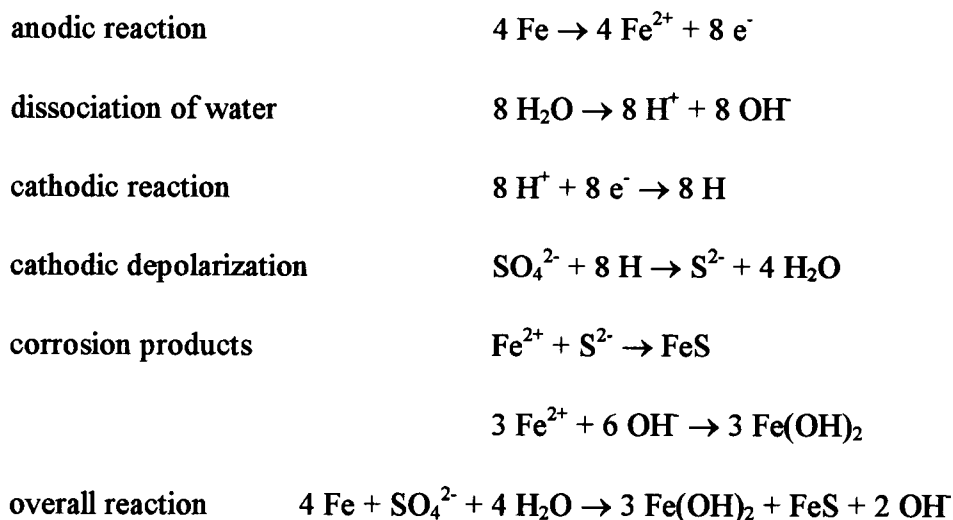


However, in the absence of oxygen, i.e., under anaerobic conditions, water reduction occurs:

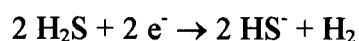


Consequently, removal of the end-products in the above cathodic reactions will accelerate the overall process of metal dissolution. It is now well established that under anaerobic conditions, sulfate-reducing bacteria are the main culprits, due to their capacity to oxidize hydrogen and to produce highly corrosive hydrogen sulfide.²⁰

The concept of anaerobic corrosion can be dated back as early as 1934 when von Wolzogen Kuhr and van der Vlugt²¹ introduced a mechanism of anaerobic corrosion with the presence of sulfate-reducing bacteria at the corrosion site:



Under anaerobic conditions, build-up of hydrogen produced by the cathodic reaction is expected to limit the dissolution of the iron at the anode. The ability of sulfate-reducing bacteria to use this cathodic hydrogen for dissimilatory sulfate reduction will offset the balance in favor of anodic reaction (Figure 1-1). This is referred to as the classical cathodic depolarization theory.²² Much research has been carried out over the years with hydrogenase-positive or -negative strains of sulfate reducing bacteria to support the depolarization theory.²³⁻²⁶ These studies have demonstrated how SRB use cathodic hydrogen. It was found that SRB were capable of removing and using hydrogen generated at cathodic sites on mild steel or platinum working electrodes. Polarization curves showed that the mild steel electrode was depolarized in the presence of the bacteria. Based on the study of the nature of sulfides and their corrosive effect on ferrous metals,²⁷⁻²⁸ it was found that hydrogen sulfide and iron sulfide also contributed to the higher corrosion rate. In the presence of hydrogen sulfide, the corrosion potential of steel becomes more negative due to the formation of iron sulfide. The cathodic process maintains the reversible potential and the exchange current density, but the hydrogen ion diffusion control gradually disappears with increasing hydrogen sulfide concentration. The corrosion product, iron sulfide, has good electronic conductivity, a low overvoltage for hydrogen evolution, a noble electrode potential, and a defect structure. These properties all contribute to the iron sulfide being an excellent cathode to iron in a galvanic corrosion cell. There is evidence showing that the cathodic reactant, when SRB are present, at neutral pH values is, in fact, hydrogen sulfide:



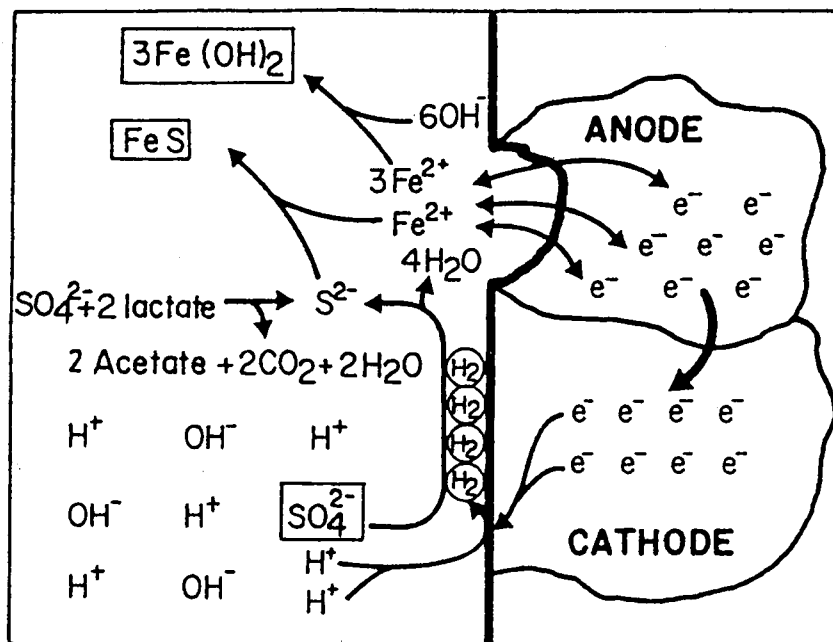


Figure 1-1. Anaerobic corrosion in the presence of sulfate reducing bacteria on an iron surface.

With the further generation of hydrogen sulfide, hydrogenase may have an important secondary role through its removal of molecular hydrogen.²⁹ However, it is more reasonable to consider the reaction as an additional hydrogen discharge from hydrogen sulfide besides the main hydrogen reduction.²⁷ In summary, sulfate-reducing bacteria play a major role in the overall corrosion process either directly, by depolarization of the cathodic reaction due to their ability to oxidize cathodic hydrogen, or indirectly, by producing sulfide as an end-product of their metabolism, which then gives rise to cathodically active iron sulfide, or by the additional hydrogen discharge from hydrogen sulfide.

1.4.2. Iron Oxidizing Bacteria Corrosion

There are few literature reports available regarding the biocorrosion mechanism caused by iron bacteria, although a great number of case histories associated with iron oxidizing bacteria has been reported. The stalked *Gallionella* and the filamentous iron oxidizing bacteria such as *Sphaerotilus* are most often associated with tubercle formation. The raised hard deposits, largely consisting of ferric hydroxide, are formed by the aerobic oxidation of iron and manganese to the higher valency state. Once the tubercle is formed, a crevice region develops under which crevice corrosion may occur.^{20,30} This explanation does not seem fitting in the case of stainless steel. When a nodule is formed, corrosion has already taken place to a considerable extent. Therefore, the protective passive film has

already broken down, and because of the inherent susceptibility of stainless steels to localized corrosion, corrosion would be expected to propagate.

Jones' depiction of the ecology of iron bacteria, as shown in Figure 1-2,¹⁸ may help to understand the corrosion due to iron oxidizing bacteria. Jones states: "The feature common to all sites where iron bacteria develop is the presence of a redox gradient, usually dominated by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. The scale of the gradient in space or time controls the extent to which the iron bacteria grow and develop. Thus, in the water column of a stratified lake, the iron bacteria may be found in a depth zone covering several meters and over which sharp gradients of oxygen and Fe^{2+} concentrations are observed." This description indicates that iron oxidizing bacteria survive in water that contains traces of oxygen and high concentrations of Fe^{2+} . Such a local environment could be developed at some locations on stainless steel, such as welds. Presumably, breakdown of the passive film by the highly oxidizing $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple may give rise to localized corrosion especially when chloride ions are present.

1.4.3. Catalysis of Cathodic Reduction

It has been observed that the corrosion rate of stainless steel in natural seawater is always higher than in artificial seawater. This was attributed to a biofilm formed on the stainless steel surface.³¹ Formation of this biofilm moves the free corrosion potential in the noble direction and shifts the cathodic polarization curve of oxygen toward higher current densities. However, when sodium azide, which inhibits the respiratory activity of

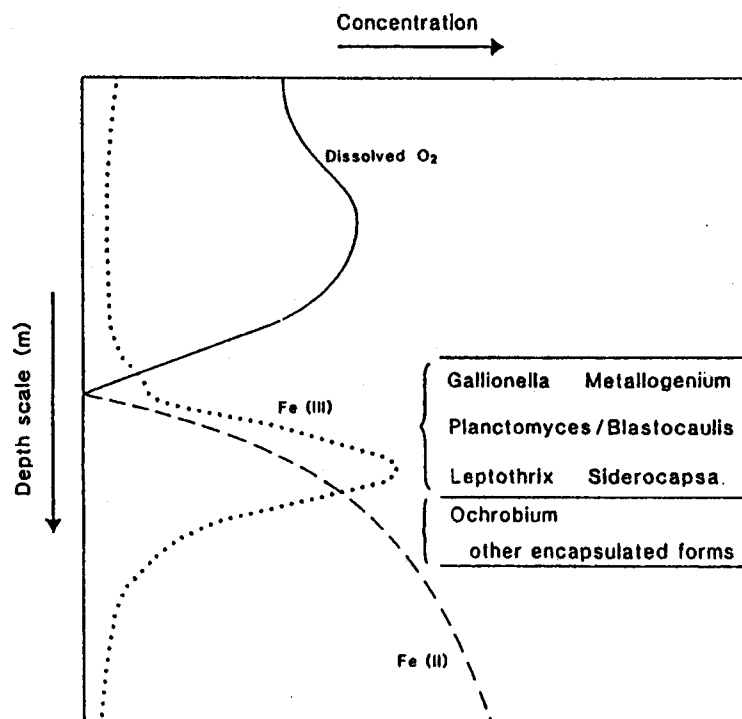


Figure 1-2. Zonation of iron bacteria along gradients of Fe^{2+} and oxygen concentration in a stratified eutrophic lake.

bacteria, was added to the natural seawater after the ennoblement in the corrosion potential in the presence of the biofilm, the original corrosion potential was restored.³² The point was that adding sodium azide decreased the bacterial activity, but it did not remove the biofilm from the stainless steel surface. Because some enzymes, after adsorption on the surface of an electrode, can accelerate the trend of various electrochemical reactions according to hitherto little known bioelectro-catalytic mechanisms, the most likely explanation seemed to be enzymic catalysis of the oxygen reduction reaction. Johnsen and Bardal investigated the cathodic behavior of stainless steel immersed in natural seawater by conducting cathodic polarization to specific potentials and then examining the changes in current density with time.³³ The cathodic current density, after a constant value for the first few days, showed an increase at the constant potentials. The increase in the cathodic current density arose as an extracellular slime built up on the stainless steel surface. This production of slime resulted in an accumulation of heavy metal ions in the slime, which caused the exchange current density of the oxygen reaction to increase.

Chandrasekaran and Dexter recently have proposed an ennoblement model in which bacterial consortia and a combination of chemical mechanisms are required for ennoblement.³⁴ The authors experimentally demonstrated the presence of hydrogen peroxide within the biofilm by showing that the cyclic-voltammogram oxidation peak from a biofilmed platinum electrode matched the oxidation peak from a bare platinum electrode with addition of hydrogen peroxide, as shown in Figure 1-3. Reduction in pH and production of hydrogen peroxide within the biofilm were primary contributors to

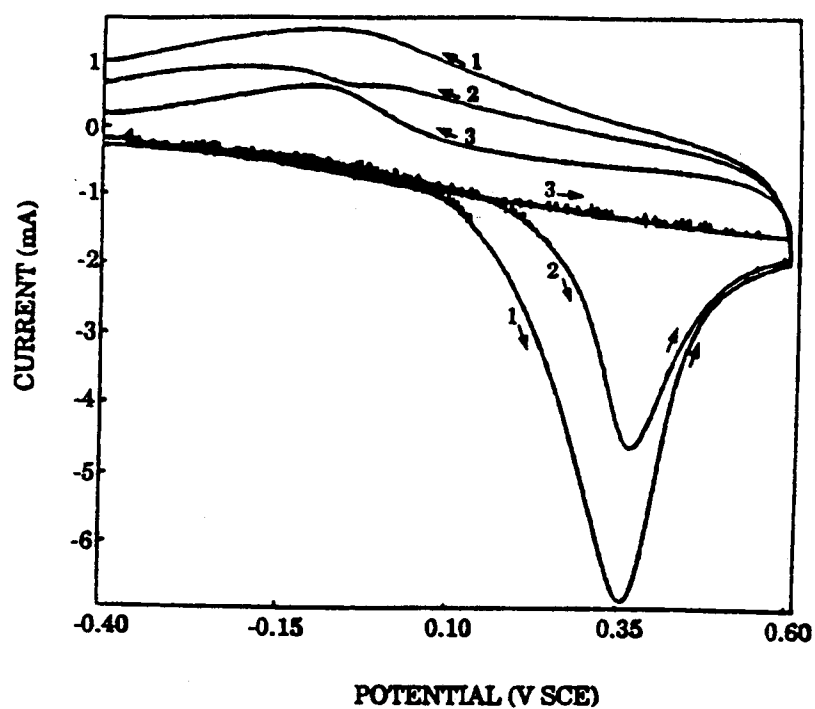


Figure 1-3. Cyclic voltammogram of biofilmed platinum electrodes (curves 1 and 2), and a bare platinum electrode (curve 3) in natural seawater.

ennoblement. It is known that when molecular oxygen in solution in an electrolyte is cathodically reduced, hydrogen peroxide is formed as an intermediate product:

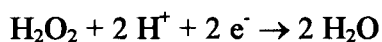
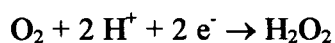


Figure 1-4 shows two equal consecutive waves, the first of which corresponds to the reduction to H_2O_2 , and the second of which corresponds to the reduction to H_2O .³⁵

Therefore, whether or not the H_2O_2 can be detected depends on how fast the second reaction occurs. If bacteria are able to inhibit the reduction to water, hydrogen peroxide can be observed during oxygen reduction.

1.4.4. Other Forms of Biocorrosion

Corrosion may occur on a submerged metal surface as a result of uneven colonization of the surface by microorganisms. As the surface-associated microbes replicate, microcolonies of each species are formed. The microcolonies are distributed in an uneven manner with some areas of the surface being less heavily colonized and more exposed to the bulk aqueous phase than other areas. Consequently, an oxygen concentration cell is likely to develop where an uncolonized area of the surface, in contact with the oxygenated bulk aqueous phase, meets an area covered by a colony of oxygen-respiring bacteria. The area under the microcolony is anodic to the area exposed to the bulk aqueous phase (Figure 1-5).³⁶

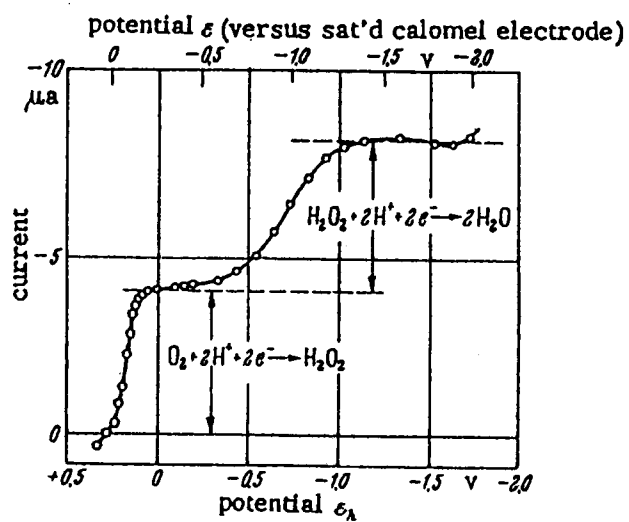


Figure 1-4. Polarogram of O_2 reduction at the dropping Hg electrode.

Differential Aeration Cell

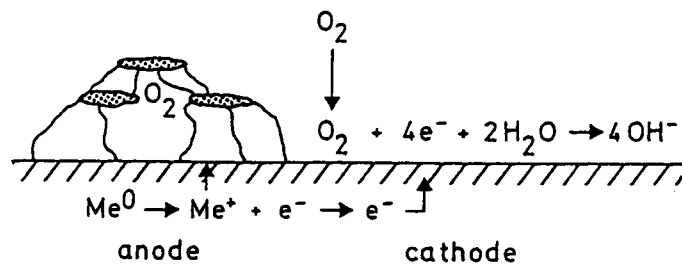


Figure 1-5. Differential aeration cell resulting from heterogeneous distribution of biofilm forming microorganisms over the surface.

Bacterial biofilms develop in all aquatic systems. Studies of biofilms in natural aquatic systems indicate that 10 to 14 days are usually required to reach climax populations and fully developed community structures.³⁷ The matrix is typically a highly hydrated anionic polysaccharide polymer containing large amounts of various uronic acids.³⁸ Early recognition of the phenomenon of microbially influenced corrosion speculated that products of bacterial metabolism exerted corrosive effects on metals without the necessity of sustained bacterial contact with these surfaces. Some bacteria produce and excrete organic acids as by-products of fermentation of organic substrates. When the rate of production is greater than the rate of use by other microbial populations in the biofilm, the acids may accumulate and create localized gradients in pH at the metal surface. As a result, the local environment becomes corrosive to the metal. Many microorganisms produce hydrogen as a product of carbohydrate fermentation. The production of hydrogen by bacteria at a crack tip could lead to stress corrosion cracking and corrosion fatigue. It was reported that hydrogen generated within a pure-culture film resulted in readily measurable absorption of hydrogen to steel.³⁹ Geesey and colleagues have shown that the deposition of two different anionic polysaccharide polymers on adjacent areas of a metal surface is sufficient to cause corrosion, even in the absence of bacteria.⁴⁰ All microorganisms that colonize metal surfaces produce polymers and form a gel matrix on the metal. In general, exopolymers are acidic and contain functional groups that bind metals.⁴¹ The role of metal binding is related to corrosion in two ways: (1) if the concentrated metal is more noble than the ions in the surface lattice then dissolution of ions from the surface would be expected, and (2) if the surface ions are noble to the ions

concentrated by the exopolymer, then that metal would oxidize in preference to the surface ions, thus preventing corrosion.⁴² Furthermore, there are considerable differences in binding capacity between individual metal ions and specific exopolymers. The extent of the binding is dependent on environmental factors, such as pH, redox potential, and competing ions.⁴³

Fouling refers to the undesirable formation of inorganic and/or organic deposits on surfaces, leading to unsatisfactory equipment performance or reduction in equipment lifetime. Biofilms cause fouling of industrial equipment such as heat exchangers, pipelines, and ship hulls, resulting in reduced heat transfer, increased fluid frictional resistance, and increased corrosion. Cathodic protection has long been recognized as an effective corrosion control method, especially in seawater where conductivity is sufficiently high that a reasonably uniform current distribution can be obtained. In addition, the inorganic chemistry of seawater permits the formation of beneficial calcareous deposits on the metal surface during cathodic protection. However, formation of biofouling or biofilms before and during cathodic protection may have influence on the effectiveness of cathodic protection. Dexter et al. have found that it is possible for a primary marine biofilm to either enhance or decrease the effectiveness of cathodic protection, depending on the applied current density.^{44,45} Bacterial settlement and reproduction were reduced by cathodic protection in the initial stages of biofilm formation. However, this effect was less relevant when the steady state of growth was reached.⁴⁶ Maxwell found that cathodic protection using sacrificial materials inhibited SRB developing on steel surfaces in seawater.⁴⁷ The main consequence of biofilm formation on protected surfaces appeared to

be an increase in the current density necessary to polarize the metal to the protection potential. The presence of large numbers of cells on cathodically-protected surfaces indicated that, in the event that cathodic protection was intermittent, discontinuous, or discontinued, the corrosion attack due to the microorganisms would be more aggressive.⁴⁸

1.5. Understanding of Stainless Steels Regarding Corrosion

Stainless steels are well known for their corrosion resistance in various corrosive media. Chemical composition is a controlling factor responsible for this unique feature. The alloys must have at least 12% chromium content to minimize corrosion occurrence. The addition of chromium causes various chemical and physical transformations. Therefore, to understand the corrosion resistance of stainless steels and associated welds, it is first necessary to consider microstructures and constitutions of the stainless steels.

1.5.1. Equilibrium Diagrams

The most basic of the phases derives from the allotropic forms of iron, which can be seen by examining the Fe-Cr binary phase diagram in Figure 1-6.⁴⁹ Between 1400°C (2552°F) and 1539°C (2802°F), pure iron exists as body-centered cubic (bcc) delta ferrite, δ . Between 910°C (1670°F) and 1400°C (2552°F), iron is face-centered cubic (fcc), called austenite, γ . Below 910°C (1670°F), iron transforms back to ferrite again, termed alpha ferrite, α . In the center of the phase field, identified as σ , is an intermetallic

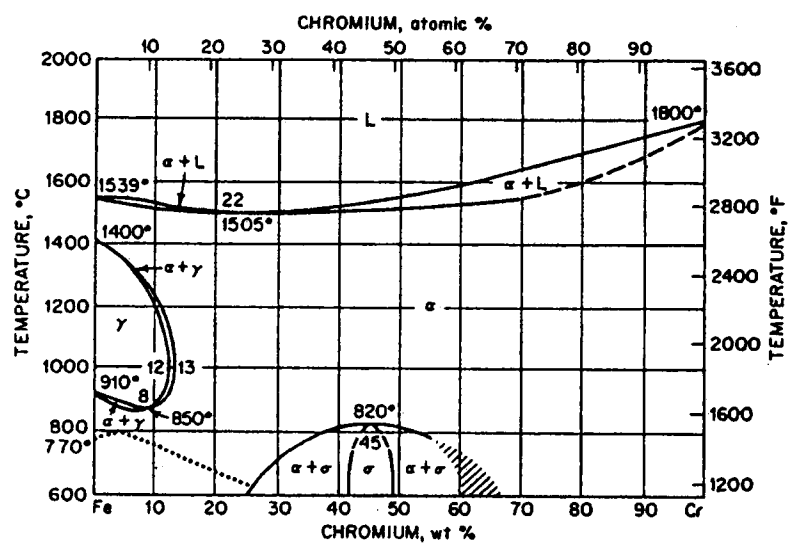


Figure 1-6. Fe-Cr equilibrium diagram.

compound, the sigma phase.

Attention is directed to the left-hand side of the diagram. The addition of chromium up to about 7% reduces the transformation temperatures of both bcc to fcc and fcc to bcc. Above 7%, the temperature interval over which austenite exists gradually decreases until at about 13% chromium, no transformation occurs, and ferrite exists at all temperatures. Thus, chromium is said to be a ferrite former. Austenitic stainless steels all contain more than 16% chromium. From Figure 1-6, it is apparent that chromium contents of this magnitude would render the alloys totally ferritic. This effect is counteracted primarily by addition of nickel to the iron-chromium binary system. The binary iron-nickel phase diagram is shown in Figure 1-7,⁵⁰ and demonstrates a sharp contrast to the effect of chromium in terms of γ phase stabilization. In Figure 1-7, the austenite field is broadened by increasing additions of nickel. Therefore, nickel is called an austenite former. In practice, at lower temperatures, equilibrium constituents do not form as predicted since nickel as a substitutional element diffuses very slowly in iron. Normal cooling rates, especially during welding processes, are insufficient to permit the diffusion necessary to achieve equilibrium.

In iron-chromium-nickel ternary systems of normal austenitic stainless steels, the alloys first solidify either into an alpha plus gamma field or a single alpha field depending on the specific composition. Then, with reducing temperature, the austenite field expands until, at about 1100°C (2012°F), the alloys may fall completely into the austenite field. The best way to visualize the phase relationships is by using pseudobinary sections, such that by keeping one of the elements constant, binary diagrams are obtained as sections

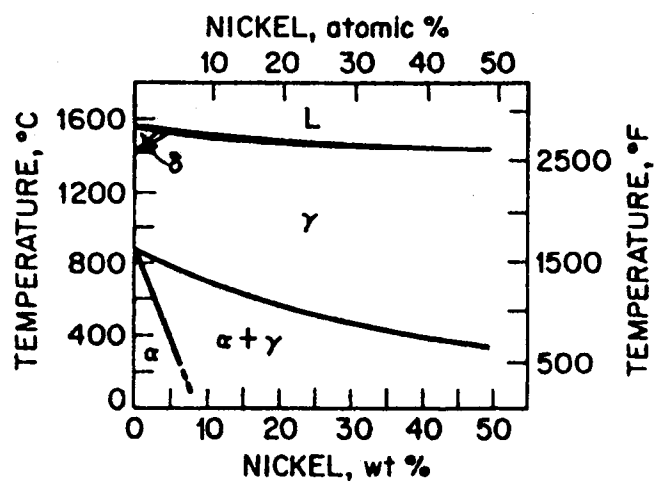


Figure 1-7. Fe-Ni equilibrium diagram.

through the ternary diagram. Figure 1-8⁵¹ shows the sections for constant iron contents of 50%, 60%, 70%, 80%, and 90%, respectively. Figure 1-8 represents equilibrium diagrams. The dashed lines used to separate the phase fields at lower temperatures mean that the transformations are not observed under practical conditions. An alloy cooled from the γ field across dashed lines will remain austenitic. At 70%, 80%, and 90% iron, the $\gamma \leftrightarrow \alpha + \gamma$ boundary slants backward such that a fully austenitic alloy close to a boundary at 1000°C (1832°F) can contain some ferrite when cooled. At lower iron contents, 50% and 60%, the $\gamma \leftrightarrow \alpha + \gamma$ boundary does not curve, so that an austenitic alloy tends to remain so at all temperatures. As iron content decreases, the $\alpha + \gamma$ field also broadens, so it is possible that some alloys in this range may not be fully austenitic.

There are various other elements present in Fe-Cr-Ni alloys, which have significant effects on phase equilibrium. Initial work by Schaeffler,⁵² as well as further improvement by DeLong⁵³ that incorporated the effect of nitrogen, was intended to define the effect of composition on the weld metal constitution. Elements were characterized as either austenite or ferrite formers according to their influence on α or γ phase stabilization. For given compositions of various elements, the percentage of ferrite to gamma phase can be determined from the Schaeffler or DeLong diagram. Therefore, a major heat treatment in austenitic stainless steels is the solution anneal intended to dissolve any constituents except austenite that may be present.

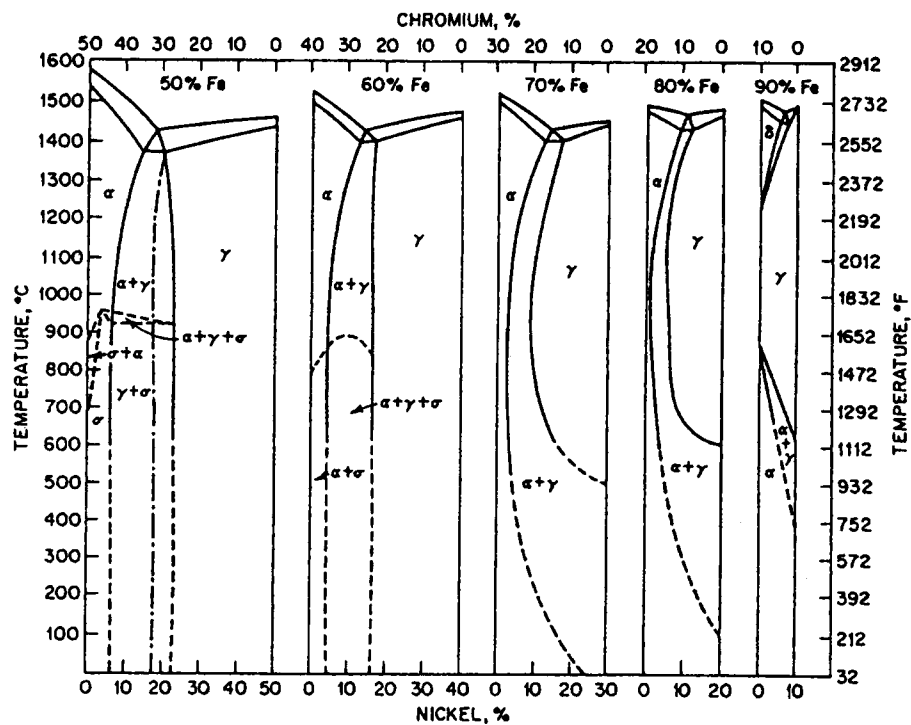


Figure 1-8. Cross sections of Fe-Cr-Ni ternary system.

1.5.2. Carbide Precipitation

In practical applications, a good solution anneal treatment can not be maintained in many situations such as welding of stainless steel. As a result, precipitation occurs within a certain range of temperatures caused by the welding thermal cycle. Austenitic stainless steels contain up to 0.08% or 0.15% carbon. Below about 1000°C (1832°F), the solid solubility for carbon is reduced tremendously. As a result, carbides precipitate mainly as $M_{23}C_6$, where M stands for strong carbide forming elements like Cr, Fe, or Mo. The precipitation of these carbides occurs at the grain boundaries, and is one of the causes of intergranular corrosion in the heat affected zone of austenitic stainless steel welds. The precipitation occurs very rapidly at ferrite/austenite interfaces, followed soon afterwards by precipitation at grain boundaries. The temperatures of the precipitation range from about 500°C (932°F) to 950°C (1742°F). $M_{23}C_6$ is primarily chromium carbide in which the iron may substitute partially for chromium. During the initial stages of $M_{23}C_6$ carbide precipitation, the iron content is quite high. With increasing precipitation, the chromium content increases. Increasing the original annealing temperature and grain size accelerates precipitation of $M_{23}C_6$.

One measure adopted to control $M_{23}C_6$ precipitation is to reduce the carbon content. Consequently, the precipitation reaction is sufficiently suppressed because of the lack of carbon. In addition, titanium or niobium can be added into stainless steel to form a stabilized grade alloy due to formation of carbides (TiC and NbC). In terms of heat treatments, these alloy additions can be viewed in two ways. When the alloys are

employed primarily as stabilized grades to prevent subsequent intergranular corrosion, they are often given a stabilizing heat treatment at temperatures of 850°C (1562°F) to 900°C (1652°F). This treatment precipitates TiC or NbC such that the matrix carbon content is effectively reduced. Thus, the detrimental $M_{23}C_6$ precipitation is avoided. Alternately, the alloys may be annealed to dissolve as much of the TiC or NbC as possible and then placed in service at some temperature within the precipitation range. The strength is increased due to subsequent intragranular MC precipitation. The MC carbides usually precipitate intragranularly. However, exposure to extraordinarily high austenitizing temperatures may result in precipitation at grain boundaries. This phenomenon, occurring at weld fusion areas, leads to the knife-line attack.

1.6. Corrosion of Austenitic Stainless Steel Welds

Stainless steel corrosion is closely related to welds on which localized corrosion occurs. In many cases, localized corrosion occurs in the heat-affected zone. Various forms of corrosion can be found on the stainless steel weldment. In general, the following types of corrosion can be characterized in terms of their forms as well as the associated environments.

1.6.1. Intergranular Corrosion

Intergranular corrosion is always a significant issue in stainless steel welds because sensitization can lead to severe damage on welds if improper welding procedures or heat treatments are applied. The mechanism responsible for sensitization has been briefly reviewed and involves carbide precipitation, which results in chromium depletion along grain boundaries. However, the intergranular corrosion can occur without chromium carbide precipitation. In welding of austenitic stainless steels, a low percentage of ferrite usually is introduced into the weld metal to avoid hot cracking and fissuring. The introduction of ferrite can lead to the sigma phase formation, which adversely affects corrosion resistance of the alloy.

Zingales showed that the sigma and related phases could be responsible for significant intergranular corrosion on austenitic stainless steel by doing the Strauss test.⁵⁴ In presence of ferrite, the sigma precipitation occurred in grain boundaries growing into the ferrite and retained a form of a continuous network, which led to severe corrosion. If sufficient sensitizing time and temperature were provided, it caused a quantitative transformation of the ferrite to the sigma. As a result, a globular shape of the sigma phase might be present, which had less effect on intergranular corrosion.

The content and morphology of delta ferrite in an austenitic stainless steel weld affect corrosion behavior of the alloy. Anodic polarization was used to study the corrosion behavior of austenitic stainless steel weld and clad metal.⁵⁵ While the results showed that delta ferrite had adverse effects on corrosion resistance as the alloy was in the

active region, there were little or no significant influences on corrosion behavior when the alloy was in the passive region. Delta ferrite effects on corrosion were also studied using the accelerated immersion tests specified by ASTM A 262.⁵⁶ The results were consistent with the anodic polarization results that delta ferrite was not harmful under passive conditions. Furthermore, delta ferrite was beneficial in controlling intergranular corrosion.

If non-sensitizing carbides are first precipitated on grain boundaries by a brief high temperature exposure, sensitization can develop during subsequent thermal treatments at unexpectedly low temperatures. This behavior has been termed low temperature sensitization. Juhas studied type 316 stainless steel with variations in carbon and nitrogen content exposed to a high temperature thermal cycle and then followed by a long term isothermal, low temperature heat treatment.⁵⁷ The corrosion tests indicated that grain boundary chromium depletion did not occur with this heat treatment. The low temperature exposure did not increase the susceptibility to intergranular corrosion.

1.6.2. Pitting and Crevice Corrosion

Pitting corrosion in austenitic stainless steel welds is a problem in acidic, oxidizing, and chloride-containing environments. Attack is likely to occur at the phase boundaries where the segregation of impurities (P, S) toward the delta-ferrite/austenite interfaces exists. This location is also the region where the final stage of solidification has occurred.

Grekula studied the effect of solidification mode and impurities on pitting corrosion of 316 stainless steel welds.⁵⁸ The sulfur content had a small effect on corrosion

resistance in the primary austenitically-solidifying welds. However, sulfur content had a significant influence on corrosion resistance of the primary ferritically-solidifying welds. The last interdendritic regions to solidify in primary austenitic welds and the delta-ferrite/austenite phase interfaces in primary ferritic welds are the most susceptible sites for pit initiation. When austenite was the leading phase during solidification, pits initiated at the interdendritic regions and grew along the austenite-dendrite core. When ferrite was the leading phase, pits initiated at delta ferrite/austenite interfaces and grew into the austenite.

Gill has studied the pitting resistance of 316L stainless steel weld metal in as-deposited and thermally-aged conditions by determining the critical pitting potential in an acid chloride solution.⁵⁹ After aging at temperatures of 500°C (932°F) to 700°C (1292°F) for up to 500 hours, the pitting corrosion resistance of the weld metal had decreased. The decrease in the critical pitting potential upon aging was due to precipitation of the various secondary phases that were transformed from delta ferrite. Delta ferrite and sigma remained unattacked during pit growth because of their relatively nobler electrochemical potentials.

Gill has also studied the pitting resistance of 316L stainless steel weld metal in the as-welded and stress-relieved conditions as a function of heat input.⁶⁰ The pitting potential in an acidic chloride solution decreased as the heat input was increased. The decrease in the pitting resistance on increasing heat input was due to enhanced segregation of chromium and molybdenum to delta ferrite. As a result, the enriched Cr and Mo delta ferrite left relatively low Cr and Mo in the adjacent austenite phase. A stress-relief heat

treatment at 800°C (1472°F) for 10 hours decreased the pitting resistance because of the transformation of ferrite to the sigma phase. The influence of heat input on the pitting corrosion resistance of 304 stainless steel weld metals containing different amounts of nitrogen also was studied.⁶¹ It was reported that the pitting resistance decreased slightly as the heat input was increased. This was balanced mainly by an addition of nitrogen in the welds. At a constant heat input, the nitrogen content in the welds increased as the volume percent of nitrogen in the shielding gas was increased. However, as the heat input was increased, the nitrogen content in the welds decreased at the same volume percent of nitrogen in the shielding gas.

1.6.3. Stress Corrosion Cracking (SCC) of Stainless Steel Welds

Stress corrosion cracking involves a combination of stress and an aggressive environment, which causes crack growth where the action of each alone would not. Corrosion fatigue involves a combination of fatigue and an aggressive environment, which causes crack growth much faster than the fatigue alone. Essentially, stress corrosion cracking and corrosion fatigue are different from corrosion in terms of the types of investigations: corrosion deals with material loss; stress corrosion cracking and corrosion fatigue deal with the fracture mechanics type behavior of growing cracks. Because there is no general rule for crack growth as a function of the stress intensity factor, K , in a corrosive environment, the controlling factor is to assure that the design stress intensity factor is lower than the value of the critical stress intensity factor for stress corrosion

cracking, K_{ISCC} . The K_{ISCC} value depends on environmental variables that are associated with the corrosion process.

Austenitic stainless steels are widely used in the welded condition especially in chemical, petrochemical, thermal power, and nuclear industries, where they are subjected to stresses in corrosive environments. As general rules of thumb, three conditions which act concurrently will possibly result in SCC: (1) a tensile stress of 14,000 psi or greater; (2) a temperature of 150°F (65°C) or higher; and (3) 100 ppm chloride or greater, in solution.⁶² However, many studies have showed stress corrosion cracking at room temperature.

Rao investigated the room temperature stress corrosion cracking resistance of austenitic stainless steel welds with different ferrite contents.⁶³ The results showed that the delta ferrite content in austenitic stainless steel welds had a predominant effect on the room temperature stress corrosion cracking behavior. As the ferrite contents increased, the SCC resistance decreased. Post weld heat treatments on austenitic stainless steel welds were examined for the resistance to room temperature stress corrosion cracking.⁶⁴ The specimens were post-weld heat-treated at 600°C (1112°F), 800°C (1472°F), and 1000°C (1832°F) for 1, 10, and 100 hours. The results indicated that postweld heat treatments at 600°C (1112°F) and 800°C (1472°F) decreased the SCC resistance of the stainless steel welds with delta ferrite. The decrease was attributed to the network of delta ferrite caused by the heat treatments. The postweld heat treatment at 1000°C (1832°F) improved the SCC resistance. It was concluded that failure due to stress corrosion cracking in austenitic weld metals was due to the combined action of (1) ferrite or sigma

dissolution, which is accelerated by applied load, and (2) the stress corrosion cracking in austenite.

Raja studied the effect of applied potentials on room temperature stress corrosion cracking of austenitic stainless steel welds.⁶⁵ Open-circuit potential was measured as a function of exposure time with application of a constant load. The open-circuit potential at SCC failure was taken as the steady state rest potential. The results indicated that the applied anodic potentials on the rest potential decreased the time to failure drastically. On the other hand, the applied cathodic potentials upon the rest potential increased the time to failure.

1.6.4. Weld Oxide Induced Corrosion

Welding is a necessary means to construct piping and pressure vessel systems for chemical and nuclear industries. Because corrosion control in such industries is an important issue, the application of corrosion resistant materials is necessary. Stainless steels are widely used in the industries because of their corrosion resistance. In the construction of piping and pressure vessel systems, welding is a necessary occurrence and usually leads to a decrease in corrosion resistance. The weld oxide produced during welding is detrimental to corrosion resistance of stainless steels. Kearns⁶⁶ and Turner⁶⁷ investigated the weld oxide effect on corrosion resistance of stainless steels. Their test procedures and test results are briefly reviewed here in order to fully understand the background of this issue.

1.6.4.1. Materials

Turner selected AISI type 304L and 316L stainless steels for his study. Kearns used AL-6XN, AL-904L, and 317LX stainless steel alloys as the base materials on which surface oxides would be produced, which typically contained 18%-21% Cr, 4.2%-6.3% Mo, and 24%-25% or 14% Ni. It is noted that the materials used by Kearns contained relatively higher than 2% contents of molybdenum, which inherently improves the corrosion pitting resistance.

1.6.4.2. Oxide Selection

Typical welding parameters ($I=120\text{A}$, $E=14\text{V}$, $v=2\text{ mm/s}$) for GTAW of 2 mm thick sheet were selected to produce the welds in Turner's study. Three characteristic welding oxides were selected in terms of their interference colors, i.e., straw-colored, blue, and green-brown. Distances from the fusion boundary to these oxides were measured. A welding mathematical model that is a function of welding parameters and material properties was used to calculate peak temperatures during welding. They were 1472°F (800°C), 1832°F (1000°C), and 2192°F (1200°C), corresponding to the oxides of straw-colored, blue and green-brown, respectively. The oxides were reproduced by furnace-heating the stainless steels at these temperatures and controlling the exposure time. The colors of these oxides were compared to ones of the true weld oxides using a stereomicroscope.

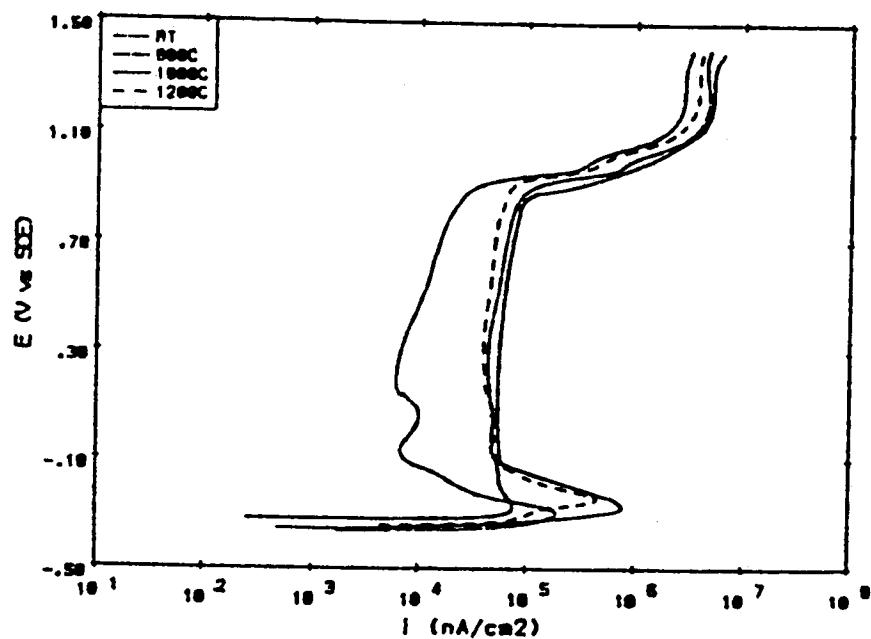
Kearns used two methods to produce weld oxide. First, welds were made by bead-on-plate GTAW welding on 1/4 inch thick hot rolled, annealed, and pickled plates in air. A thermocouple was attached to the underside of the plate so that the peak temperature (heat tint temperature) was measured during welding. The welding current was varied from 50A to 250A to give different energy inputs. As a result, different oxides on the underside of the plates were produced according to the different peak temperatures determined by the different energy inputs. These oxides were designated by the peak temperatures that the underside of the plates had experienced. They were 445°F (229°C), 709°F (376°C), 972°F (522°C), 1232°F (667°C), and 1499°F (815°C). Another set of samples was prepared in an argon atmosphere. Secondly, stainless steel plates of 0.62 inch thickness and 0.036 inch thickness were used to produce the oxides through "Gleeble" resistance heating techniques. Peak temperatures based on the first method were chosen in the Gleeble simulation. They were 350°F (176°C), 750°F (399°C), 1050°F (566°C), 1200°F (649°C), 1450°F (788°C), and 1700°F (927°C).

In Turner's study, the peak temperatures that represented the oxides with three typical colors were based on calculations through the mathematical model. Therefore, the calculated peak temperatures used to identify the oxides in colors may not be the true peak temperatures. The straw-colored oxide was produced at the peak temperature of 1472°F (800°C) using 304L and 316L stainless steels. However, at a peak temperature of 1499°F (815°C), the oxide color was blue or rose using 317LX or AL-904L in Kearns' study. In addition, because the welding oxides formed in shorter times and with mechanical strain due to the thermal stresses, the oxides produced by the furnace treatments did not

adequately represent the weld oxides formed at the peak temperatures during welding. Kearns used true weld oxides and simulated oxides produced in the Gleeble. However, the peak temperatures only ranged from 350°F (176°C) to 1700°F (927°C) and also did not cover the higher temperatures at which the oxides formed.

1.6.4.3. Corrosion Tests

Potentiodynamic polarization techniques were applied to characterize the corrosion properties of the oxides in both studies. Turner used a 0.4 N H₂SO₄ solution to obtain anodic polarization behavior (see in Figure 1-9) and then calculated corrosion rates corresponding to critical current densities and passive current densities. The oxides were also tested in a chloride-containing solution (290 ppm Cl⁻) to evaluate the pitting potential (Figure 1-10). Kearns used a modified version of ASTM specification G-5 (10 wt% FeCl₃ solution at 50°C (122°F)) to test the oxides and obtained the pitting or crevice breakdown potential (Table 1-1). Kearns also ran immersion tests with crevices per ASTM G-48 using the same solution (Table 1-2). Kearns' test results did not significantly differentiate corrosion resistance between the tinted samples and the untinted samples (argon shielded). In general, the test solutions were too aggressive, especially 10% FeCl₃. As a result, the heat tinted and untinted samples were not readily distinguished in corrosion behaviors (E_{corr} and E_p , etc.).

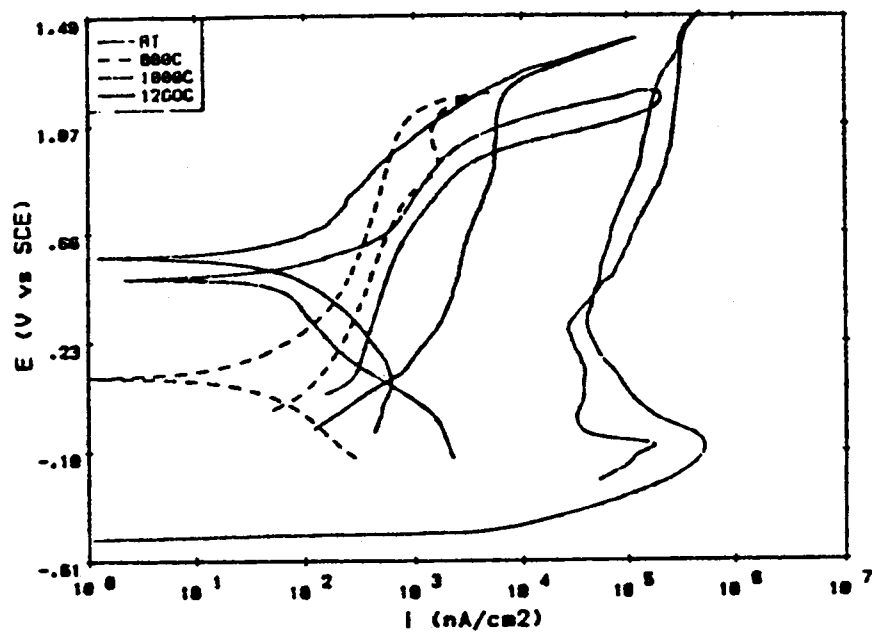


*Corrosion Rates (mpy) for AISI Type 316L and 304L Oxides
in Sulfuric Acid Solutions*

Temperature (°C)	Type 316L		Type 304L		Actual Welded Samples Type 304L	
	i_{pass}	i_{crit}	i_{pass}	i_{crit}	i_{pass}	i_{crit}
RT ^(A)	~5	—	3.06	102.96	3.06	102.96
800	4.22	18.99	18.04	35.84	89.58	321.42
1000	6.90	18.24	18.61	348.56	154.0	1174.54
1200	14.81	263.46	24.45	287.43		

^(A) RT = room temperature.

Figure 1-9. Potentiodynamic polarization curves for the oxides on type 304L in 0.4N H₂SO₄ solution.



*Electrochemical Pitting Parameters for AISI Type 316L
in 0.005 N NaCl + 0.025 N Na₂SO₄*

Temperature (°C)	E _p (V)	E _p - E _{corr} (V)
RT ^a	1.230	1.334
800	1.123	1.143
1000	0.882	0.889
1200	—	—

Figure 1-10. Polarization pitting scans for the various oxides on type 316L in a 0.025N Na₂SO₄ + 0.005N NaCl solution.

Table 1-1. The corrosion data from the anodic polarization results.

I. Welded Samples

Alloy	Welding Amperage	Potential, Volts (vs. SCE)			Remarks [#]
		Ecorr	Ep	Er	
T-317LX	50	0.27	0.27	0.14	P&C
	100	0.27	0.27	0.14	P&C
	150	0.30	0.30	0.16	P&C
	200	0.31	0.32	0.16	P&C
	250	0.22	0.23	0.10	P&C
AL 904L	50	0.40	0.42	0.14	P&C
	100	0.44	0.44	0.14	P&C
	150	0.39	0.40	0.16	P&C
	200	0.27	0.28	0.14	P&C
	250	0.24	0.25	0.14	P&C
AL 6XN	50	0.52	>1.0	*	N.A.
	100	0.56	>1.0	*	N.A.
	150	0.56	0.80	0.60	P&C
	200	0.40	0.87	0.40	P&C
	250	0.30	0.89	0.40	P&C

II. Welded Samples Shielded by Argon (Untinted)

Alloy	Welding Amperage	Potential, Volts (vs. SCE)			Remarks [#]
		Ecorr	Ep	Er	
T-317LX	Base	0.28	0.28	0.08	P&C
	50	0.26	0.28	0.12	P&C
	100	0.28	0.30	0.15	P&C
	150	0.28	0.30	0.14	P&C
	200	0.33	0.36	0.16	P&C
	250	0.32	0.35	0.14	P&C
AL 904L	Base	0.41	0.42	0.13	P&C
	50	0.38	0.38	0.16	P&C
	100	0.38	0.38	0.17	P&C
	150	0.37	0.37	0.16	P&C
	200	0.35	0.35	0.14	P&C
	250	0.35	0.35	0.17	P&C
AL 6XN	Base	0.52	0.80	*	C
	50	0.48	0.86	*	P
	100	0.49	0.89	*	Light C
	150	0.53	0.91	*	P
	200	0.55	0.89	*	C
	250	0.56	0.91	*	C

Table 1-1. (continued)

III. Gleeble Samples

Alloy	Welding Amperage	Potential, Volts (vs. SCE)			Remarks [#]
		Ecorr	Ep	Er	
T-317LX	176	0.14	0.14	0.16	P&C
	399	0.20	0.20	0.16	P&C
	566	0.19	0.20	0.16	P&C
	649	0.23	0.23	0.15	P&C
	788	0.05	0.08	0.15	P&C
	927	-0.16	-0.10	0.12	P&C
AL 904L	176	0.36	0.70	0.14	P&C
	399	0.40	0.64	0.14	P&C
	566	0.39	0.41	0.16	P&C
	649	0.36	0.37	0.18	P&C
	788	0.40	0.44	0.24	P&C
	927	0.44	0.46	0.26	P&C
AL 6XN	176	0.48	0.91	0.52	Slight C
	399	0.52	0.92	0.64	Light P
	566	0.57	0.88	*	Light C
	649	0.52	0.86	*	C
	788	0.48	0.89	*	C
	927	0.24	0.92	*	C

* No Hysteresis Loop

N.A. = No Attack, P = Pits, C = Crevice

Ecorr = Corrosion Potential, Ep = Pitting Potential, Er = Repassivation Potential

This table is from Kearns (Ref. 66)

Table 1-2. The welded samples were exposed to the 10% FeCl₃ solution at 50°C per ASTM G-48 crevice test.

MAXIMUM PIT DEPTH IN HEAT TINTED REGIONS

Alloy	Peak Temp. (°C)	Max. Pit Depth (mm)	Center-line to Deepest Pit (mm)	Color of Oxide at Deepest pit	Number of Pits
T-317LX	229	0.1	6	Straw	2
	376	0.7	2	Blue	10
	522	0.8	0	Blue	>50
	667	0.7	0	Blue	>70
	815	0.9	4	Blue	>70
AL 904L	229		Crevice attack only		
	376	<0.1	3	Blue	7
	522	0.7	0	Blue	25
	667	0.9	0	Blue	50
	815	1.1	5	Rose	50
AL 6XN	229		Crevice attack only		
	376		Crevice attack only		
	522		Crevice attack only		
	667		Crevice attack only		
	815		Crevice attack only		

1 x 2 inch (2.5 x 5.1 cm) welded samples were exposed to a 10% FeCl₃.6H₂O solution at 50°C (122°F)

This table is from Kearns (Ref. 66)

1.6.4.4. Auger Analysis

Turner analyzed the oxides produced by furnace heating and also actual weld oxides having the three characteristic colors. Depth profiles of the alloy elements were obtained by sputtering the oxide and underlying surface. Oxide thicknesses were measured at the half-maximum value of the oxygen signal. As a result, the corresponding sputtering times of 1.5, 2, and 10 minutes were necessary to penetrate the 1472°F (800°C), 1832°F (1000°C), and 2192°F (1200°C) oxides in 304L. Turner's interpretations of the results are summarized. Chromium content at the surface of oxide was low in comparison to chromium in the matrix. After the oxide had been sputtered off, chromium enrichment was found in the underlying metal of all three oxide samples (Figure 1-11). Because chromium was enriched at these low depths, further penetration into the metal revealed chromium depletion.

Kearns also applied the depth profile to present chemistry information on the oxide samples. Reducing the oxygen concentration to a minimum by sputtering was used to measure the oxide thicknesses. For instance, it took 6 minutes to penetrate the oxide with a peak temperature of 972°F (522°C). Chromium enrichment and depletion relative to the matrix were found as the sputtering time increased (Figure 1-12). However, Kearns indicated that Cr enrichment occurred in the oxide layer and Cr depletion occurred in the underlying metal. Although Kearns and Turner basically had the same results of Auger chemical analysis, the interpretations of the data were different. This was mainly due to the different criteria used to establish the oxide thicknesses. Kearns pointed out that the

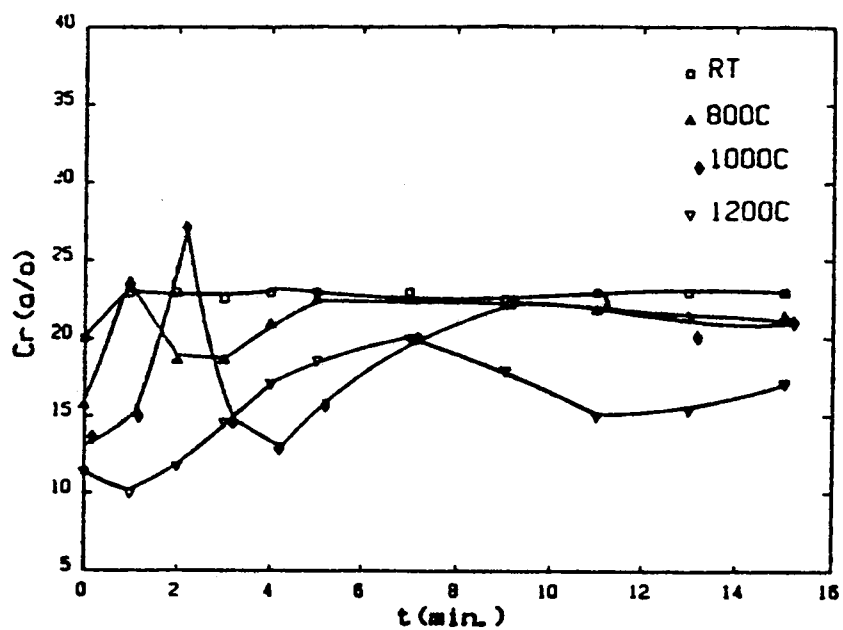


Figure 1-11. Comparison of the chromium depth profiles for the natural and high temperature oxides produced on type 304L.

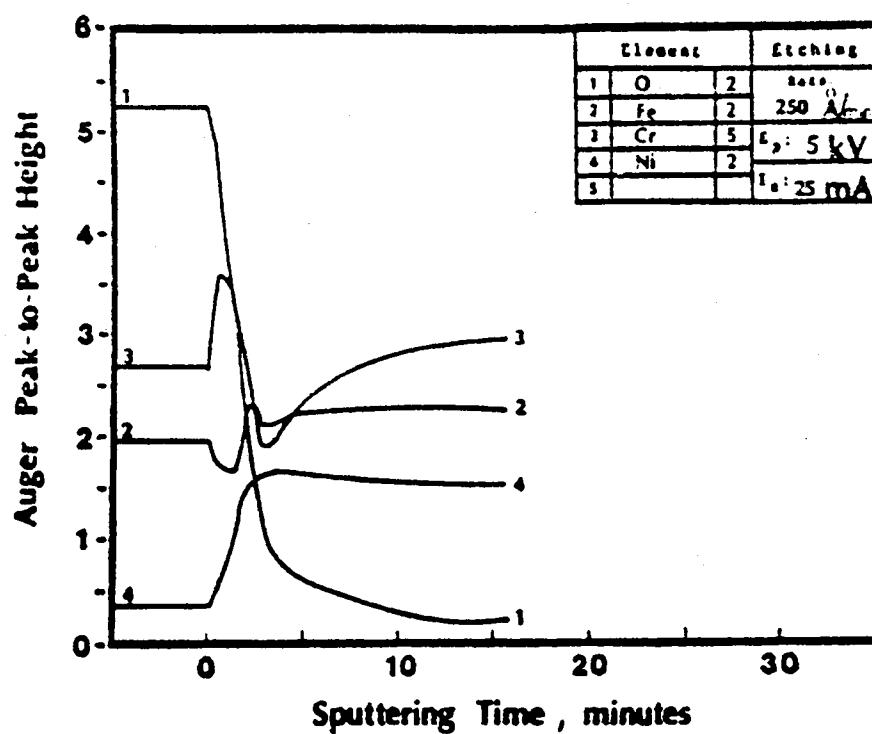


Figure 1-12. Auger sputter depth profile of the heat tint oxide on an AL 904L alloy sample. The peak temperature on the heat tinted surface during welding was 522°C.

chromium enrichment in the oxide was proportional to the chromium depletion in the base metal. The Cr depletion in the base metal would be susceptible to preferential corrosion attack should localized spalling or cracking of the chromium-enriched surface film occur. Turner applied the theories of surface oxidation and substrate diffusion to explain the chromium depletion in both the oxide and base metal. However, the reason for the chromium enrichment in the profile remained unclear. In both studies, the chromium oxide and the chromium metal were unable to be distinguished in the depth profiles. Therefore, defining the oxide thickness was always difficult. In addition, iron and nickel data were not accounted for in the data explanations. As a result, it is incomplete to characterize the oxide without taking into account the presence of iron and nickel oxides, which were also present in the weld oxide.

Surface treatments to reduce heat tint effects on the corrosion resistance of austenitic stainless steels were summarized by Tuthill⁶⁸ and Kearns.⁶⁹ Passivation, pickling, electrochemical cleaning, and mechanical cleaning were used mainly for stainless steel surface treatments. Effective passivation treatments were obtained using nitric-acid-based solutions. To remove heat tint, embedded iron particles, heat treating scale, and other surface defects produced during fabrication, pickling was used with nitric-hydrofluoric-based solutions. Electrochemical cleaning had the same effect as pickling. It removed imperfections from stainless steel surfaces. Mechanical cleaning included abrasive blasting, brushing, and grinding. These mechanical cleaning processes should be performed carefully; otherwise, iron contaminants and a rough cold-worked surface would

lead to crevice corrosion. Better performance was achieved using mechanical cleaning, followed by pickling.

1.7. Summary

Based on this literature review, it is seen that bacteria are capable of exacerbating service environments causing materials to be less corrosion resistant. Microbially influenced corrosion is associated not only with the service environment but also with the materials themselves. Studies of microbially influenced environments can not give a satisfactory explanation for the lower corrosion resistance of carbon steels and stainless steels. For instance, in stainless steel, most of MIC cases indicate that the corrosion occurs at welds rather than base metal. Therefore, studies on material resistance to MIC are as important as studies of the environments altered by bacteria. This proposal began with the idea that real situations may be simulated to generate MIC in the field and in the laboratory in order to differentiate the resistance to microbial corrosion of various stainless steel weldments. The specimens, the bacteria, and the experimental conditions were carefully considered in an attempt to simulate real world exposure. An experimental procedure was employed to simulate a hydrostatic test procedure, wherein a slow solution flow was provided into the corrosion cell for a short period of time, then the system was exposed to stagnant water for three months. The field site was selected on the basis of previous occurrences of MIC associated with untreated well water at the Palo Verde Nuclear Generating Station near Phoenix, Arizona.

CHAPTER 2

EXPERIMENTAL PROCEDURES

The objective of this research is to study microbially influenced corrosion of austenitic stainless steel weldments in fresh water systems. Therefore, the initial experiments were focused on investigations of the microbial effects on corrosion resistance of the stainless steel weldments. As the research progressed, it was found that the corrosion had been occurring exclusively on the welding oxide region of the stainless steel weldments. As a result, the purposes of the experiments were directed to study the corrosion resistance of the various oxides produced on the stainless steel during welding. Finally, the surface analyses on the oxides were conducted using scanning electron microscopy, x-ray photoelectron spectroscopy, and Auger electron spectroscopy.

2.1. Stainless Steel Weldments

The stainless steel weldments to be tested in corrosion experiments were from 12-inch diameter, schedule 10, austenitic stainless steel pipes. Each pipe contained a circumferential weld. The pipe materials were 304L or 316L stainless steel and the filler materials were 308L or 316L stainless steel. There was a variety of combinations of the

welding parameters to give thirteen different stainless steel pipes which were designated by the pipe number.

2.1.1. Stainless Steel Pipes

The stainless steel pipes were welded by Douglas Bros. Company (Portland, ME) using Gas Tungsten Arc Welding (GTAW) on the root pass and Shielded Metal Arc Welding (SMAW) on the second pass. The joint ends, as sketched in Figure 2-1, were prepared by machining. The shield backing was made by baffling on each pipe end and purging the ID root with argon gas. The pipe was manually welded in the horizontal rolled position. The filler wire with diameter of 3/32 or 1/8 inch was added during welding. The arc and the travel speed were adjusted to fuse both sides of the weld joint and the filler metal to give an ID root with 1/32 to 1/16 inch reinforcement. The subsequent pass was made by SMAW using commercial filler metals. The interpass temperature was maintained approximately at 350°F and also the internal purge was remained during the subsequent welding.

The thirteen pipes, designated by their numbers (without No. 10), are listed in Table 2-1. The No. 1 through No. 5 pipes were welded with the above welding procedure specification using 304L as the pipe material and 308L as the filler metal. A 3/32 inch gap between the joint ends was placed to give a full penetration of the joint so that a sound weld was produced. Pipe No. 1 having an as-welded surface, on which no treatment was given after the welding, refers to a base case of the 304L stainless steel pipe (Figure 2-2).

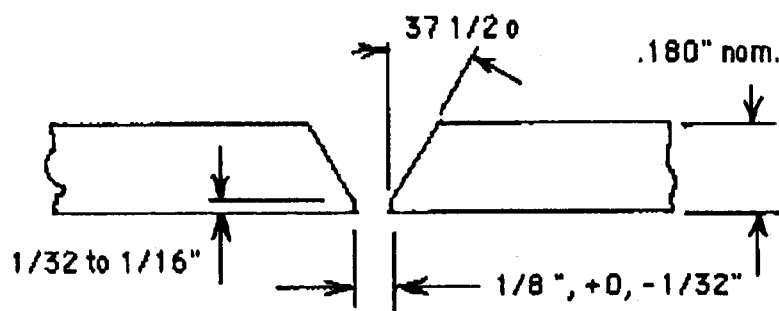


Figure 1. Joint design for 12 in. schedule
10 stainless steel pipe

Figure 2-1. Joint design for 12 inch, schedule 10 stainless steel pipe.

Table 2-1. The Stainless Steel Pipes and Their Welding Procedure Parameters.

PIPE NUMBER	PIPE MATERIAL	FILLER MATERIAL	GAP (INCH)	PENETRATION	TREATMENT	REMARKS
1	304L	308L	3/32	Full	None	Reference
2	304L	308L	3/32	Full	Pickled	Surface studies
3	304L	308L	3/32	Full	Electropolished	Surface studies
4	304L	308L	3/32	Full	SA+WQ+Pickled	Effect of soln. anneal
5	304L	308L	3/32	Full	Ground	Surface studies
6	304L	316L	3/32	Full	None	Filler metal evaluation
7	304L	308L	3/32	Full	Purge rem. aft. RP	Surface studies
8	304L	None	None	Full	Fuse root pass	Surface studies
9	304L	None	None	Incomplete	None	Crevice evaluation
11	316L	316L	3/32	Full	None	Reference
12	316L	None	None	Full	Fuse root pass	Surface studies
13	316L	None	None	Incomplete	None	Crevice evaluation
14	316L	316L	3/32	Full	Purge rem. aft. RP	Surface studies

Pipe No. 2 has a pickled ID surface and pipe No. 3 has an electropolished surface, both prepared for surface studies. Pipe No. 4 was heat-treated to study effects of heat treatment after the welding. Pipe No. 5 has a ground surface, also for surface studies. Pipe No. 6 was welded using 304L as the pipe material and 316L as the filler metal to evaluate effects of filler material. Pipe No. 7 was welded according to the welding procedure specification for the root pass. However, the internal ID purge was removed for the second pass so that a heavy oxide was produced on the ID surface because of the heat from the subsequent pass. Pipe No. 8 and pipe No. 9 used 304L as the pipe material and were welded without the root gap and without the filler metal. Pipe No. 8 has a full penetration weld produced by fusing the root pass. In contrast, pipe No. 9 has an incomplete penetration weld. As a result, an artificial crevice geometry was created on the ID surface of the pipe. Pipes No. 11 through pipe No. 14 are the 316L stainless steel pipes. Pipe No. 11 was welded using 316L as the pipe material and 316L as the filler metal. Once again, this weld refers to a base case of the 316L stainless steel pipe. Pipes No. 12 and No. 13 have similarity with pipes No. 8 and No. 9, wherein a crevice was formed on the ID surface of pipe No. 13. Pipe No. 14 was welded with the removal of the ID purge after the root pass, resulting in thick oxide formation on the ID surface of the pipe.

2.1.2. Corrosion Test Coupons

Corrosion test coupons of the stainless steel weldments were sectioned from the circumferential pipe welds into a size of 2.5 inch long and 1 inch wide. The test coupons

were to be mounted into a corrosion cell such that electrochemical corrosion measurements could be made during exposure to microbial environments. Thus, some necessary means were adopted to isolate electrical contacts necessary for the electrochemical measurements from the corrosion environment. Specifically, electrical contact was made on the back side of each coupon (pipe OD surface). Each coupon was coated with Amercoat 90 epoxy (Ameron, Brea, CA) except for an exposed window on the test surface (pipe weld ID surface). As illustrated in Figure 2-3, the window of material exposed to the electrolyte contained all weldment regions — base metal (region not modified by welding), heat-affected zone (region not melted but modified microstructurally by welding), fusion zone (region melted by welding), and heat-tint area (surface area covered by visible welding oxide). The original ID surface of the pipe was carefully preserved during the preparation of the corrosion test coupons so that the as-fabricated surface was maintained for corrosion studies.

Coupon No. 1 (from pipe No. 1) prior to corrosion tests is shown in Figure 2-4. As mentioned in the previous section, this as-welded coupon represents a reference case for the 304L stainless steel weldments in this whole research study. It is seen that the welding oxide is evident even though the pipe ID surface and the melting pool were protected from oxidation by argon shielding gas, indicating that it is very difficult to achieve an ideal surface protection during welding on an industrial production scale. The oxide region or heat-tint area covers the fusion and heat-affected zones and extends into

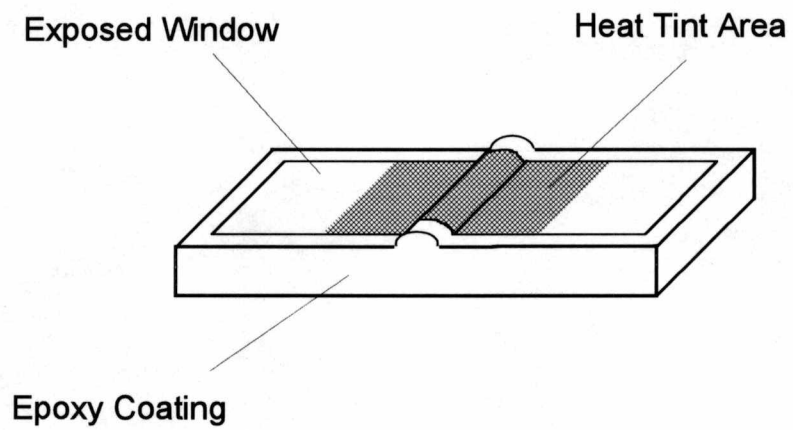


Figure 2-3. The corrosion test coupon of the stainless steel weldment sectioned from the circumferential pipe weld.



Figure 2-4. Coupon No. 1 having an as-welded surface prior to corrosion test.

the base-metal. Coupon No. 2, shown in Figure 2-5, had been pickled according to the ASTM 380 specification for stainless steel pipe, i.e., 2% HF + 10% HNO₃ + H₂O for 15 mins at 110°F. Coupon No. 3 (Figure 2-6) was electropolished by Fin-Tech Inc. (Houston, TX). Both these coupons (Figures 2-5 and 2-6) have experienced a chemical process to remove the welding oxide. Coupon No. 4 was solution annealed at 1900°F for 1 hour and then water quenched to room temperature. It was found that even though the coupon was capsulized into a vacuum quartz tube and then subjected to the heat treatment, an oxide scale still was formed during the water quench (wherein the quartz tube was fractured). Consequently, the coupon was annealed in air, water quenched, and then pickled to remove the oxide scale formed during the heat treatment. Coupon No. 5 (Figure 2-7) was ground using a portable polishing wheel to remove the weld reinforcement as well as the welding oxide. Coupon No. 7, as shown in Figure 2-8, exhibits a heavy oxide scale as a result of the purge removal after the root pass. Coupon No. 9 (Figure 2-9) reveals a crevice geometry on the ID surface because of the incomplete penetration weld. The rest of the coupons had a similar appearance to one of the above descriptions.

2.2. Microbially Influenced Corrosion Tests

The microbially influenced corrosion tests were divided into two parts: Tennessee River water laboratory tests and Arizona ground water field tests. The laboratory tests mimicked a Tennessee River fresh water system which had caused MIC attack in many

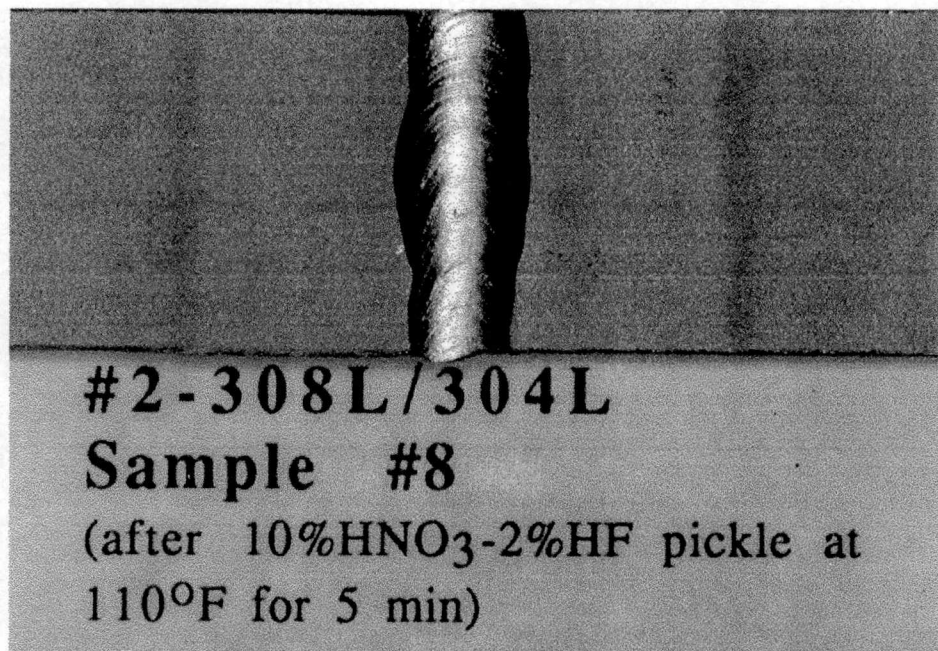


Figure 2-5. Coupon No. 2 having a pickled surface prior to corrosion test.

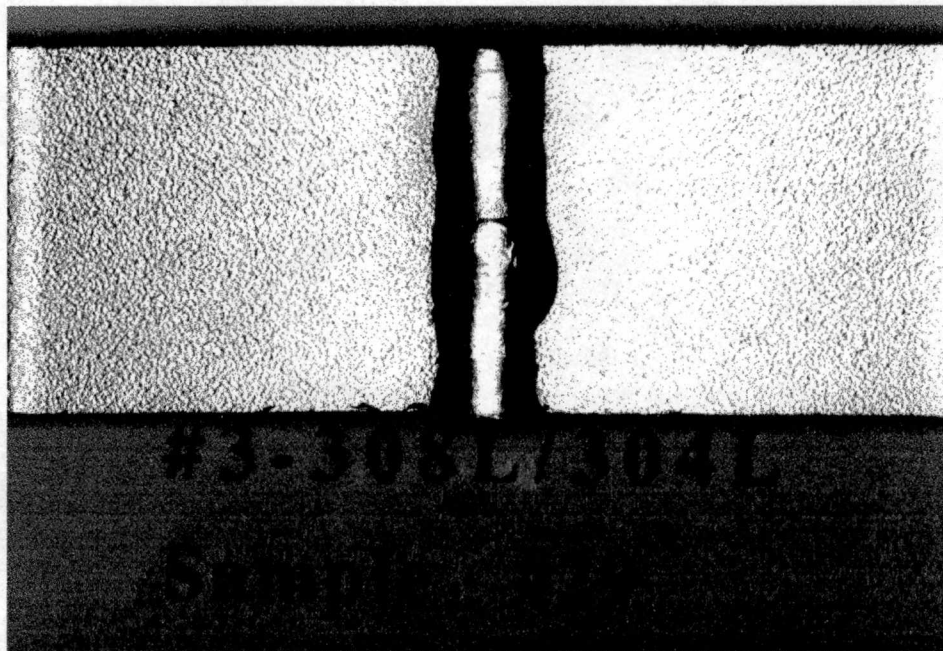


Figure 2-6. Coupon No. 3 having an electropolished surface prior to corrosion test.

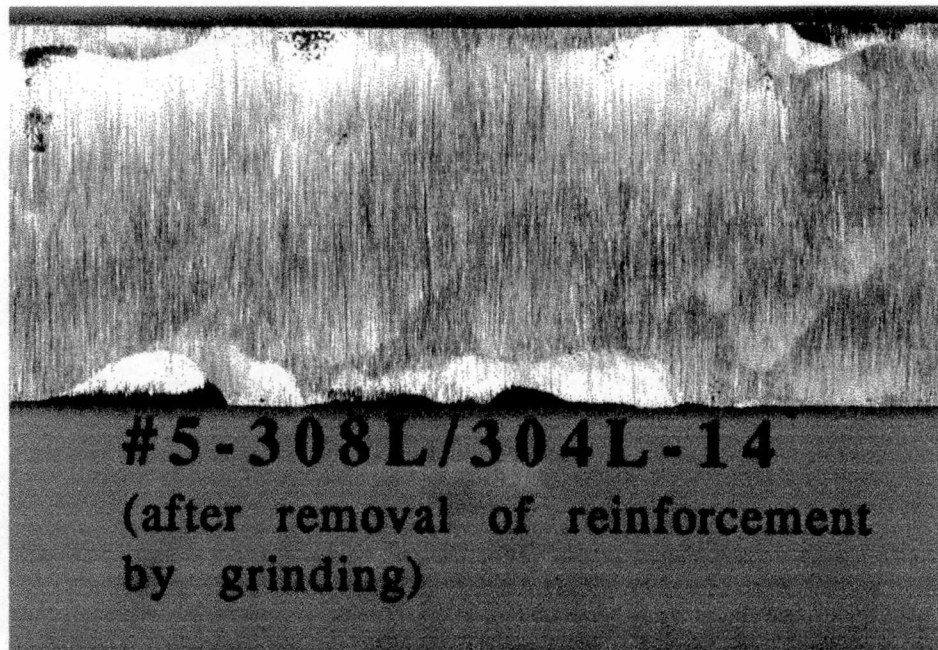


Figure 2-7. Coupon No. 5 having a ground surface prior to corrosion test.

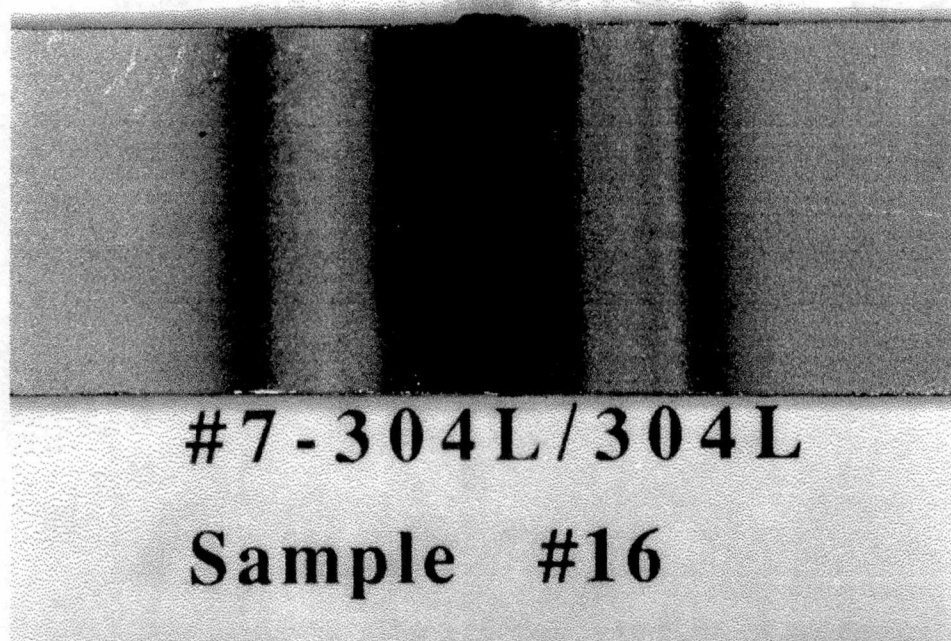


Figure 2-8. Coupon No. 7 having a heavy oxide surface prior to corrosion test.

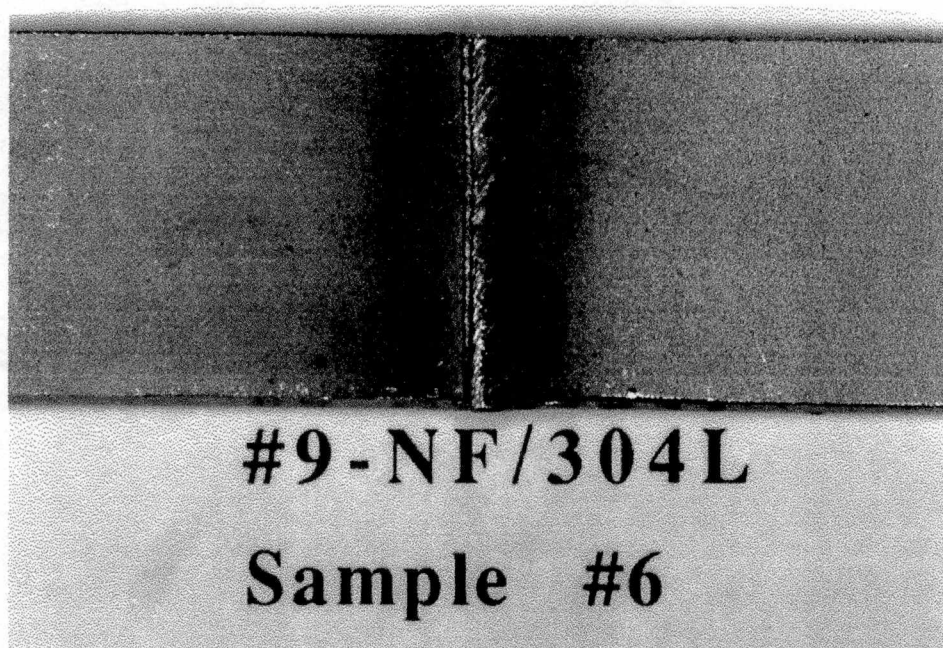


Figure 2-9. Coupon No. 9 having a crevice surface prior to corrosion test.

Tennessee Valley Authority power plants. The field tests were conducted at the Palo Verde Nuclear Generating Station near Phoenix, Arizona, which had experienced MIC occurrences associated with untreated ground water.

2.2.1. Tennessee River Water Laboratory Testing

The laboratory tests used a synthetic Tennessee River water, a consortium of ten bacteria strains, and a specific experimental procedure. Based on reported MIC case histories, a procedure in which MIC was most likely to occur was selected to simulate a process of an industrial piping system experiencing a hydrostatic test following a stagnant water exposure. The corrosion behaviors of the stainless steel weldments and the bacterial activities were monitored electrochemically during exposure. Finally, the results of the corrosion data and bacteria counts were evaluated on each of the weldments.

2.2.1.1. MIC Experimental Setup

A experimental setup (Figure 2-10) including a corrosion cell, a solution supply system, and an electrochemical measurement system, was designed for the MIC laboratory tests. The corrosion cell having dimensions of 2 x 2 x 48 inches was fabricated from Plexiglas. Thirteen corrosion coupons with ID weld surfaces exposed were mounted on the bottom of the cell and sealed with silicone. The solution system consisted of the medium reservoirs, as well as a waste vessel, to provide continuous culture conditions for



Figure 2-10. Laboratory experimental setup showing corrosion cell, solution supply system, and electrochemical measurement system.

bacterial growth. Solution inlets were equally spaced along the length of the cell to obtain a good distribution of the nutrient supply. The solution overflowed through outlets at each end of the cell. Each specimen was provided with separate reference and counter electrodes for electrochemical measurements, shown in Figure 2-11. A platinum electrode was placed in the corrosion cell to provide the redox potential of the electrolyte. The test cell, including the test specimens, was ethylene-oxide-gas sterilized before the laboratory tests.

2.2.1.2. Microorganism Selection

All bacteria in the consortium were isolated from Tennessee Valley Authority (TVA) and Duke Power Company field sites at which MIC had been identified. The consortium, identified in Table 2-2, was cultured in the laboratory. It includes aerobic bacteria, facultatively anaerobic bacteria, as well as sulfate reducing bacteria. The aerobic and facultatively anaerobic bacteria were maintained in trypticase soy agar slants. The sulfate reducing bacteria were retained in anaerobic tubes filled with broth. The bacteria were transferred into trypticase soy broth before applying them into the corrosion cell.

2.2.1.3. Simulated Tennessee River Water

The base solution for the laboratory tests was prepared to simulate the components of Tennessee River water in light of TVA reports on river chemistry, as shown in

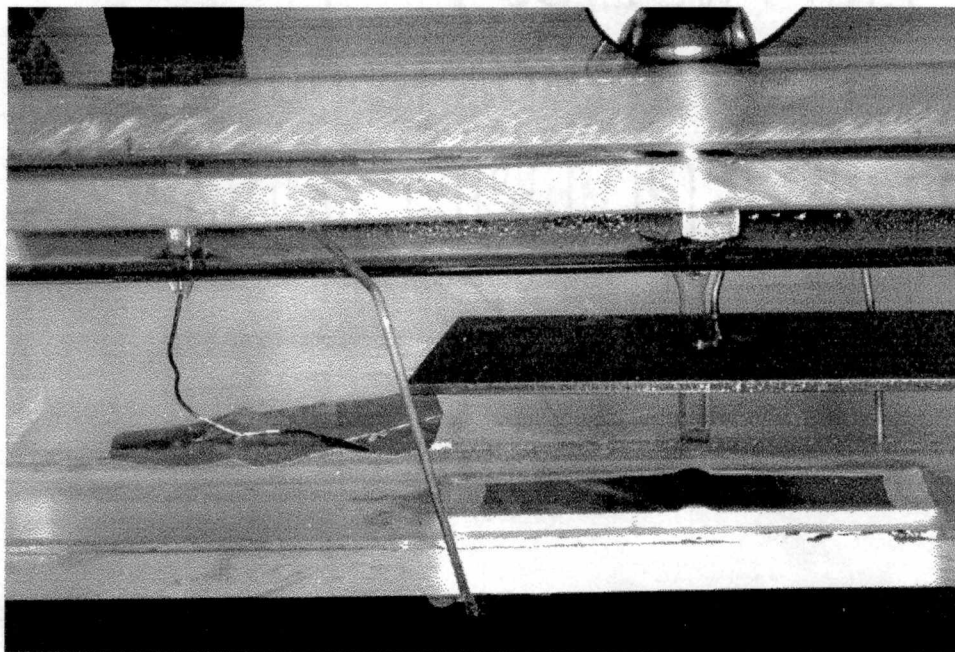


Figure 2-11. Close-up view of the corrosion cell showing the working electrode (stainless steel weldment), the counter electrode, the reference electrode, and the platinum electrode.

Table 2-2. Bacteria Consortium in the Laboratory Tests

TVA Organism	Duke Power Organism	SRB Organism
#261 <i>Acinetobacter</i> sp.	(A) <i>Bacillus megaterium</i>	<i>Desulfovibrio gigas</i>
#327 <i>Acinetobacter</i> sp.	(C) <i>Bacillus thuringiensis</i>	Duke Power SRB
#345 <i>Vibrio</i> sp.	(H) <i>Bacillus cereus</i>	
#347 <i>Pseudomonas</i> sp.		
A6F <i>Shigella</i>		

Table 2-3. It is seen that nutrients (sodium lactate, trypticase soy, and sodium succinate) were added to the synthetic water with the intent of increasing the bacterial aggressiveness while maintaining a basic fresh-water supply. The chloride concentration also was increased from approximately 10 ppm to 100 ppm with the intent of more closely simulating other fresh water systems. The solution, vessels, and tubing were autoclave-sterilized before each test.

2.2.1.4. Laboratory Test Procedure

Triplicate laboratory experiments lasting approximately 90 days were conducted in the microbial environment. The experiment began by filling the corrosion cell with the sterilized solution. The bacterial consortium was then inoculated into the corrosion cell. Then, a continuous nutrient flow was pumped into the corrosion cell at a 5% dilution rate for 14 days. After 14 days, the solution supply system was shut off and the specimens were maintained in a stagnant batch condition. During the exposure, the open circuit potentials (OCP) of the specimens were monitored and periodic electrochemical impedance spectroscopy (EIS) measurements were made. A laboratory control experiment was conducted under the same experimental conditions except that the bacterial consortium was not added to the base electrolyte. After each run of the tests, the specimens were photographed to characterize the corrosion surfaces.

Table 2-3. Basal Solution of the Laboratory Tests.

Composition	mg/L	30 L (g)
1. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	13.30	0.40
2. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	56.60	1.70
3. NH_4Cl	5.00	0.15
4. NaCl	115.00	3.46
5. KCl	0.17	0.005
6. KH_2PO_4	0.17	0.005
7. NaHCO_3 *	0.5	0.015
8. Sodium Lactate	0.06 ml	1.89 ml
9. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.27	0.0082
10. Trypticase Soy	1.00	0.03
11. Sodium Succinate	210.00	6.30
12. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.01	0.0004
pH=7.3 adjusted with HCl and NaOH		
* Postautoclave add No.7 plus trace element		
Each liter contains: 100 ppm chloride, 5.42 ppm Sulfate, 0.1 ppm Manganese, 0.002 ppm Iron, 53 ppm Organic Carbon (25% from Sodium Lactate, 75% from Sodium Succinate).		

Trace Element Solution SL7, 1 ml for 1 liter medium	
HCl, 25%	10 ml
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	1.5 g
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	190 mg
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	100 mg
$\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$	70 mg
H_3BO_3	62 mg
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	36 mg
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	24 mg
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	17 mg
Distilled Water	add 1 L
At first the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is covered with the concentrated HCl to dissolve insoluble iron (III) hydroxides, which are normally present in Fe (II) salts as oxidation products by air	

2.2.1.5. Post-Test Bacteria Counting

Biological scraping samples were collected from the surface of each specimen at the end of the bacterial run to obtain bacteria counts. The samples were injected into tubes containing a mineral salt buffer. A one-ml aliquot of each sample was preserved in 2.5% gluteraldehyde for Acridine Orange Direct Counts (AODC). AODC stains were made for each of the samples to determine total numbers of bacteria. A one-ml aliquot was serially diluted and spread plates were made using heterotrophic aerobic colony forming unit media to obtain viable numbers of aerobic bacteria.

2.2.2. Arizona Ground Water Field Testing

Field tests are generally more acceptable than laboratory tests in determining true behavior because they are directly applicable to service conditions. The field tests described below were conducted at the Palo Verde Nuclear Generating Station. OCP measurements were made during the exposure. The corrosion surfaces were characterized after the tests, and microbiological analyses were conducted.

2.2.2.1. Corrosion Experimental Setup

Two electrochemical cells, each having dimensions of 2 x 2 x 48 inches, were fabricated from Plexiglas, as shown in Figure 2-12. The duplicate cells were set up and

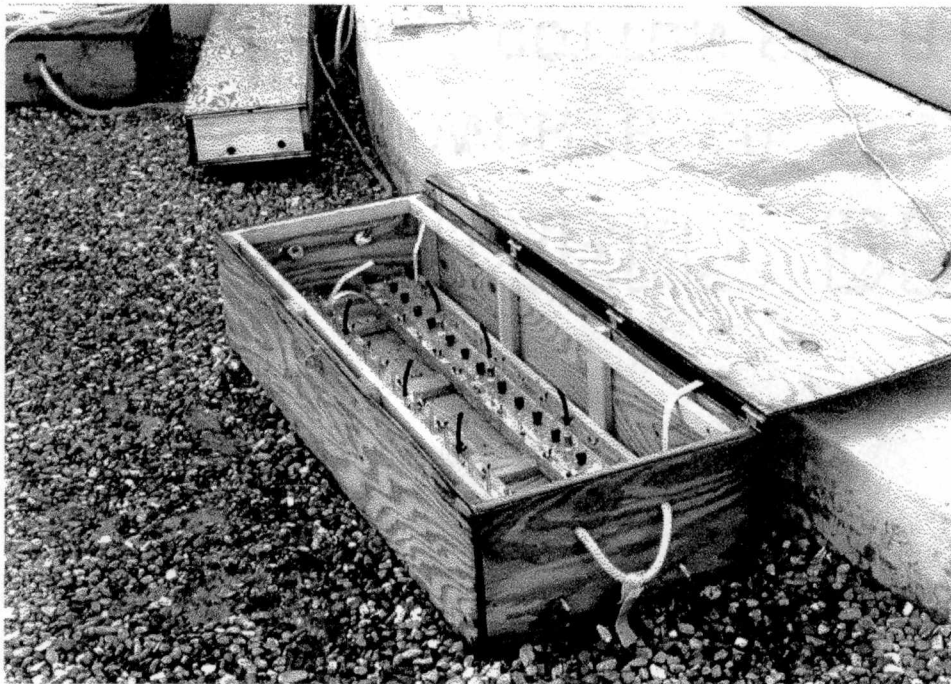


Figure 2-12. The experimental setup at the field site showing the two parallel corrosion cells in the wooden box.

run simultaneously. The thirteen specimens with ID weld surfaces face-up were mounted on the bottom of each cell with silicone sealant. Each specimen had a separate reference electrode holder for electrochemical measurements. A platinum electrode was placed in each cell to provide the redox potential of the water. The water inlet was located at one end of each cell and the outlet at the other in order to simulate a real pipe geometry. An on-line pressure regulator and a water filter of 50 μm pore size were placed before the inlet of the cells. Both cells were placed in a wooden box to eliminate sunlight so that algae growth would not occur.

2.2.2.2. Field Test Procedure

The coupons were exposed to the well water (pumped directly from the underground source) at the field site for 140 days, as shown in Figure 2-13. The temperature of the well water varied from 15 to 23°C. Chlorides were 126-635 ppm and oxygen was 1.0 ppm. Table 2-4 gives the inorganic chemical analysis of the water flowing through the test system. The volumetric flow rate was controlled by a needle valve at approximately 10 liters per hour, corresponding to a flow velocity of 1.08×10^{-3} meters per second (3.54×10^{-3} feet per second). Periodically, open circuit potential data were collected with a portable electrometer and a saturated Ag/AgCl reference electrode from all thirteen weldment coupons and the platinum electrode for each cell. At the end of the exposure, each coupon was photographed in the cell. Biological scraping samples were taken from typical corrosion coupons.



Figure 2-13. The field site at the Palo Verde Nuclear Generating Station near Phoenix, Arizona.

Table 2-4. Chemical Composition of the Well Water

Fluoride	6.9 ppm
Nitrates (as N)	2.0 ppm
Calcium	13 ppm
Chloride	226 ppm
Magnesium	6.3 ppm
Sodium	250 ppm
Sulfate	96 ppm
Hardness	58
TDS	740
Alkalinity	144
pH	8.1
Dissolved Oxygen	1.0 ppm

2.2.2.3. Microbiological Analyses

Efforts were made to search for the existence of bacterial colonization on the coupon surfaces after the exposure. Samples for scanning electron microscopy (SEM) observation were preserved with gluteraldehyde after exposure. They were dehydrated and critical-point dried in the laboratory. The first step in the SEM examination was accomplished using secondary electron imaging with part of the nodule removed from the corrosion coupon surface. The SEM specimen was coated with a 8-nm-thick film of gold-palladium. Under a 6 keV incident beam, the specimen charged. The energy of the incidence beam was reduced to 1 keV in an attempt to avoid charging. It was shown that even at the lower energy the specimen still appeared to be negatively charged. Examination also was conducted by backscatter electron imaging. Energy dispersive spectroscopy (EDS) data were collected at 10 keV from several areas of the specimen.

All microbiological tests were conducted on water samples taken directly from each of the test cells, and on samples taken from nodules found on the coupon surfaces. Nodules were scraped into tubes containing a mineral salt buffer, and then shaken to obtain an even distribution of microbial cells. A one-ml aliquot of each sample was preserved in 2.5% gluteraldehyde for Acridine Orange Direct Counts (AODC). One ml aliquots were then added to test tubes containing 9-ml of culture media for sulfate-reducing or sulfur-oxidizing bacteria. A dilution series was then carried out for each sample to determine the numbers of bacteria present.

2.2.2.3.1. Acridine Orange Direct Counts

AODC stains were made for each of the samples to determine total numbers of bacteria. AODC slides also were examined for evidence of iron bacteria of the species *Gallionella*, which can be tentatively identified by the presence of twisted inorganic stalks that are secreted by each cell.

2.2.2.3.2. Sulfate Reducing Bacteria

All samples were cultured anaerobically in American Petroleum Institute Sulfate Media to test for the presence of sulfate reducing bacteria. Samples were incubated at 30°C for one month. The reduction of sulfates to sulfides causes the tube contents to turn black and is read as a positive test result for SRB.

2.2.2.3.3. Sulfur Oxidizing Bacteria

All samples were cultured in a medium suitable for the detection of sulfur oxidizing bacteria of the species *Thiobacillus*. Samples were incubated at 30°C for one month. The presence of sulfur oxidizing bacteria was determined by turbidity, the precipitation of elemental sulfur, and a drop in the pH due to production of sulfuric acid.

2.2.2.3.4. pH Measurement

The pH of the water samples was checked with pH paper. Fluid was withdrawn from the interior of the nodules using a syringe with a small gauge needle in order to check the pH in the tubercles.

2.3. Advanced MIC and Crevice Corrosion Tests

The previous Tennessee River water laboratory tests and Arizona ground water field tests indicated that the aggressiveness of the corrosion environments and a crevice geometry caused by the welding oxide and the overlapping epoxy coating were associated with the test results. Therefore, some necessary adjustments in the Tennessee River water laboratory MIC tests were made and more tests regarding possible mechanisms were conducted. Finally, crevice corrosion tests were carried out using the Arizona ground water.

2.3.1. MIC Tests

The advanced MIC tests employed almost the same experimental setup as the one in the Tennessee River water laboratory test. A few changes were made to adapt the tests to new experimental conditions. A small beaker-type electrochemical cell was used to run the tests more efficiently (Figure 2-14). Each cell was able to contain two weldment

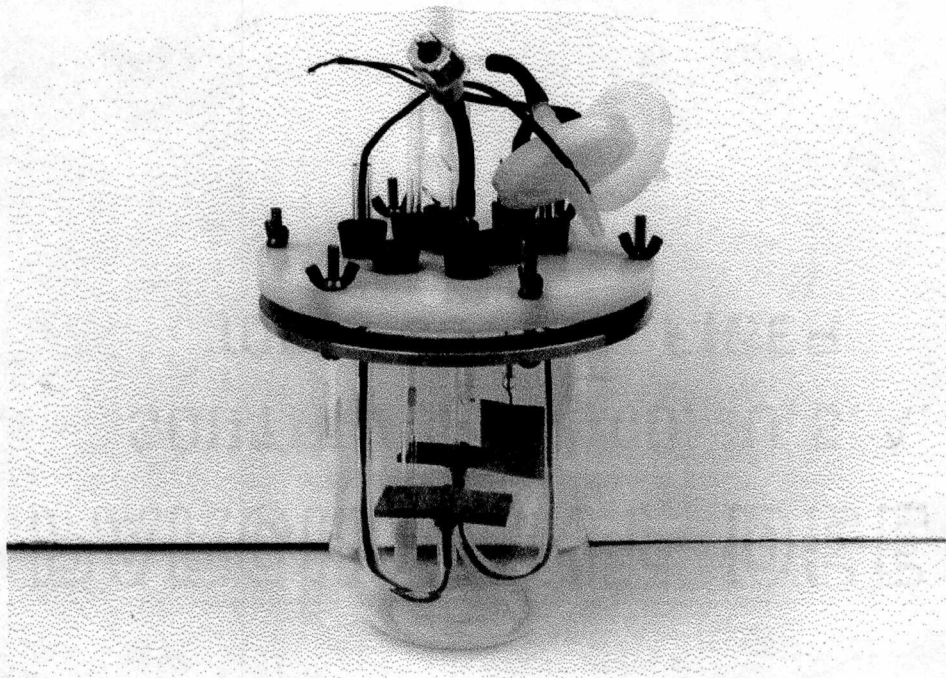


Figure 2-14. Corrosion cell for advanced MIC corrosion tests.

coupons, a necessary platinum electrode, and a reference electrode. Solution inlet and outlet as well as an air sparger were properly placed into the cell. Solution flow was pumped in and out with a controller so that a precise dilution rate of replenishment was reached. The cell was sealed using a Teflon lid with an o-ring and proper numbers of rubber stoppers. As a result, the cell was isolated from the laboratory-air environment and air was allowed into the cell only through a 0.2 μm air filter. Again, the cell was gas-sterilized before any test. The exposed window of the corrosion coupon also was changed in terms of the coating area. Only the edges of the corrosion coupon were covered by epoxy coating, rather than overlapping the coating onto the ID surface, so as to eliminate a possible crevice geometry. Later, it turned out that this coating method made a significant difference in the corrosion behavior of the stainless steel weldments. In the advanced MIC tests, only the as-welded and pickled specimens (304L/308L) were run because the welding oxide was determined to be mainly responsible for the observed corrosion behavior.

2.3.1.1. Adjusted MIC Testing

A few adjustments on the composition of the basal solution were made to increase the solution aggressiveness. The iron content in the solution was increased from 0.002 ppm to 0.1 ppm. The content of trypticase soy, a nutrient for general aerobic bacteria, was doubled to reach a level of 2 mg/L. Either iron bacteria *Gallionella*, or sulfur oxidizing bacteria *Thiobacillus*, both of which were known to cause corrosion problems,

was combined with the bacteria consortium to increase bacterial aggressiveness. A new bacteria inoculation procedure was also used such that after inoculating the bacteria into the corrosion cell, the solution supply was shut off for 24 hours, whereby the bacteria were allowed to adhere to the specimen surface, and then the solution flow was restored. As a result, a chance for bacteria attachment was granted and the detachment was minimized. A stabilized solution flow was maintained during the remaining exposure (two weeks) and more bacteria were inoculated during exposure if necessary. The open-circuit potential measurement was carried out throughout exposure. The following tests were conducted:

- (1) Specimen: two as-welded 304L/308L weldments.
Bacteria: the consortium.
Condition: one coupon at the water level, the other was totally immersed.
- (2) Specimen: two as-welded 304L/308L weldments.
Bacteria: the consortium + *Gallionella*.
Condition: none.
- (3) Specimen: two as-welded 304L/308L weldments.
Bacteria: the consortium + *Thiobacillus*.
Condition: none.
- (4) Specimen: four as-welded 304L/308L weldments.
Bacteria: the consortium.
Condition: imposed aeration.
- (5) Specimen: two as-welded 304L/308L weldments.
Bacteria: A6F single strain.
Condition: none.

2.3.1.2. Potentiostatic Constant-Potential Testing

Potentiostatic constant-potential tests were conducted on as-welded 304L/308L specimens at +500 mV (SHE) to examine the anodic current density responses with and without the bacteria addition. The experiments were started by monitoring the open-circuit corrosion potentials for approximately two days in the sterile control solution. For the bacterial run, the bacteria were inoculated into the test cell after 17 hours. A potential of +500 mV(SHE) was potentiostatically applied 48 hours after inoculation. For the control run, a potential of +500 mV (SHE) was applied after the first 48 hour exposure. The resulting anodic current densities were measured as a function of exposure time. After an overall exposure time of five days, the experiments were terminated and visual examinations of the specimens were conducted.

2.3.1.3. Anodic Polarization Testing

Anodic polarization measurements were made on the as-welded and pickled 304L/308L specimens in bacterial and control solutions. The experimental procedures followed those of the initial tests so that good growth of bacteria was assured before anodic polarization measurements were made. These anodic polarization tests were duplicated to attest corrosion behavior of the stainless steel weldments. Another specimen with an as-welded surface was pickled in 10% nitric plus 2% hydrofluoric acid at 110°F for 15 minutes (as in the initial tests) to remove the weld oxides. The passive film possibly

formed during the pickling treatment was removed by immersion in 10% hydrochloric acid for 10 minutes. Furthermore, the specimen was cathodically cleaned by applying a potential of -1200 mV versus the standard hydrogen electrode (SHE) for 10 minutes.

2.3.2. Control Tests

In control tests including chloride tests, flasks were used as the corrosion cells. The flask was sealed with a rubber stopper and aerated through the 0.2 μm airfilter. Consequently, the chance of having the cell contaminated was reduced to the minimum. To maintain the initial conditions of the corrosion coupon, all specimens with as-welded surfaces were coated with epoxy overlapping the test coupon surface; thus, the crevice geometry (if any) was retained.

2.3.2.1. Contamination Testing

Because there was concern regarding possible contamination of the initial control experiment, additional control experiments (no bacterial inoculation) were designed to test specimens over conditions ranging from the worst possible air-borne-contamination situation to the best control condition. The control tests were conducted under four different conditions:

- (1) The simulated Tennessee River water solution with nutrient additions and with the cell open to air and thereby subjected to air-borne contamination during the 90 day exposure.

- (2) The same solution and nutrient additions as in (1) but with the cell sterilized and isolated from the air environment (0.2 μm filter) under the same conditions as in the initial laboratory control tests.
- (3) The same arrangement as in (2) but with no nutrients added to the solution.
- (4) The same arrangement as in (3) but with a biocide (Kathon 886 MW, Rohm and Haas Co., Spring House, PA) added to the solution.

2.3.2.2. Chloride Testing

In order to evaluate chloride concentration effects, additional 96-day control experiments were conducted in the sterilized solution. The specimens employed were as-welded 304L/308L weldments with the crevice geometry associated with the epoxy overlapping the test surface. The test solutions were the simulated Tennessee River water containing 100 ppm chloride, 10 ppm chloride, and no chloride.

2.3.3. Crevice Testing

The UT and LaQue crevice-corrosion assemblies (to be described in next sections) were mounted in a test cell made from a 5-inch diameter PVC pipe. The test cell contained replicate UT creviced 304L/308L specimens, as well as replicate UT non-creviced 304L/308L control specimens, in both the as-welded and pickled conditions. Replicate LaQue creviced specimens of 304L and 316L base-metal plates also were placed in the test cell. The specimens were exposed to the Arizona ground water using most of the previous parameters in order to maintain the same test conditions as in the initial tests.

The tests were run for 148 days. After transferring the cell to the laboratory, the coupons were visually examined and photographed.

2.3.3.1. Crevice Assembly for Weldment

Current ASTM standard techniques for conducting crevice-corrosion tests on non-flat specimens, such as weldments with reinforcements, are not available. Therefore, a part of this study involved designing a special crevice-forming assembly which would allow the evaluation of the crevice-corrosion resistance of all areas in the non-flat weldment coupons, i.e., base metal, fusion zone, heat-affected zone and heat-tint area.

University of Tennessee (UT) crevice-corrosion assemblies were designed and fabricated for the weldment specimens, as shown in Figure 2-15. The assemblies utilized 3/8-inch diameter low-halide silicone rubber rods (GE RTV 664) which were formed by casting into polytetrafluoroethylene (PTFE) molds. The silicone rods were uniformly compressed over the length of the weldment coupon and held in place by bolted backing plates, with a torque of 0.23 m-N (2 in-lb) applied to each bolt. The assembly produced a crevice geometry by means of an inert material over all regions of the weldment specimen, including the weld reinforcement. The assembly also was modified to produce a "non-creviced" condition in the heat tint area. Short segments of silicone rod, 3/8-inch in length, were compressed at the top and bottom of each end of the coupon for support, touching only base metal, not the heat-tint area. Thus, no crevice was produced over the weld-modified surface region. The weldments selected for evaluation with the UT

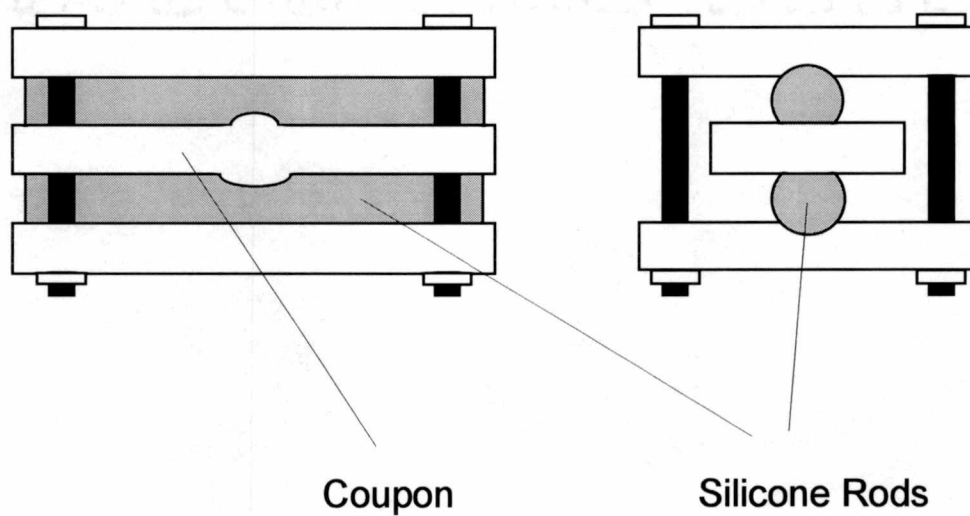


Figure 2-15. UT designed crevice test assembly for the stainless steel weldments.

crevice-corrosion assemblies were the as-welded 304L/308L coupons and the as-welded and pickled 304L/308L coupons.

2.3.3.2. Crevice Assembly for Base Metal

In addition, creviced, flat, base-metal specimens were fabricated for the study by Mr. Stanley Pikul at the LaQue Center for Corrosion Technology, Inc., Wrightsville Beach, NC. 304L and 316L sheets were employed and multiple crevice assemblies were used for forming the crevice sites. Each crevice assembly consisted of two nonmetallic segmented washers, with each washer having 20 grooves and plateaus (Anderson 20-land washers), compressed on either side of the specimen with a through-bolt / nut arrangement torqued at 8.6 m-N (75 ft-lb). Each of the 40 plateaus in contact with the metal surface provided a possible site for initiation of crevice corrosion. The specimens used in the test were 304L and 316L stainless steels.

2.4. Welding Oxide Tests

The oxide produced during welding was so crucial to this research investigation that it was necessary to extend the investigation further in order to examine the oxide characteristics associated with corrosion behaviors. In this study, the oxide characterized by its peak temperature was examined. Its corrosion behaviors in terms of pitting and crevice corrosion were investigated in different corrosion environments. The oxide

morphology, chemical composition, and the metal beneath the oxide were studied by microscopic microanalytical techniques.

2.4.1. Oxide Specimens

The oxide specimens used in the experiments included the as-welded 304L/308L weldment (as-received from pipe No. 1), the oxide on 304L by Gleeble simulation, and an as-welded 304L/308L weldment produced under a special welding procedure specification, which was designated the "heat tinted weldment specimen". In order to eliminate some factors influencing the accuracy of the microscopic analyses, the Gleeble specimens and the heat tinted weldment specimen were metallographically polished before the simulation or the actual welding was made.

2.4.1.1. The Gleeble Simulation

The Gleeble thermal simulation technique provides a practical means in the laboratory to reproduce the HAZ thermal and mechanical histories of a weld on a laboratory sample. The technique also provides a way to produce oxide on the sample associated with the thermal cycle. In this study, a Model 1500 Gleeble thermal mechanical simulator was used for preparing the welding oxide samples. The specimens were made from the pipe material (304L) which was used previously to produce the stainless steel weldments. The size of the specimen was 2.5 inch long, 0.5 inch wide, and 0.125 inch in

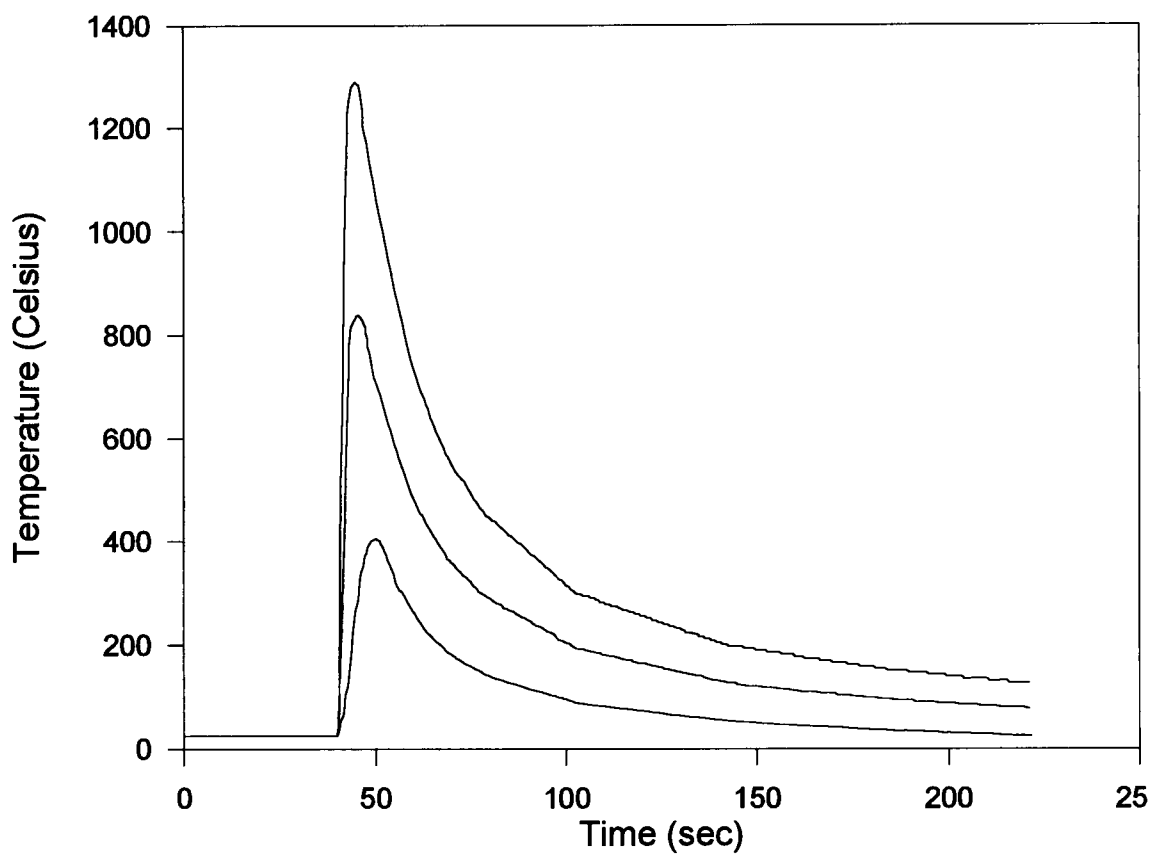


Figure 2-16. Thermal cycles with peak temperatures of 2400°F, 1600°F, and 800°F during the Gleeble simulation.

then filled by an internal process in the atom whereby an electron from a level E_Y falls into the core hole with the energy balance taken by a third electron from a level E_Z . This last electron, called an Auger electron, is then ejected from the atom with an energy E_A , given approximately by:

$$E_A = E_X - E_Y - E_Z$$

typically from 0 to 2 keV. Auger electrons from only the outermost atom layers of a solid survive to be ejected and measured in the spectrum. It is noted that the Auger energy is a function only of atomic energy levels, so that for each element in the Periodic table there is an unique set of Auger energies. Thus analysis of Auger energies immediately leads to elemental identification.

In x-ray photoelectron spectroscopy (XPS), a low energy characteristic x-ray is used as the exciting photon source. The energies of emitted electrons, called the photoelectrons, are given by:

$$E_K = h\nu - E_B$$

where E_K is the kinetic energy of the photoelectrons, $h\nu$ the incident photon energy, and E_B the electron binding energy. A series of photoelectron peaks from core levels and valence levels reflect the discrete binding energies of the electrons present in a solid. XPS has a significant advantage over AES in that non-equivalent atoms of the same element in a solid give rise to core level peaks with measurably different binding energies. This binding energy difference is called the chemical shift. The non-equivalence of atoms can arise in several ways: difference in formal oxidation state, difference in molecular environment, difference in lattice site and so on.

2.4.3.1. XPS and AES Data Analyses

XPS data were obtained using a Perkin Elmer PHI 5600 ESCA System. The data collection and analytical procedures are described in general as the following. A data survey was performed over an energy spectrum of 0-1200 eV. The photoelectron peaks in terms of their locations on the spectrum were identified by comparing to the standard handbook of XPS spectroscopy. Then, the spectral window was narrowed on each peak and the data collection sweep was increased to obtain an accurate location and a smooth curve from each peak. The Shirley background that each peak rode on was subtracted. As a result, the peak area was determined. Then, applying atomic sensitivity factors, the peak area was normalized to the corresponding atomic concentration. In case of overlapped peaks, the Asymmetric Gaussian-Lorentzian function was used to mimic each single peak and the overlapped curve was fitted by the two single peaks. Consequently, the two peaks were separated and the peak area was determined on each single peak. In obtaining the depth profile, the specimen surface was sputtered by ion beam gun and the above analytical procedures for one data cycle were repeated between each data cycle. As a result, atomic concentration as a function of the data cycle or depth was obtained.

AES data were obtained using a Perkin Elmer PHI 660 AES System. The AES data analysis procedures are similar to that in XPS analysis. Because the AES peak is small, traditionally, the AES peak is differentiated to give rise to a "peak to peak" height which corresponds to the spinodal points of the peak. The derivative peak height normalized by applying the atomic sensitivity factors leads to atomic concentration.

2.4.3.2. SEM Sample Preparation

The oxide morphology was examined by SEM on the specimen surface and cross section. The oxide on the cross section sample was coated with gold by sputtering. Then the sample was nickel-plated in the Watts solution for 20 mins with a plating current of 0.25 A. The sample was placed into a vacuum chamber for 30 mins to degas the hydrogen embedded in the nickel film during the plating before the sample was finally mounted into epoxy. The sample was polished to the metallographical finish.

2.4.3.3. XPS, AES, and SEM Tests List

XPS: As-welded 304L/308L weldment, heat-tinted 304L/308L weldment, the Gleeble specimens (2400°F, 1600°F, 800°F).

AES: As-welded 304L/308L weldment, heat-tinted 304L/308L weldment.

SEM: As-welded 304L/308L weldments (surface and cross section), heat-tinted 304L/308L weldment, the Gleeble specimens (2400°F, 1600°F, 800°F).

CHAPTER 3

RESULTS AND DISCUSSION

The results of the Tennessee River water laboratory tests and the Arizona ground water field tests will be first presented as a corrosion problem posed by the microbially influenced corrosion tests. Around this issue, the corrosion mechanisms were further studied and will be discussed by presentation of the results of the advanced microbially influenced corrosion tests and the crevice corrosion tests. Regardless of all the MIC results, which show a variety of detrimental effects on the corrosion, it seems that a major cause is traced back to an issue of the oxides formed in the welding process. Therefore, the results of microscopic analyses on the oxides will be introduced to devise plausible explanations for the corrosion causes.

3.1. Tennessee River Water Laboratory Tests

Three bacteria runs (with bacteria inoculation) and one control run (without bacteria inoculation) were conducted in the Tennessee River water laboratory tests. Herein, only the results from the third bacterial and control runs are described because of similarities of the test results in the three bacterial runs. Also, owing to a great deal of corrosion results, only typical specimens are selected to illustrate the facts which represent

the generality of all specimens. For the purpose of comparison, the data in the bacteria and the control runs are always presented simultaneously.

3.1.1. Open-Circuit Potential

Open-circuit potentials (OCP) of the specimens (#1 304L/308L with the as-welded surfaces) as a function of the exposure time, in the bacterial and the control solutions, respectively, are illustrated in Figure 3-1. For the reason that the platinum potential usually indicates the redox potential of a solution, open-circuit potentials of the platinum electrodes are also given in Figure 3-1. The solid bold lines represent the OCPs from the corrosion specimens, and the solid fine lines represent the platinum electrodes. The OCPs of specimens #7 which had a heavy oxide surface due to the shielding gas removal after the root pass, are shown in Figure 3-2. The OCPs of specimens #9 which had a crevice on the root due to the incomplete penetration, are depicted in Figure 3-3. The above three specimens are typical examples with the as-welded oxides on their surfaces. When the oxides were stripped by a chemical means (#2 304L/308L, pickled), an electrochemical means (#3 304L/308L, electropolished), and a mechanical means (#5 304L/308L, ground), the OCPs of the specimens are illustrated in Figures 3-4, 3-5, 3-6, respectively. The results of the OCP measurements exhibit two distinct potential profiles, regardless of the presence of the welding oxides. In the bacterial solution, the potential decreased shortly after the bacteria inoculation, retained the low potential as long as the solution supply was maintained, and then increased to high potential after the solution supply

2.4.2. Corrosion Tests

2.4.2.1. Crevice Corrosion Testing

Crevice corrosion tests using the UT designed crevice assembly to form the crevice geometry were conducted in the bacterial and control solutions. The Gleeble specimens were subjected to the crevice tests. The experimental procedures were in accord with those in the advanced MIC tests, in which the total exposure was about two weeks. The open-circuit potentials were measured throughout the exposures. The specimens were examined after the tests by visual observation.

2.4.2.2. Pitting Corrosion Testing

Pitting corrosion tests were conducted using the ASTM G-48 specification. The Gleeble specimens and the heat-tint specimen were tested in 6% FeCl₃ solution at room temperature for 24 hours. After the tests, the specimens were evaluated visually and the corrosion surfaces were photographed.

2.4.3. XPS, AES, and SEM Examinations

The principle of the Auger electron spectroscopy (AES) technique is that the sample is bombarded by an electron beam of 1-10 keV energy and this ejects core electrons from a level E_X in atoms in a region of the sample up to 1 μm or so deep. The core hole is

thickness. The specimen surface on which the oxide would be produced was metallographically polished. Thermal cycles with an energy input of 70 kJ/in were selected to conduct the simulation tests. The peak temperatures of the thermal cycles were 2400°F (1315°C), 1600°F (871°C), and 800°F (426°C), respectively. The tests were conducted in air. As a result, an oxygen saturated atmosphere was applied to produce the welding oxide on the specimens. The actual thermal cycles with the peak temperature of 2400°F (1315°C), 1600°F (871°C), and 800°F (426°C), are illustrated in Figure 2-16.

2.4.1.2. The Heat-Tint Specimen Prepared by GTAW

An actual welding specimen was made to produce the oxide on 304L stainless steel. Again, the pipe material (304L) was chosen for comparison with the Gleeble specimens. Two plates sized 2 x 4 x 0.125 inch were prepared for making the subsequent butt-weld. The surfaces of the plates were metallographically polished before welding. The first pass was made using GTAW with a complete argon gas backing. Then, the root weld surface appeared shiny with no evidence of oxidation. The argon gas backing was removed when the second pass was made using SMAW. As a result, the welding oxide was produced on the root weld surface owing to the heat made by the second pass. The welding environment was similar to that in the Gleeble simulation in terms of the saturated oxygen atmosphere. The oxide showed the discoloration (dark gray to straw color) on the HAZ surface.

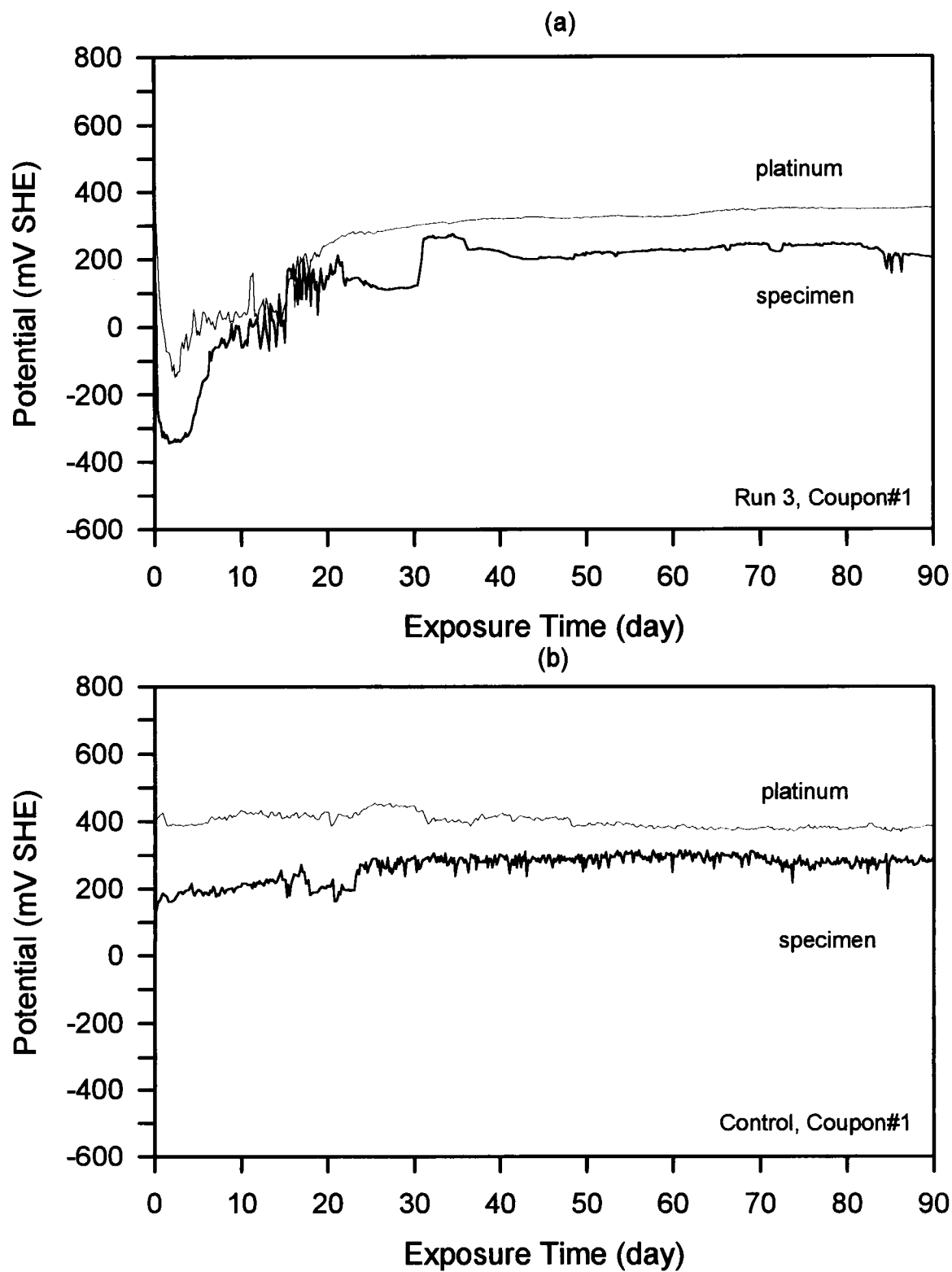


Figure 3-1. Open-circuit potentials of 304L/308L, no treatment, as a function of the exposure time, (a) Coupon #1 in Run 3, (b) Coupon #1 in Control Run.

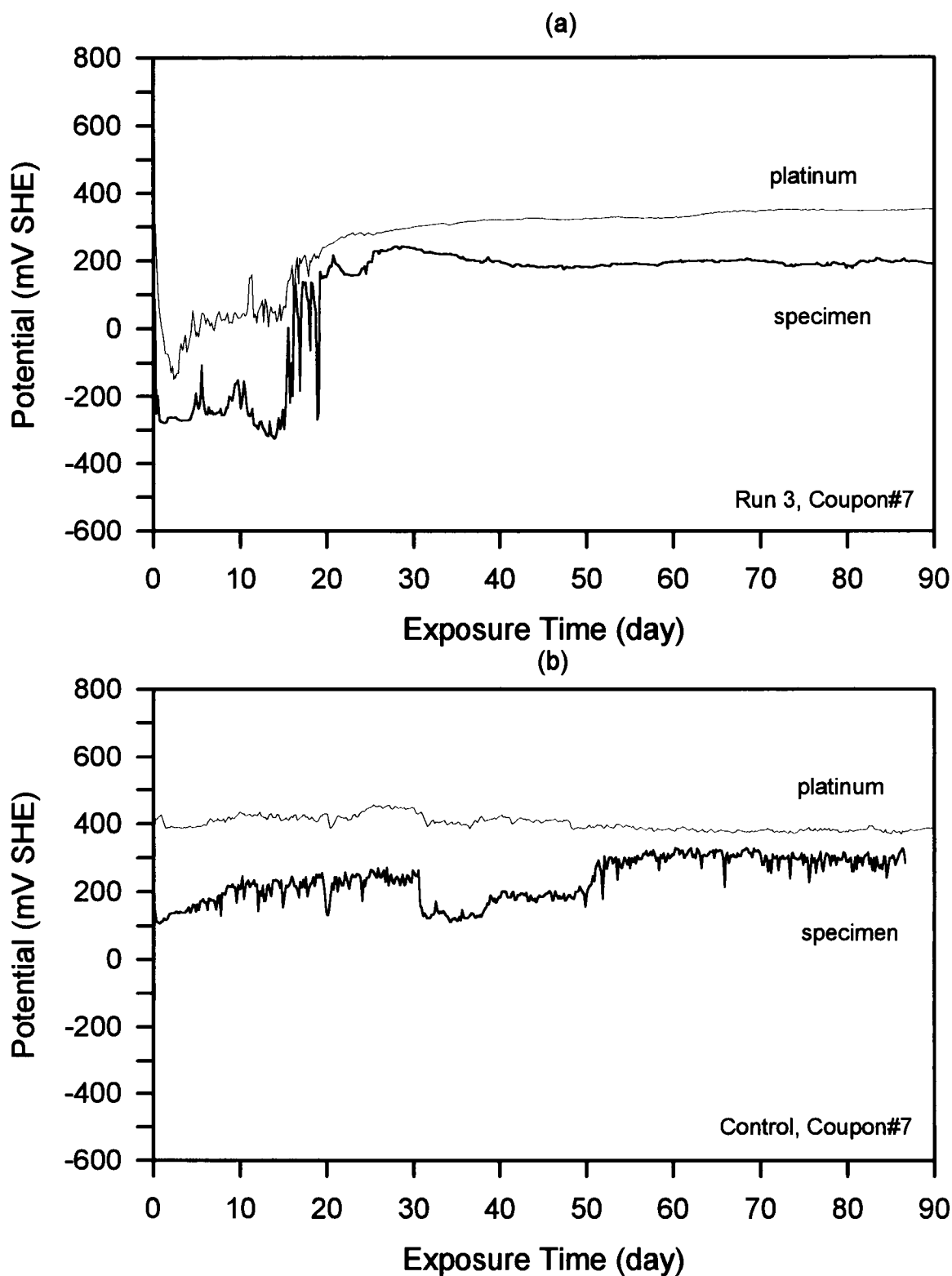


Figure 3-2. Open-circuit potentials of 304L/308L, purge rem. af. RP, as a function of the exposure time, (a) Coupon #7 in Run 3, (b) Coupon #7 in Control Run.

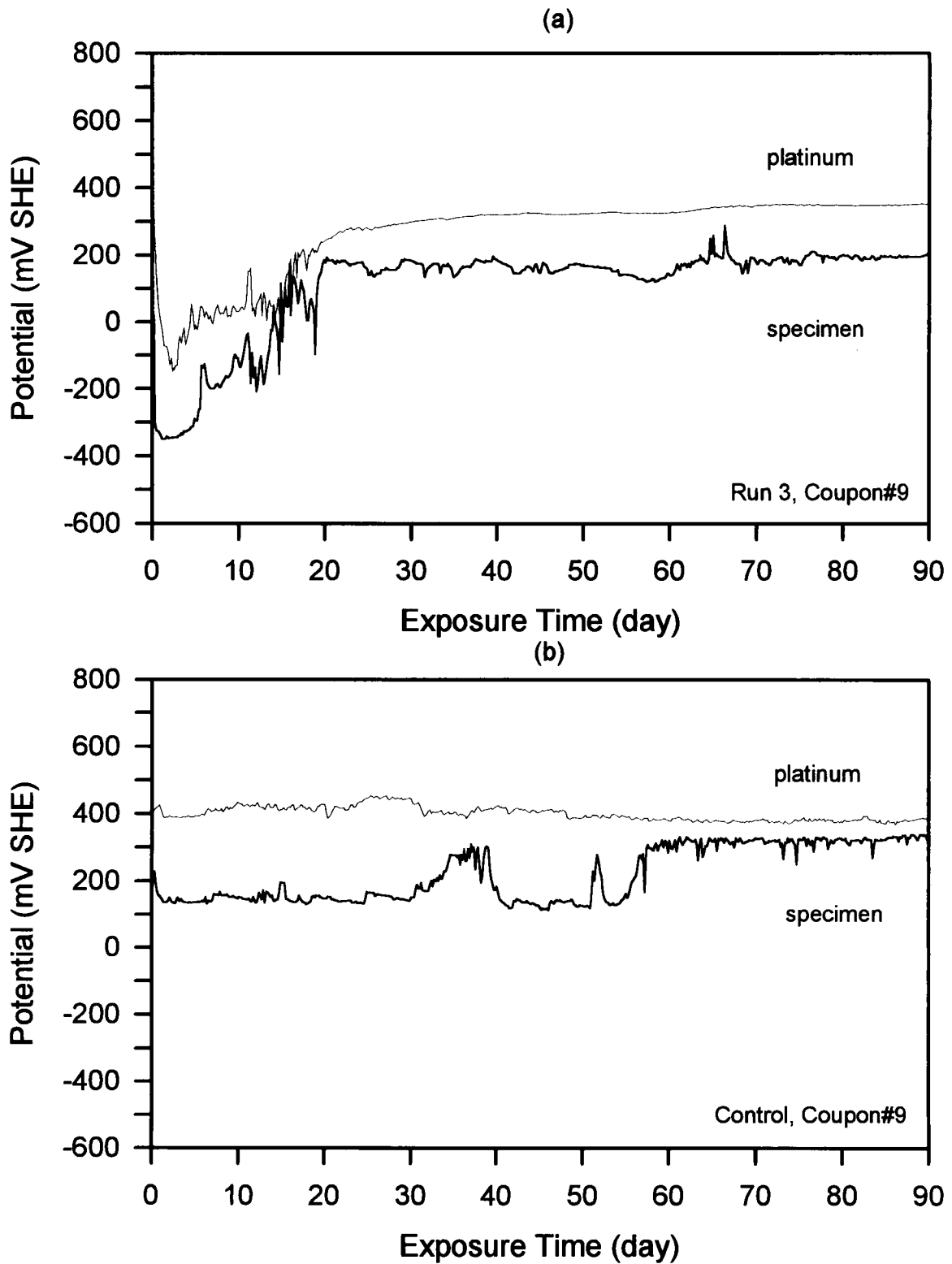


Figure 3-3. Open-circuit potentials of 304L/None, incomplete pene., as a function of the exposure time, (a) Coupon #9 in Run 3, (b) Coupon #9 in Control Run.

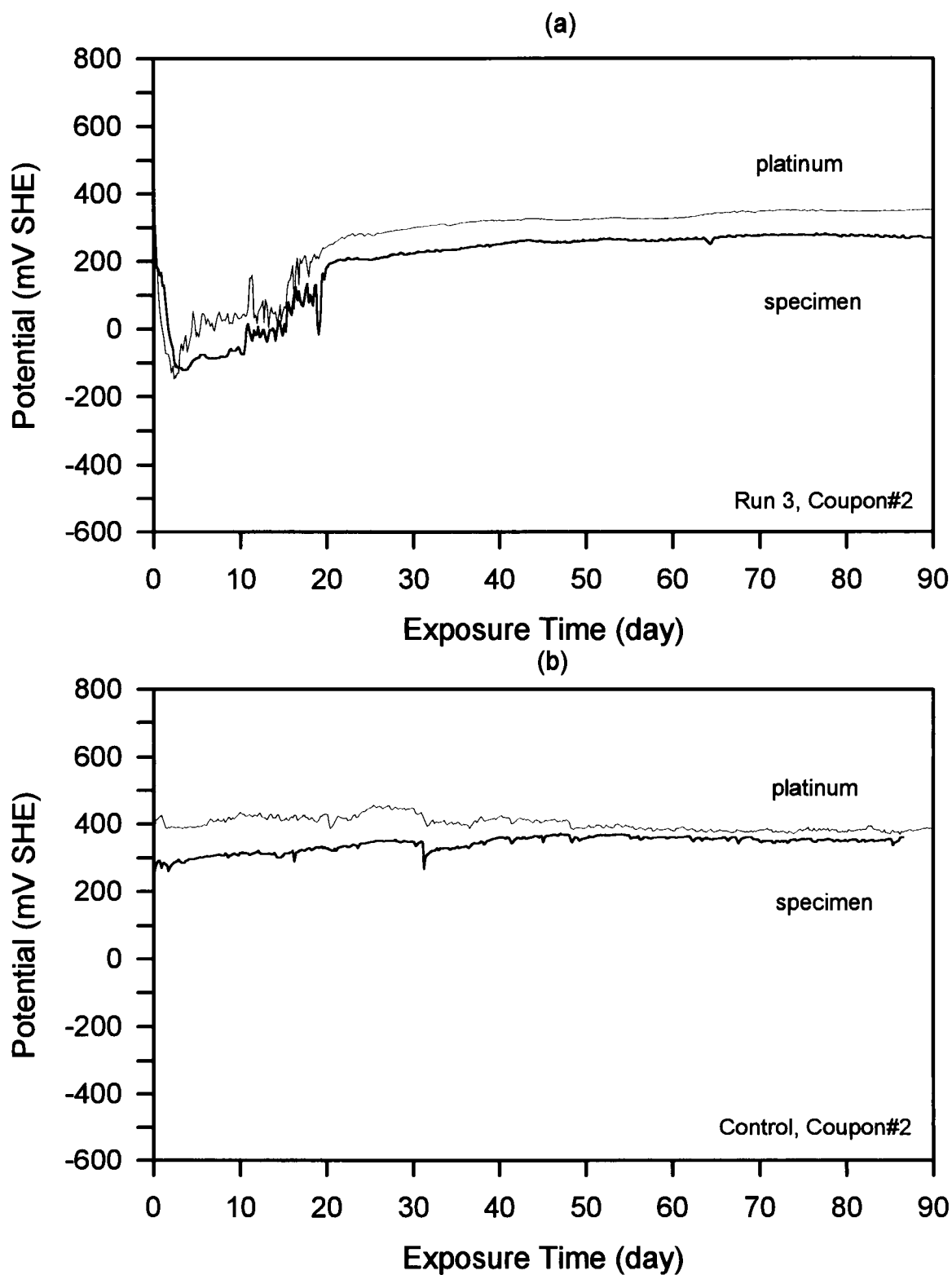


Figure 3-4. Open-circuit potentials of 304L/308L, pickled, as a function of the exposure time, (a) Coupon #2 in Run 3, (b) Coupon #2 in Control Run.

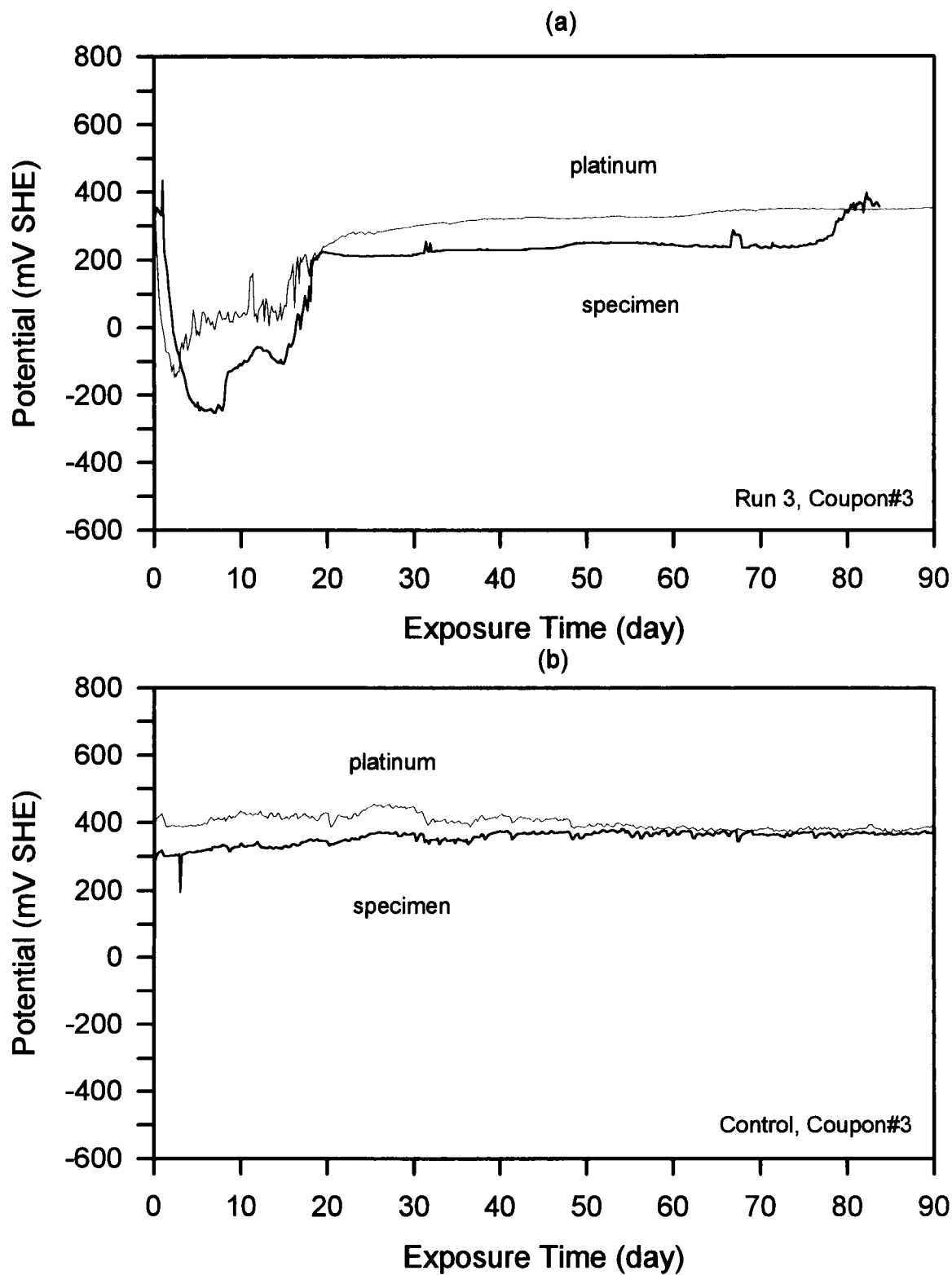


Figure 3-5. Open-circuit potentials of 304L/308L, electropolished, as a function of the exposure time, (a) Coupon #3 in Run 3, (b) Coupon #3 in Control Run.

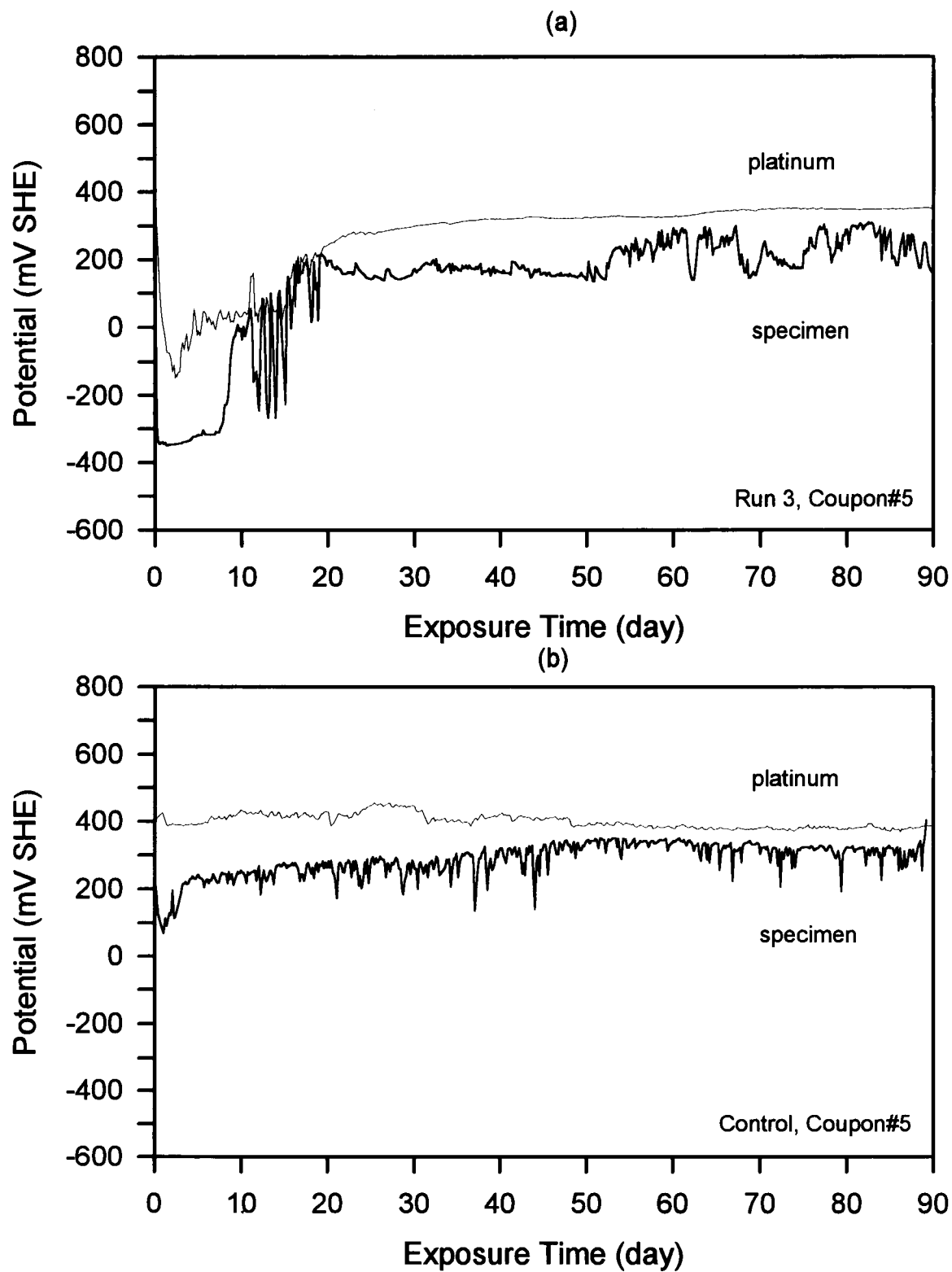


Figure 3-6. Open-circuit potentials of 304L/308L, ground, as a function of the exposure time, (a) Coupon #5 in Run 3, (b) Coupon #5 in Control Run.

was stopped. In the control solution, the potential remained at a fairly constant potential throughout the exposure. This was also true for the platinum electrodes.

The OCP data for the bacterial solution show significant differences relative to that for the control solution. For the bacterial solution, it is believed that the decrease in OCP to -250 mV(SHE) at the beginning of the bacterial exposure was caused by rapid growth resulting in a high number of bacteria.^{70,71} The bacteria possibly consumed a significant amount of oxygen and create a deoxygenated state in the bulk solution. The system then reached steady-state conditions wherein the solution flow rate and, consequently, the nutrient replacement rate, were insufficient to maintain the initial surge in bacterial activity. As a result, the number and activity of bacteria decreased and the OCP increased somewhat. When the nutrient supply was cut-off after 14 days, so that the test cell became completely stagnant, the OCP increased to +200 mV (SHE) and remained at this value until the end of the exposure. The initial decrease and subsequent increase in the OCP was not observed during the sterilized control solution run. Therefore, the significant differences in OCP are attributed to the bacterial activity reflected in the OCP values which are negative on the SHE scale with a sufficient nutrient level and positive when there is insufficient or no nutrient supply. It is known that bacteria are able to alter environments due to their metabolic processes by which local cathodic reactions are changed. Thus, it is not surprising that the bacteria caused a significant depletion of the dissolved oxygen during the initial exposure. Once the solution supply was stopped, the bacteria did not consume as much oxygen as they did when the nutrient was more

available. Consequently, the oxygen diffused back into the bulk solution and the OCPs were restored to the positive values.

3.1.2. Electrochemical Impedance Spectroscopy

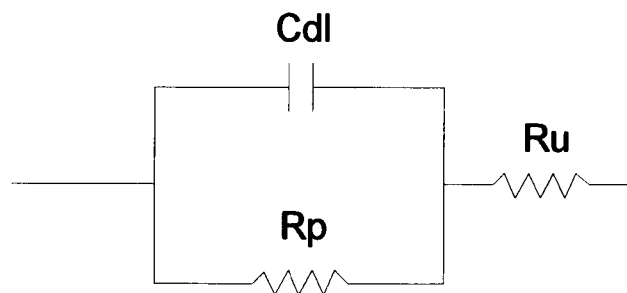
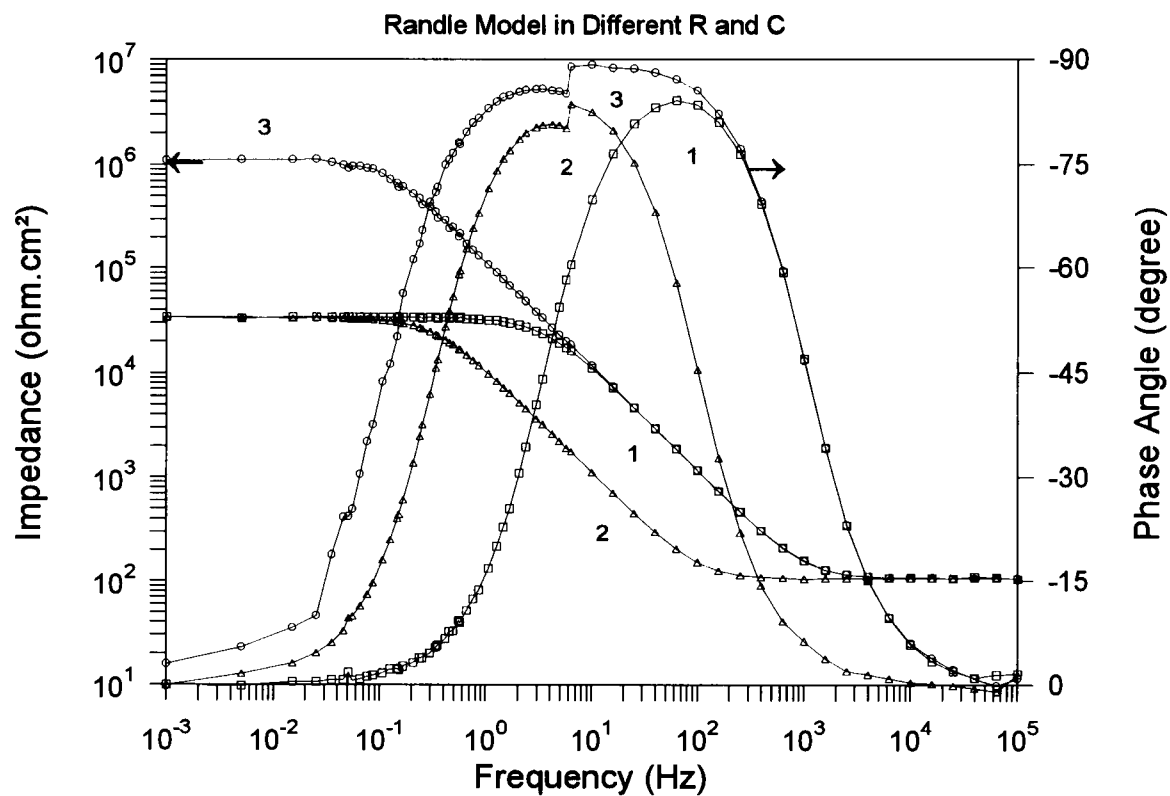
Electrochemical impedance spectroscopy (EIS) is an interesting technique for electrochemical study. Although it was brought into corrosion science in the 1970s, EIS still is not widely employed in corrosion studies. In the author's opinion, EIS should become a conventional technique and be complemented with the DC polarization techniques so as to give a full picture of an electrochemical reaction.

3.1.2.1. EIS Data Interpretation

The difficulty in interpreting EIS data is one aspect which obstructs the technique in terms of wide applications. Since the EIS is based on the same electrochemical theory as DC polarization, the data interpretation should be similar in the sense that a slight polarization is employed in the anodic and the cathodic directions. Because frequency is used as a measurement parameter, the EIS adds another dimension to study electrochemical reactions, i.e., it provides kinetic information associated with the charge transfer of electrochemical reactions. In most cases, the electrochemical interface associated with coupled half-cell electrochemical reactions can be represented by the simple Randle model, provided that the electrochemical interface is without dielectric

coating and is not in diffusion control, which normally is true since most measurements are made at the OCP and Tafel behavior is retained. The Randle model is illustrated in Figure 3-7, where R_p is the polarization resistance, C_{dl} is (could be) the double layer capacitance, and R_u is the uncompensated resistance. EIS results of the Randle model constituted from the corresponding electrical circuits (different R_p and C_{dl}) are also illustrated in Figure 3-7. The half-cell reactions are kinetically in equilibrium at corrosion potential. Within a high frequency range, the charge transfer rate of either the anodic or the cathodic half-cell reaction is not affected because of the high frequency of the perturbing current. The electrochemical interface is "transparent" to the applied current. Consequently, the uncompensated resistance is detected. In the frequency vicinity of the charge transfer rate, it is conceivable that the charge transfer rate (current) will be perturbed, in other words, the half-cell reactions are polarized either anodically or cathodically, so the measured impedance increases and the phase angle is altered. Within a low frequency range, the charge transfer rate is not affected because of the low frequency of the perturbing current. As a result, the pure interface resistance which is sum of the polarization resistance and the uncompensated resistance is measured. The polarization resistance related to the corrosion rate is obtained by subtracting the uncompensated resistance.

Two problems are most likely to be confronted in the EIS measurement: (1) noisy data, especially in the low frequency range; (2) the multiple time-constants (relaxation times) phenomenon. It is conceivable that 5-10 mV input signal is readily influenced by a potential fluctuation larger than 10 mV, especially in low frequencies in which the technique needs a long time to take data. Thus, it is essential for the EIS measurement to



Case 1: $R_p = 30 \text{ K}\Omega$, $C_{dl} = 1.47 \text{ }\mu\text{F}$, $R_u = 100 \text{ }\Omega$

Case 2: $R_p = 30 \text{ K}\Omega$, $C_{dl} = 14.7 \text{ }\mu\text{F}$, $R_u = 100 \text{ }\Omega$

Case 3: $R_p = 1 \text{ M}\Omega$, $C_{dl} = 1.47 \text{ }\mu\text{F}$, $R_u = 100 \text{ }\Omega$

Figure 3-7. EIS spectra of the Randle circuits with different R and C.

have a stable potential throughout the measuring time. The two or more time-constants result is one of the difficulties of interpreting the data if the electrochemical interface is not coated by any dielectric film. In most electrochemical systems, it indicates that two or more coupled half-cell reactions are occurring at the interface. In most cases, only the predominant coupled half-cell reactions are measured in a corrosion study, in other words, the reactions having the greater current densities. However, if two coupled half-cell reactions occur at about the same rate, two time-constants data possibly would be measured in the spectrum.

3.1.2.2. EIS Results

The first cycle of the EIS data was collected after a few days exposure for each run when the system reached stable conditions, more specifically, the OCPs were stabilized at about -250 mV vs SHE in the bacterial solution or at about +250 mV vs SHE in the control solution. The next cycles were made at about every 30 days exposure. Because the EIS spectra look similar for the later cycles, herein, the data from the first and the last cycles are selected to present the EIS results. The EIS Bode plots for specimen #1, specimen #2, specimen #4, and specimen #5 are illustrated in Figures 3-8, 3-9, 3-10, and 3-11, respectively.

The EIS data presented in Figures 3-8 to 3-11 showed that all specimens, either in the bacterial or the sterilized solutions, were very corrosion resistant. The data, in general, exhibited a capacitive nature at most frequencies over the range in which the

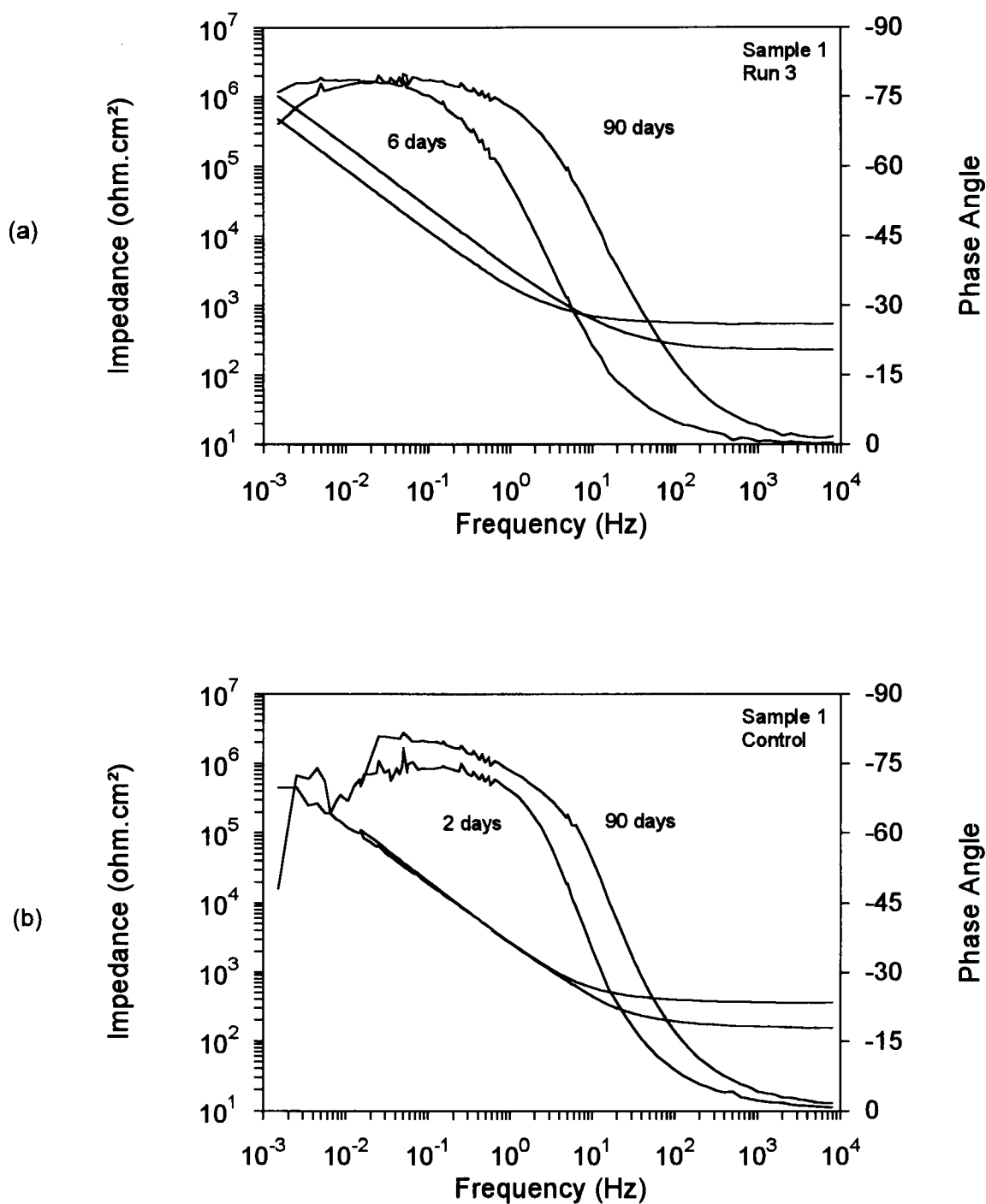


Figure 3-8. EIS spectra of 304L/308L, no treatment, collected at two exposure times, (a) Coupon #1 in Run 3, (b) Coupon #1 in Control Run.

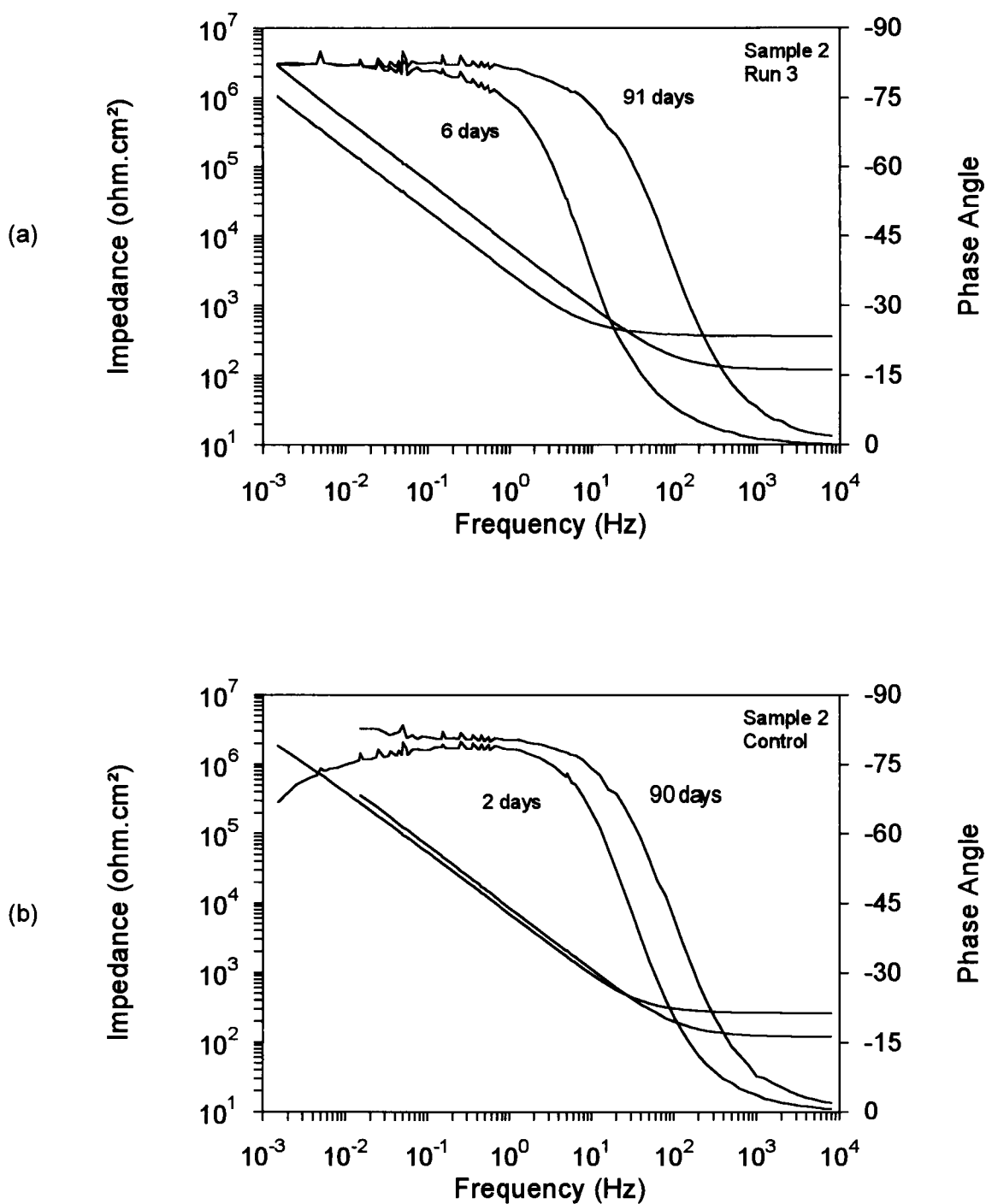


Figure 3-9. EIS spectra of 304L/308L, pickled, collected at two exposure times, (a) Coupon #2 in Run 3, (b) Coupon #2 in Control Run.

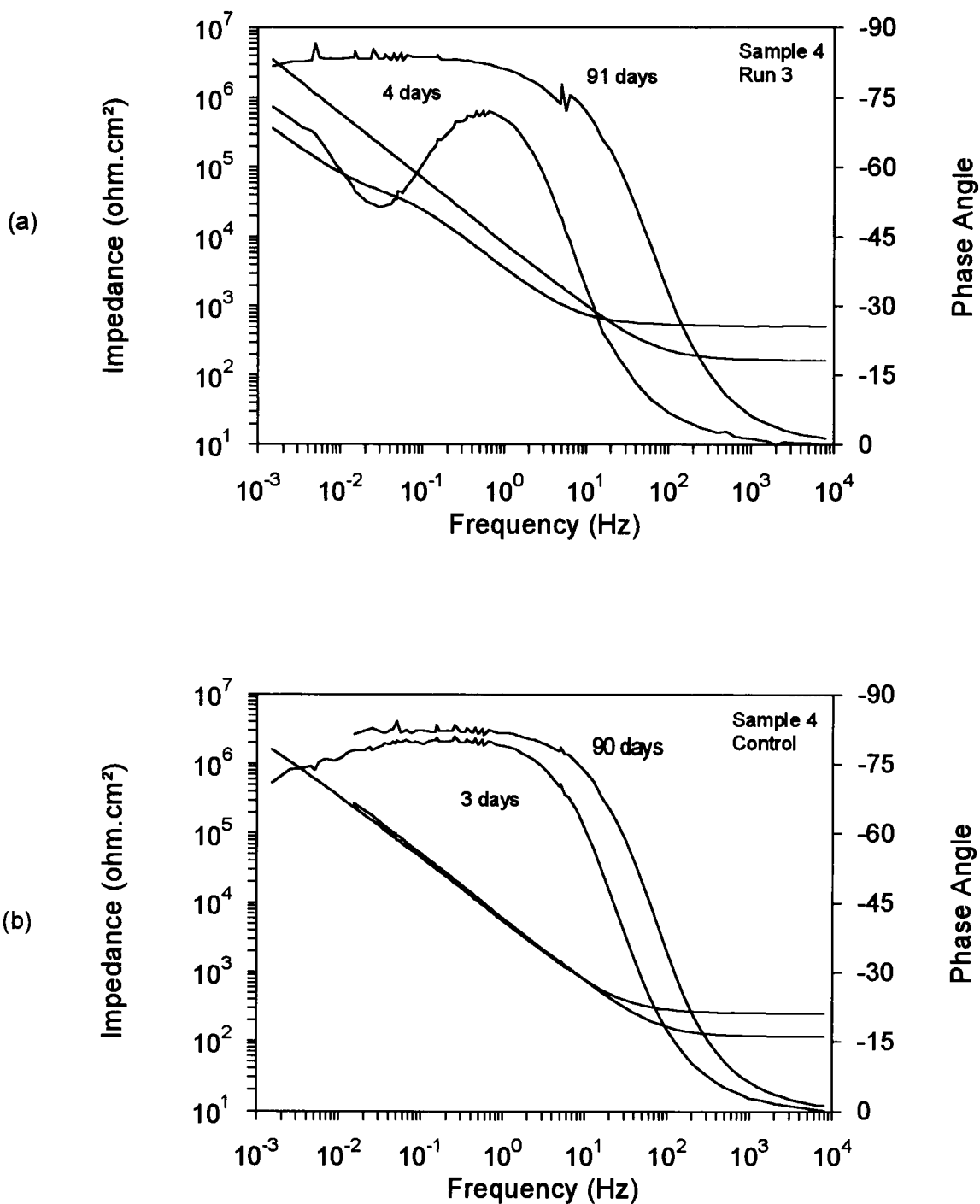


Figure 3-10. EIS spectra of 304L/308L, SA+WQ+Pickled, collected at two exposure times, (a) Coupon #4 in Run 3, (b) Coupon #4 in Control Run.

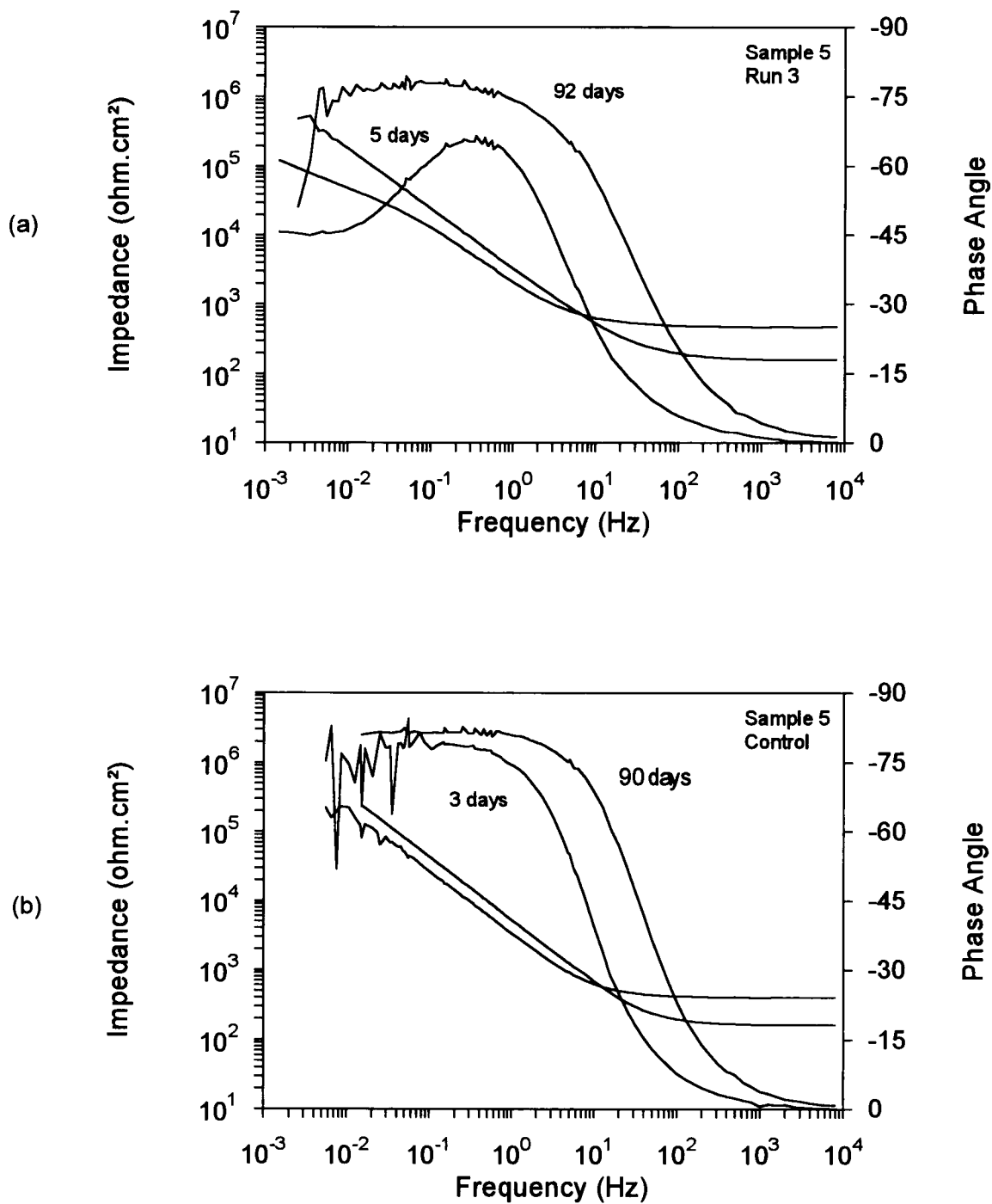


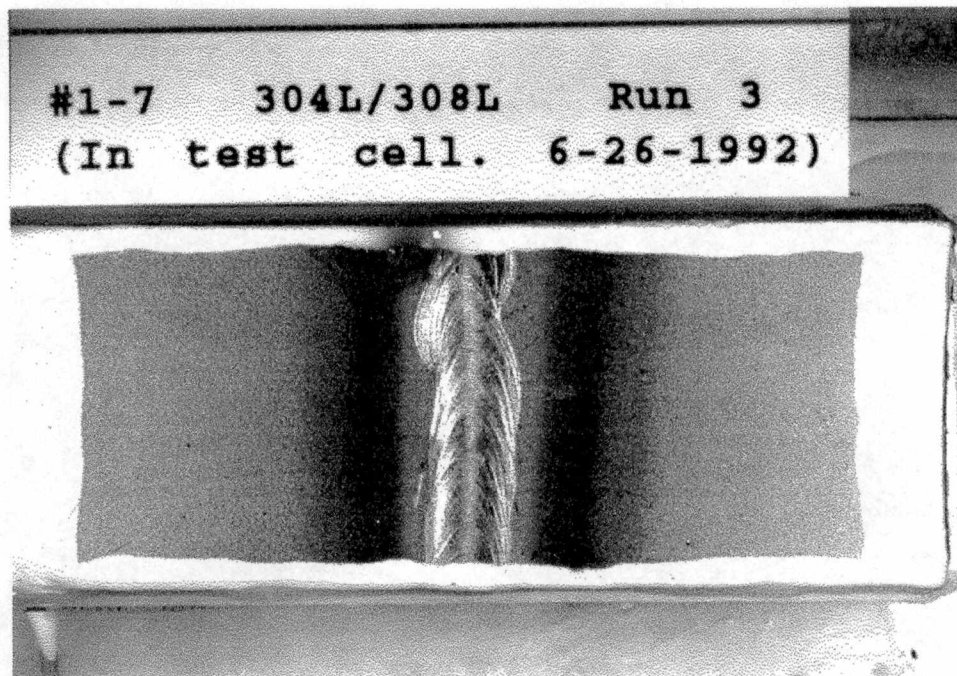
Figure 3-11. EIS spectra of 304L/308L, ground, collected at two exposure times, (a) Coupon #5 in Run 3, (b) Coupon #5 in Control Run.

impedance values were collected. This indicated a significant polarization resistance or good corrosion resistance (usually exceeding 10^6 ohm-cm^2). In the control solution (Figure 3-10, (b)), the spectra of the first and last cycles were almost the same, with only a slight discrepancy in phase angle, suggesting that a pair of coupled half-cell reactions was measured throughout the exposure. In the bacterial solution, the spectra of the first and last cycles appeared to be different in the phase angle curves. Some of them had different positions and shapes (Figure 3-9, (a)), some appeared to have more than one time-constant (Figure 3-10, (a)). It is recalled that for the bacterial runs the EIS of the first cycle was taken when the OCP was negative; in contrast, the EIS of the last cycle was obtained when the OCP was positive. The striking difference of the phase angle curves indicated that the coupled half-cell reactions occurring at the negative OCP were different from the coupled half-cell reactions at the positive OCP. If anodic reaction was the metallic ion dissolution throughout the exposure, and the cathodic reaction was oxygen reduction at the positive OCP, then the cathodic reaction at the negative OCP could have been water reduction because the dissolved oxygen was depleted in the solution by the bacterial metabolism. The EIS also suggested that at the negative potential the interface at the specimen surface had higher capacitance, which meant more charge storage during the measurements. This could have been the result of atomic hydrogen adsorption as a consequence of the water-reduction cathodic reaction. Because a decrease of polarization resistance was not observed, it seems that the different cathodic reactions were responsible for the open-circuit potential decrease and increase during the exposure for the bacterial runs. In summary, the EIS data did not show any decrease in polarization resistance. A

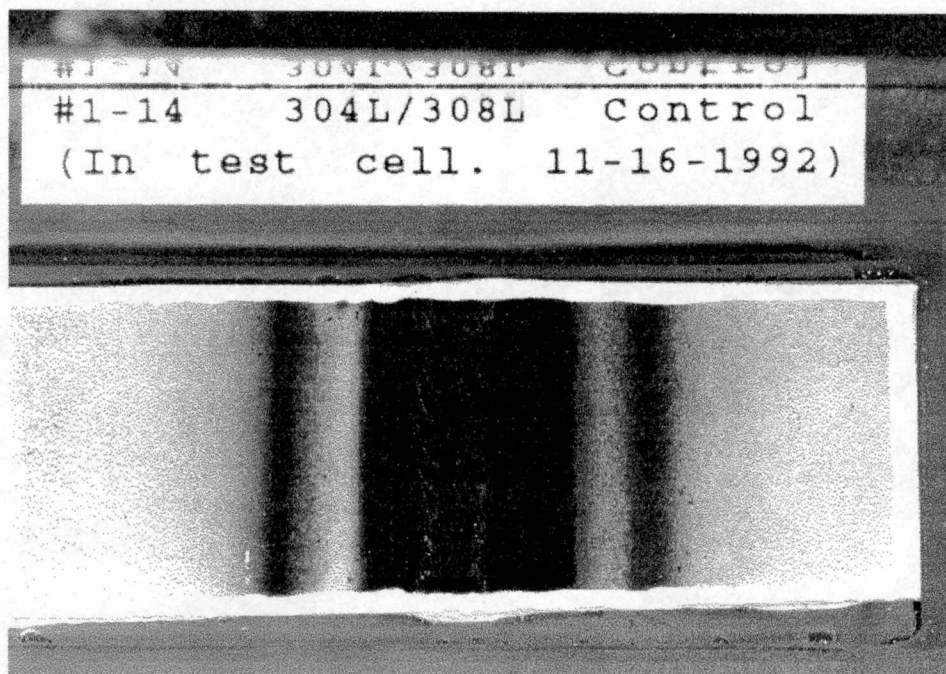
deoxygenating condition may account for the phase angle changes in the EIS spectrum for the bacterial solution.

3.1.3. Corrosion Surface Evaluation

After the 90-day exposure, the appearances of the weldments were photographed while in the corrosion cell. The weldments in order of the specimen's sequential number are shown in Figure 3-12 through Figure 3-24. The results of all bacterial runs and the control run, in terms of corrosion nodule number and size, are summarized in Table 3-1. Visual observation of the weldments after exposure showed that small corrosion nodules had formed at the epoxy interface in the weld region on all specimens except those for which the oxide layer had been removed by either chemical or electrochemical means. It is seen that specimens #2 (pickled, Figure 3-13), #3 (electropolished, Figure 3-14), and #4 (solution annealed + pickled, Figure 3-15) clearly showed corrosion resistance. Nodule formation was observed in all three runs with the bacteria inoculation after about 30 days exposure and in the control run without the bacteria inoculation. However, as shown in the Table 3-1, the numbers of nodules on each coupon for the control run was less, and the size was much smaller, compared to that for the bacterial runs. This result indicates that either the bacteria assisted the attack on the coupons or the environmental history exacerbated the corrosion since the bacteria had altered the environment before the nodule was observed. The corrosion nodules occurred at the metal/epoxy interface on the specimen surfaces in the heat tint area, as opposed to the base metal, suggesting that the

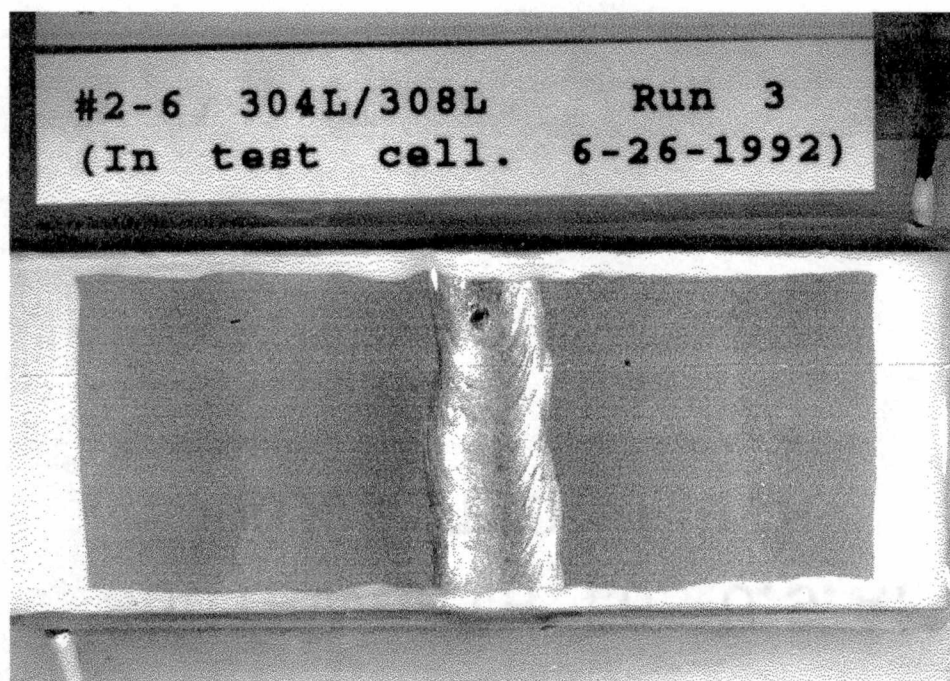


(a)



(b)

Figure 3-12. Photographs of 304L/308L, no treatment, after the exposure: (a) Coupon #1 in Run 3; (b) Coupon #1 in Control Run.

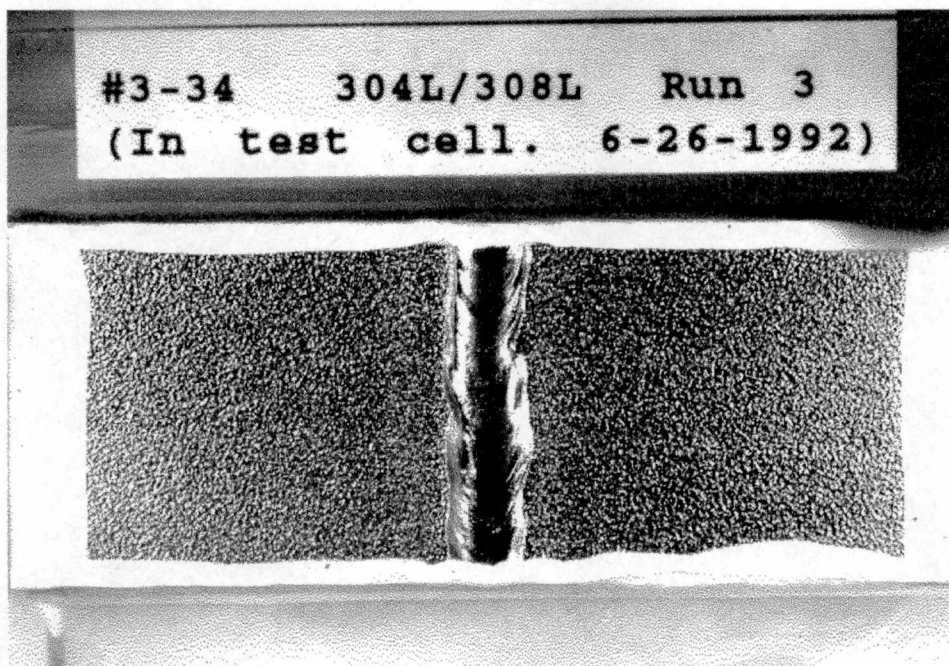


(a)

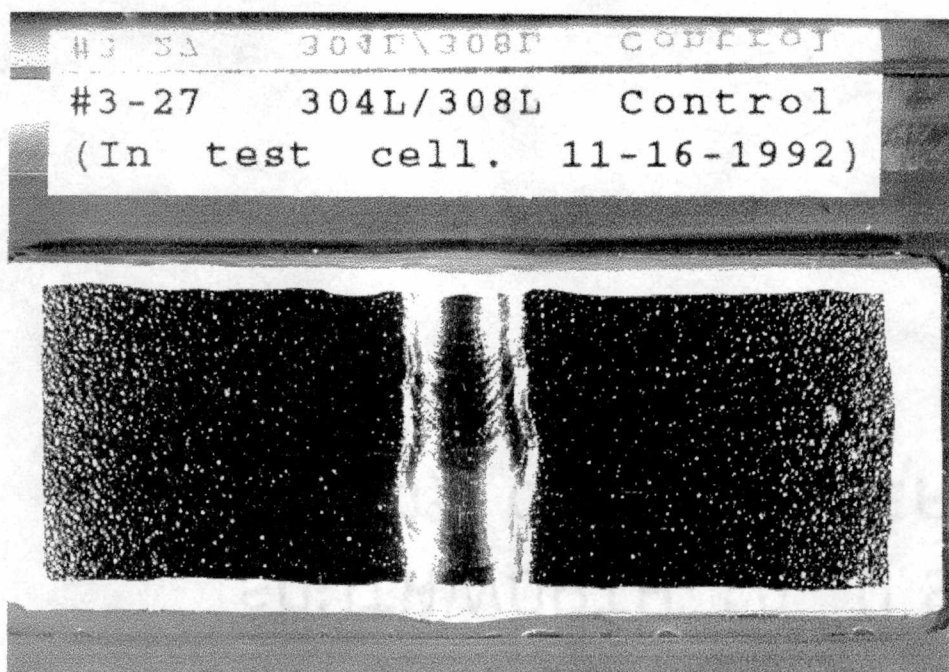


(b)

Figure 3-13. Photographs of 304L/308L, pickled, after the exposure: (a) Coupon #2 in Run 3; (b) Coupon #2 in Control Run.

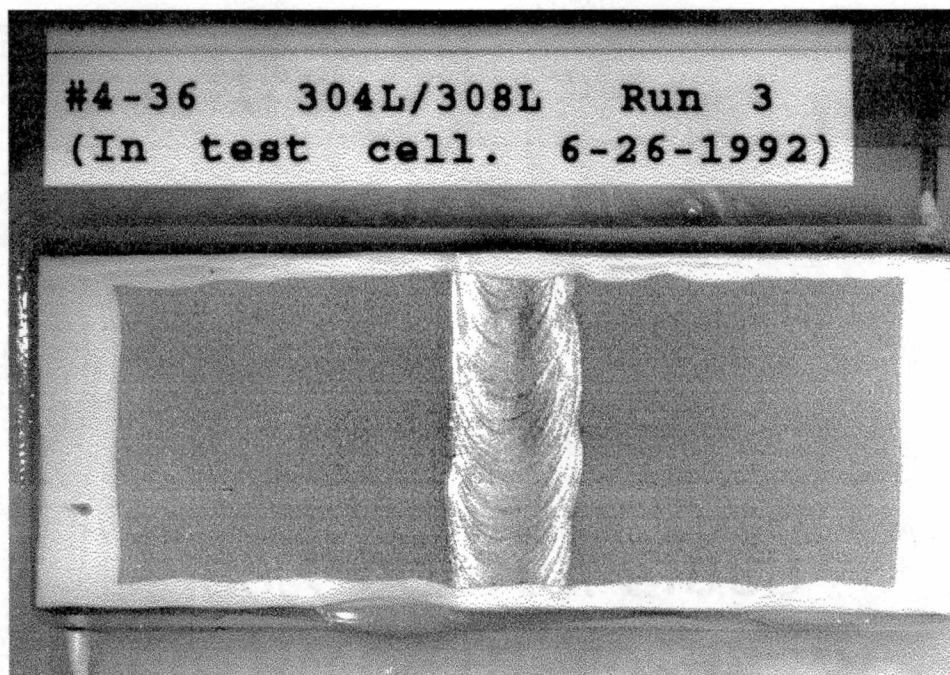


(a)



(b)

Figure 3-14. Photographs of 304L/308L, electropolished, after the exposure: (a) Coupon #3 in Run 3; (b) Coupon #3 in Control Run.



(a)

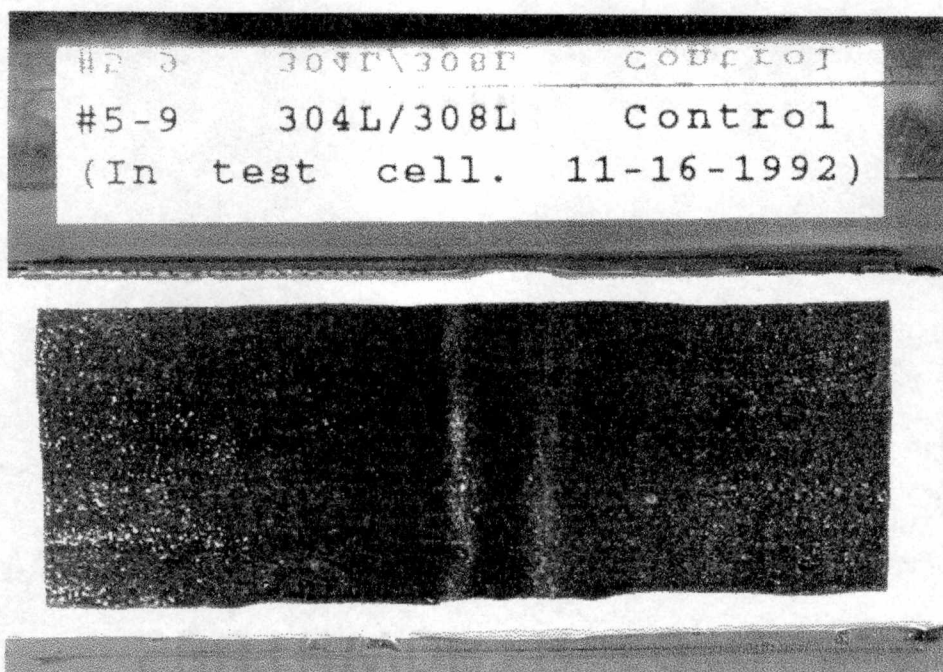


(b)

Figure 3-15. Photographs of 304L/308L, SA+WQ+Pickled, after the exposure: (a) Coupon #4 in Run 3; (b) Coupon #4 in Control Run.



(a)



(b)

Figure 3-16. Photographs of 304L/308L, ground, after the exposure: (a) Coupon #5 in Run 3; (b) Coupon #5 in Control Run.

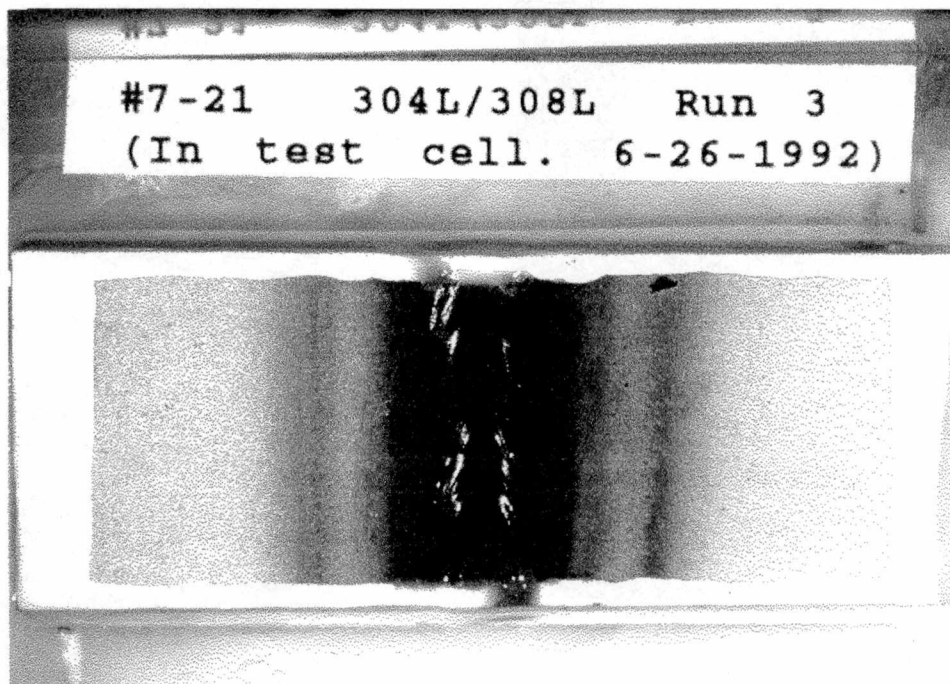


(a)



(b)

Figure 3-17. Photographs of 304L/316L, no treatment, after the exposure: (a) Coupon #6 in Run 3; (b) Coupon #6 in Control Run.

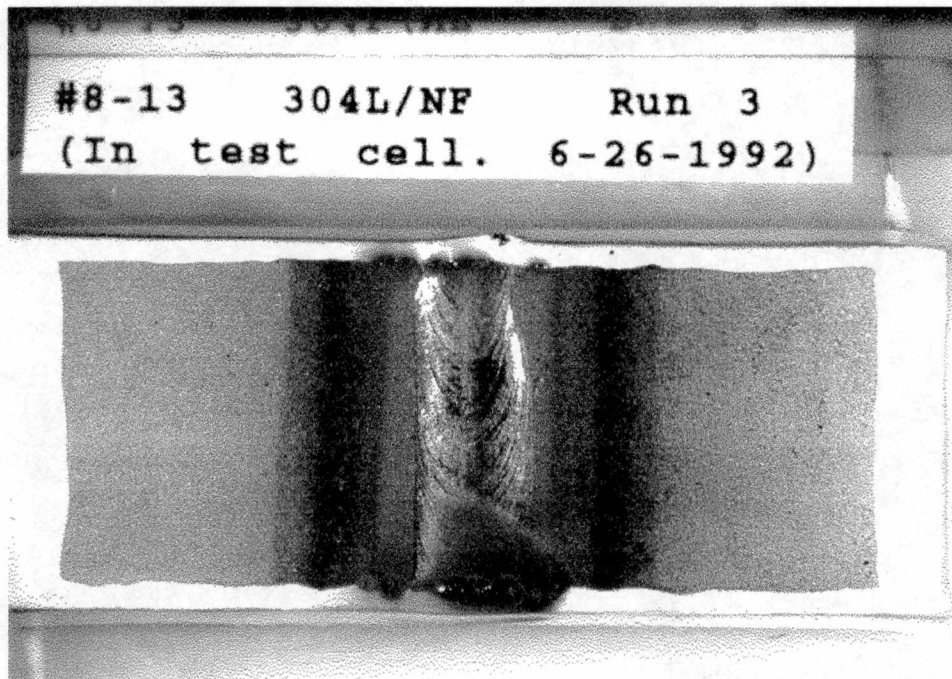


(a)

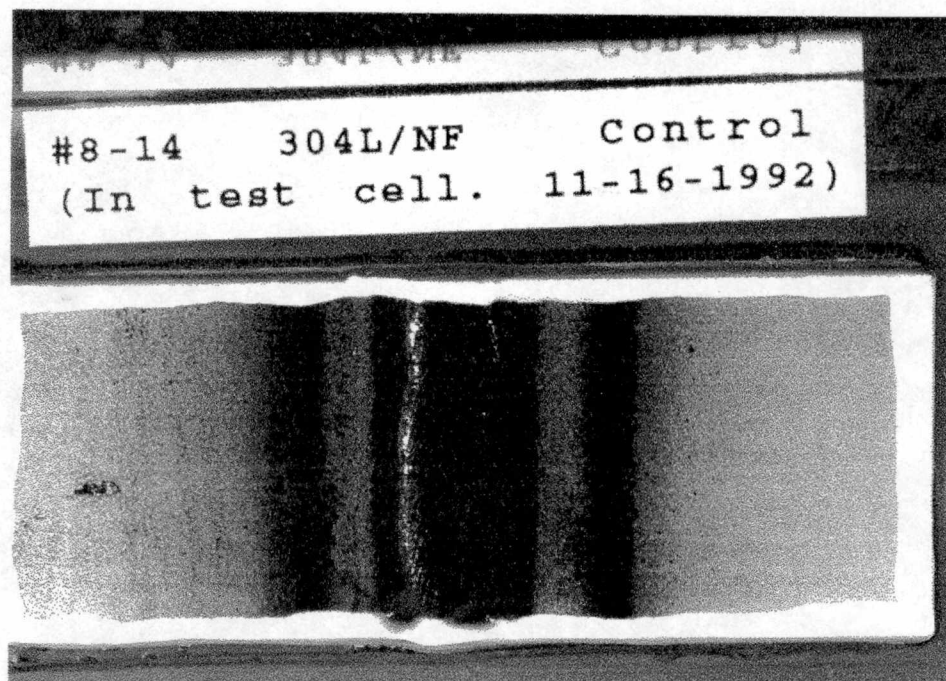


(b)

Figure 3-18. Photographs of 304L/308L, purge removal after root pass, after the exposure: (a) Coupon #7 in Run 3; (b) Coupon #7 in Control Run.

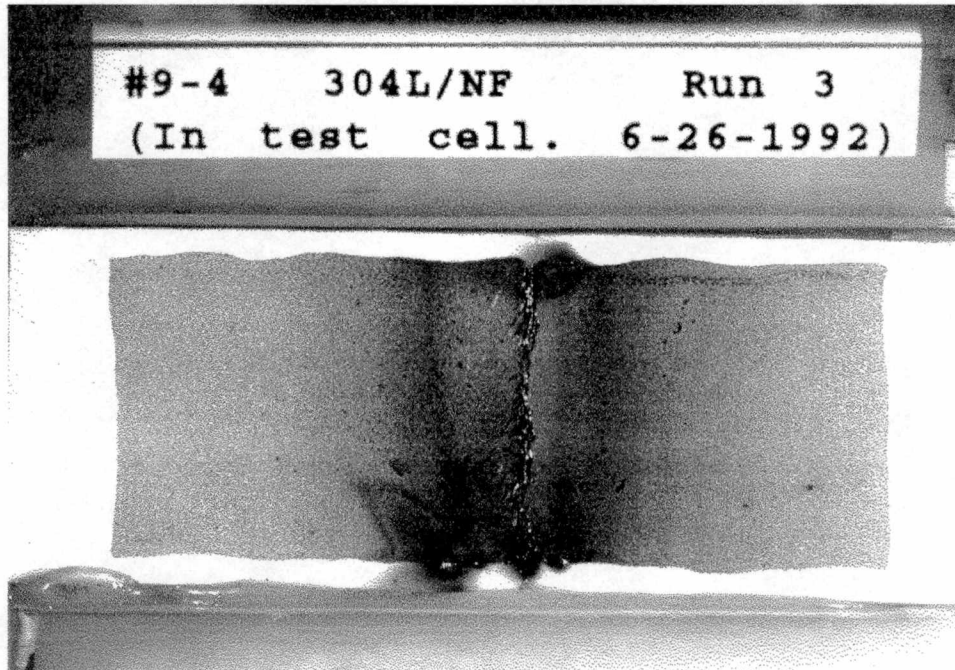


(a)

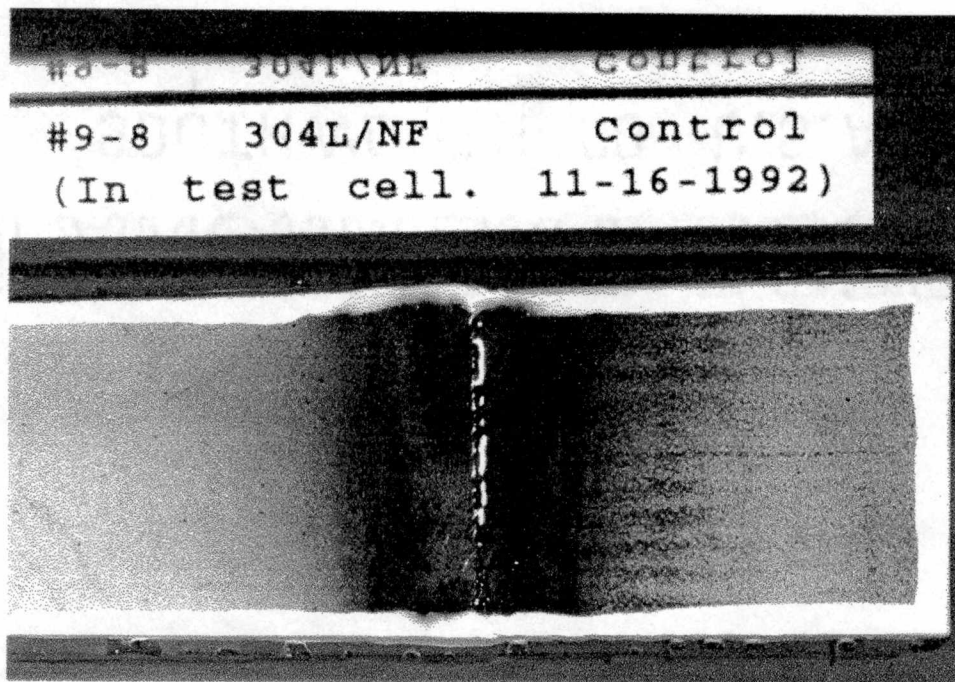


(b)

Figure 3-19. Photographs of 304L/None, fuse root pass, after the exposure: (a) Coupon #8 in Run 3; (b) Coupon #8 in Control Run.

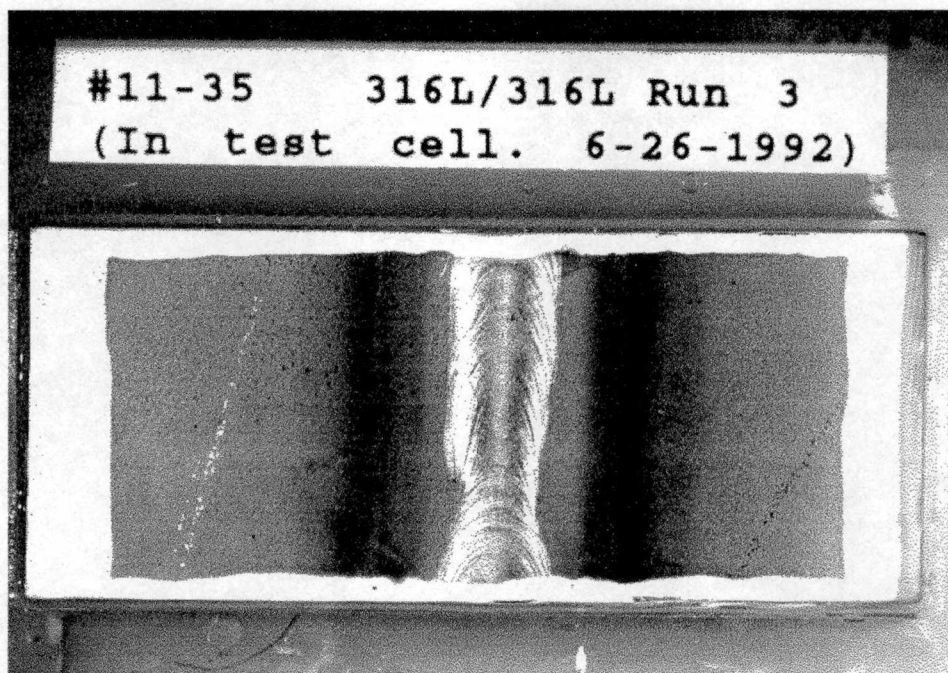


(a)

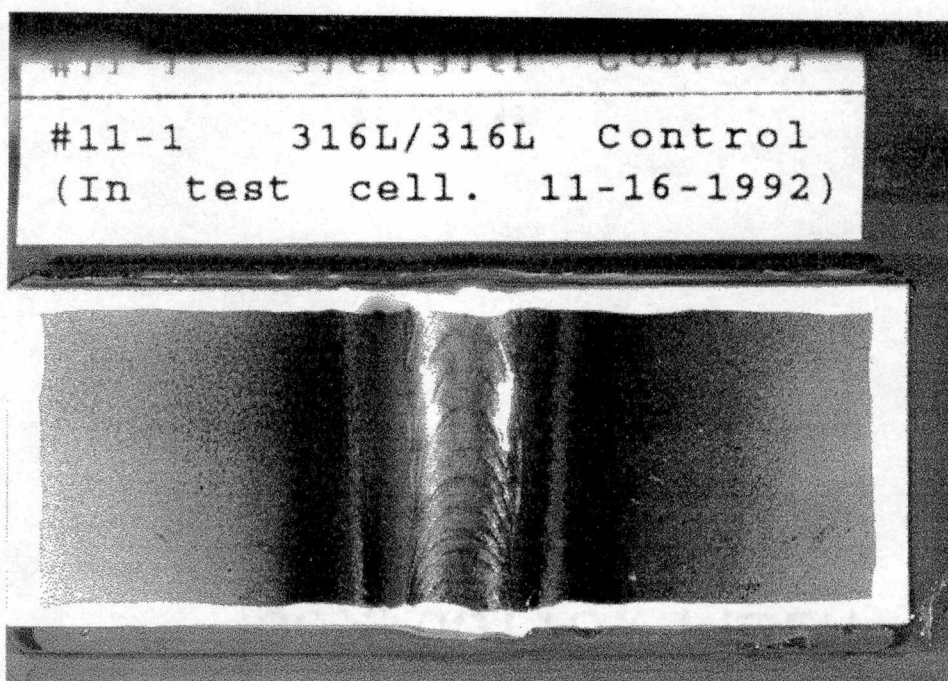


(b)

Figure 3-20. Photographs of 304L/None, incomplete penetration, after the exposure: (a) Coupon #9 in Run 3; (b) Coupon #9 in Control Run.

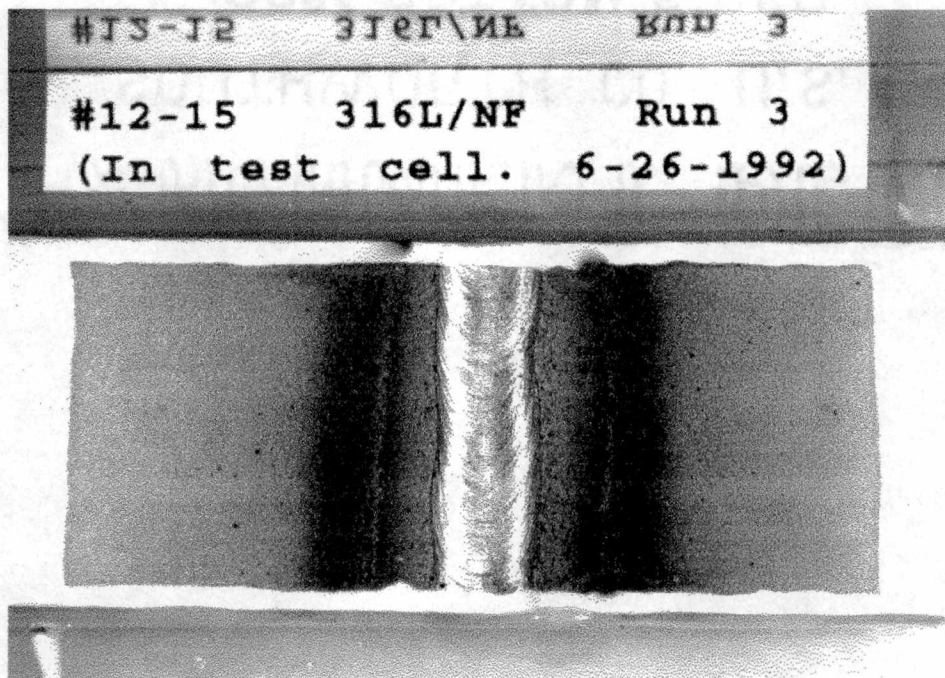


(a)

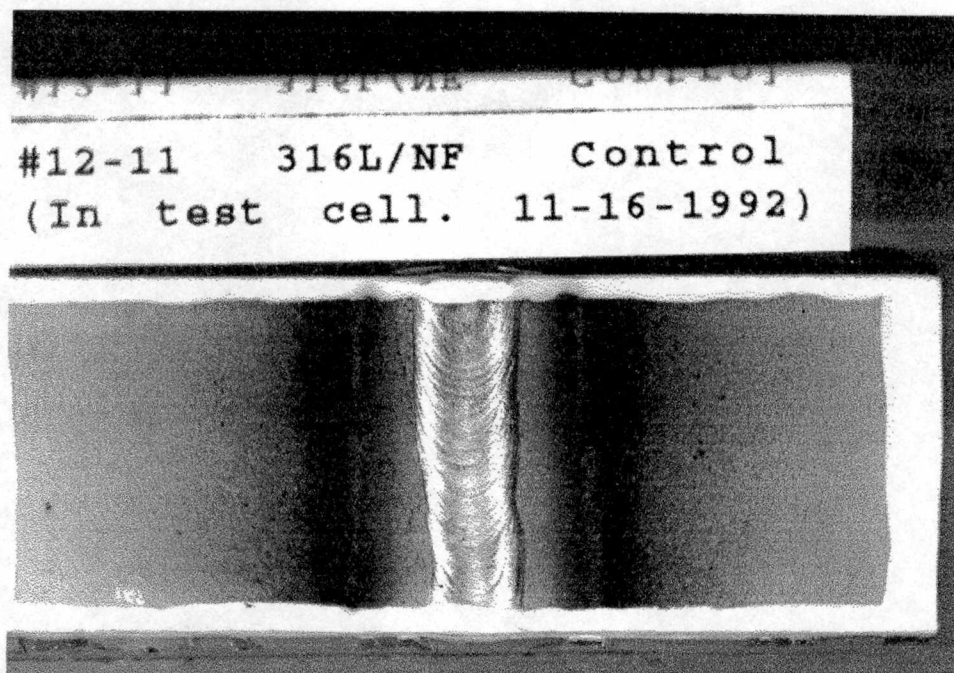


(b)

Figure 3-21. Photographs of 316L/316L, no treatment, after the exposure: (a) Coupon #11 in Run 3; (b) Coupon #11 in Control Run.

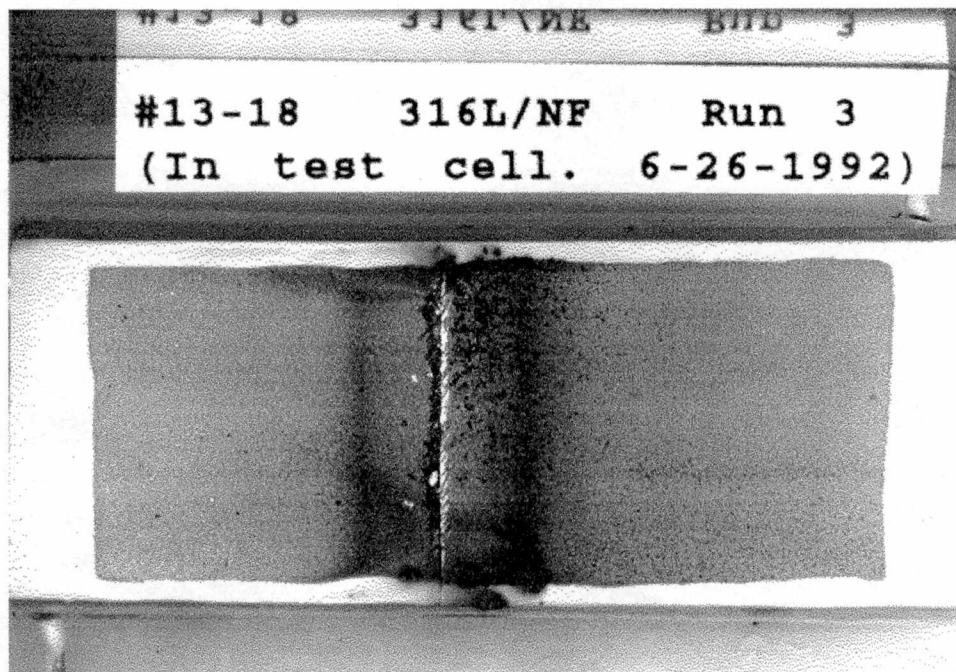


(a)

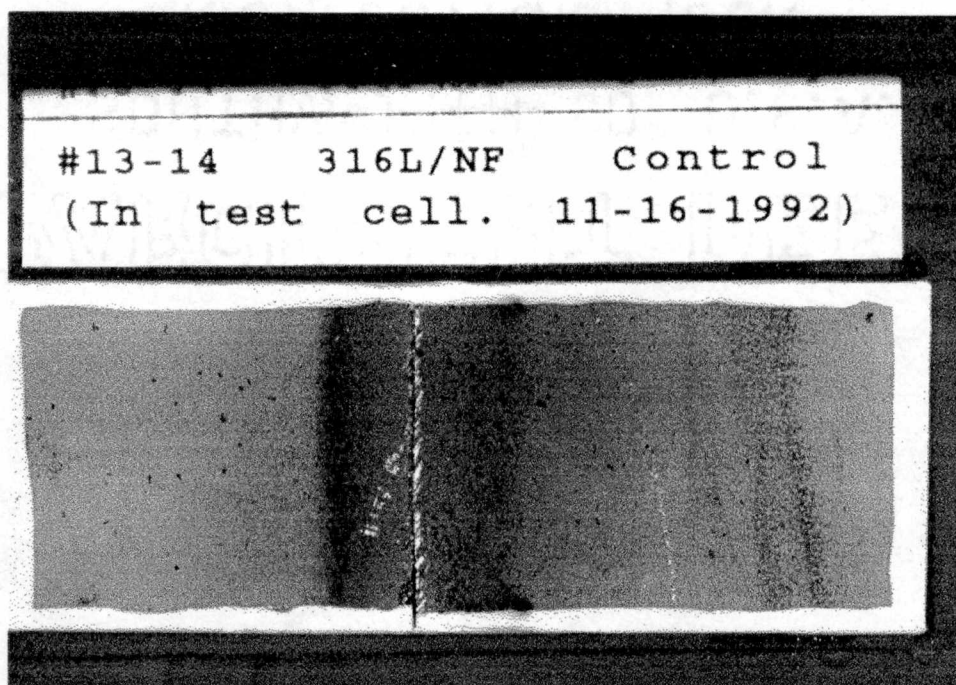


(b)

Figure 3-22. Photographs of 316L/None, fuse root pass, after the exposure: (a) Coupon #12 in Run 3; (b) Coupon #12 in Control Run.

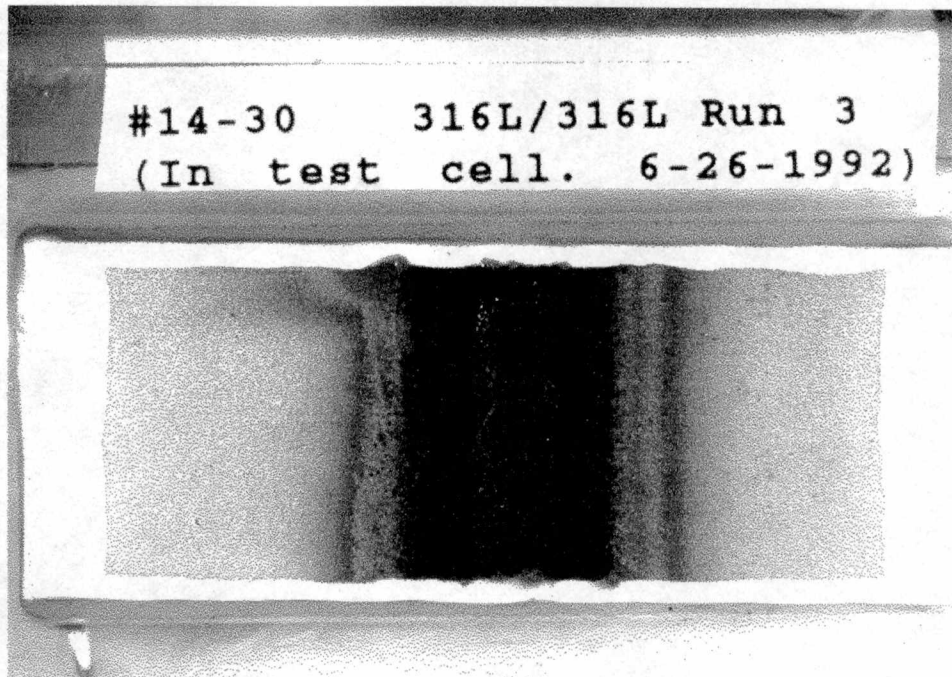


(a)

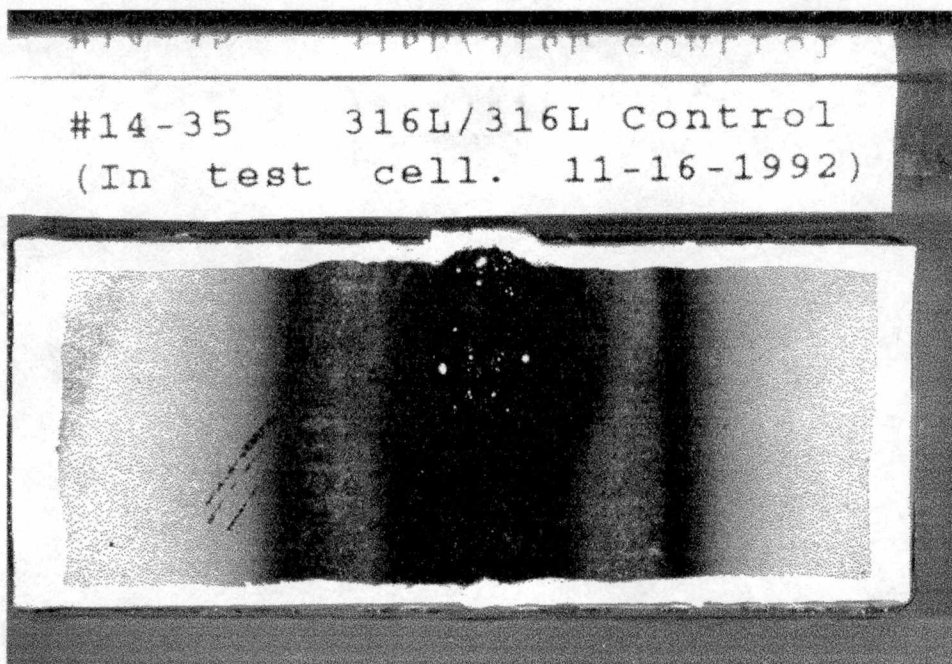


(b)

Figure 3-23. Photographs of 316L/None, incomplete penetration, after the exposure: (a) Coupon #13 in Run 3; (b) Coupon #13 in Control Run.



(a)



(b)

Figure 3-24. Photographs of 316L/316L, purge removal after root pass, after the exposure: (a) Coupon #14 in Run 3; (b) Coupon #14 in Control Run.

Table 3-1. Nodule Characterization of the Tennessee River water laboratory tests.

Coupon #	Control		Bacteria Run 3		Bacteria Run 2		Bacteria Run 1	
	Number	Size	Number	Size	Number	Size	Number	Size
1	Yes-1	L:1	Yes-2	L:4, S:1	Yes-3	L:3, S:1	Yes-1	L:3
2	No		No		No		No	
3	No		No		No		No	
4	No		No		No		No	
5	No		Yes-8	L:4, S:1	No		Yes-1	L:1
6	Yes-7	L:1, S:1	Yes-14	L:3, S:1	Yes-3	L:2, S:1	Yes-3	L:5, S:1
7	Yes-3	L:1, S:1	Yes-11	L:3, S:1	Yes-2	L:1, S:1	Yes-6	L:2, S:1
8	Yes-2	L:3, S:2	Yes-11	L:4, S:1	Yes-4	L:1, S:1	No	
9	Yes-7	L:2, S:1	Yes-5	L:3, S:2	Yes-2	L:1 S:1	No	
11	Yes-2	L:1, S:1	Yes-4	L:1, S:1	Yes-2	L:1, S:1	Yes-1	L:3
12	Yes-3	L:2, S:1	Yes-2	L:2, S:1	Yes-2	L:3 S:2	No	
13	Yes-2	L:1, S:1	Yes-5	L:3, S:1	Yes-1	L:1	No	
14	Yes-2	L:1, S:1	Yes-8	L:2, S:1	Yes-4	L:2, S:1	Yes-8	L:2, S:1

Size: L (Largest), S (Smallest), 1 (1 mm)

corrosion might be crevice-related. It is noted that nodules existed on the control specimens for which no changes in electrochemical activity (OCP or EIS) were observed. Thus, the results indicated that the observed changes in electrochemical activity were not associated with nodule formation.

3.1.4. AODC and Viable Counts

Microbiological tests on the Run 3 were conducted on samples from each specimen surface in the base metal area and from nodules found in the weld region, including the heat tint area. Samples from the bulk solution also were obtained. The results, given in Table 3-2, indicated that the number of bacteria were on the order of 10^5 to 10^7 cells/cm². It is noted that the bacteria counts of the weld regions including the nodules showed almost no difference from the counts of the base metal regions, suggesting that a biofilm covered the entire coupon surface, and that no bacterial aggregation existed on either the base or weld metal region.

3.1.5. Summary

Nodule formation was observed not only in the bacterial runs but also in the sterilized control run. Whether this could be correlated to the bacterial activities or other contributing factors was not clear based solely on the results of the Tennessee River water laboratory tests. There was suspicion that the control run might have been contaminated

Table 3-2. Total Bacteria from AODC and Viable Counts.

Sample	AODC, cell/cm ²	Viable Counts, cell/cm ²
Bulk Solution	4.3×10^5	7.0×10^5
Coupon 1 on weld	8.4×10^6	1.6×10^5
Coupon 1 on base	3.5×10^6	2.8×10^3
Coupon 2 on weld	1.1×10^7	2.1×10^4
Coupon 2 on base	8.9×10^6	1.2×10^5
Coupon 3 on weld	6.9×10^5	2.5×10^3
Coupon 3 on base	2.6×10^5	0
Coupon 4 on weld	9.2×10^4	5.8×10^2
Coupon 4 on base	9.6×10^5	1.2×10^3
Coupon 5 on weld	6.0×10^6	4.6×10^3
Coupon 5 on base	1.2×10^6	2.4×10^3
Coupon 6 on weld	3.1×10^6	8.3×10^1
Coupon 6 on base	1.2×10^6	2.0×10^5
Coupon 7 on weld	4.2×10^6	5.1×10^4
Coupon 7 on base	1.9×10^6	1.5×10^3
Coupon 8 on weld	6.0×10^7	4.9×10^5
Coupon 8 on base	9.4×10^5	9.8×10^3
Coupon 9 on weld	8.1×10^6	3.8×10^5
Coupon 9 on base	3.3×10^6	0
Coupon 11 on weld	5.6×10^5	5.4×10^4
Coupon 11 on base	2.0×10^5	1.9×10^4
Coupon 12 on weld	4.2×10^5	2.9×10^3
Coupon 12 on base	9.7×10^5	1.1×10^3
Coupon 13 on weld	7.7×10^6	2.1×10^5
Coupon 13 on base	1.7×10^7	5.8×10^3
Coupon 14 on weld	1.7×10^7	4.2×10^5
Coupon 14 on base	6.7×10^6	4.6×10^3

during the experiment. Also, the simulated Tennessee River water had a higher chloride content (100 ppm) than the actual Tennessee River water (~10 ppm). The higher chloride content could have contributed to the nodule formation. Furthermore, it was recognized that the corrosion nodule formation at the metal/epoxy interface within the weld-modified region was most-likely crevice related.

3.2. Arizona Ground Water Field Tests

Two parallel corrosion tests were performed simultaneously in the Arizona ground water field tests. The two tests produced almost identical corrosion results in terms of nodule characteristics, open-circuit potentials, and microbiological analysis. The coupons in corrosion cell 2 were selected to illustrate the corrosion surface appearance. Typical OCP curves from the as-welded and pickled coupons were chosen to represent the electrochemical results.

3.2.1. Corrosion Surface and OCP Evaluations

The surface appearances of the corrosion coupons were photographed while in the corrosion cells after the exposure. The photographs in order of the specimen number are shown in Figure 3-25 through Figure 3-37. It is seen that corrosion nodules were found on all coupons except those with chemically-cleaned surfaces (Figures 3-26, pickled; Figure 3-28, SA+WQ+Pickled), electrochemically-cleaned surfaces (Figure 3-27,

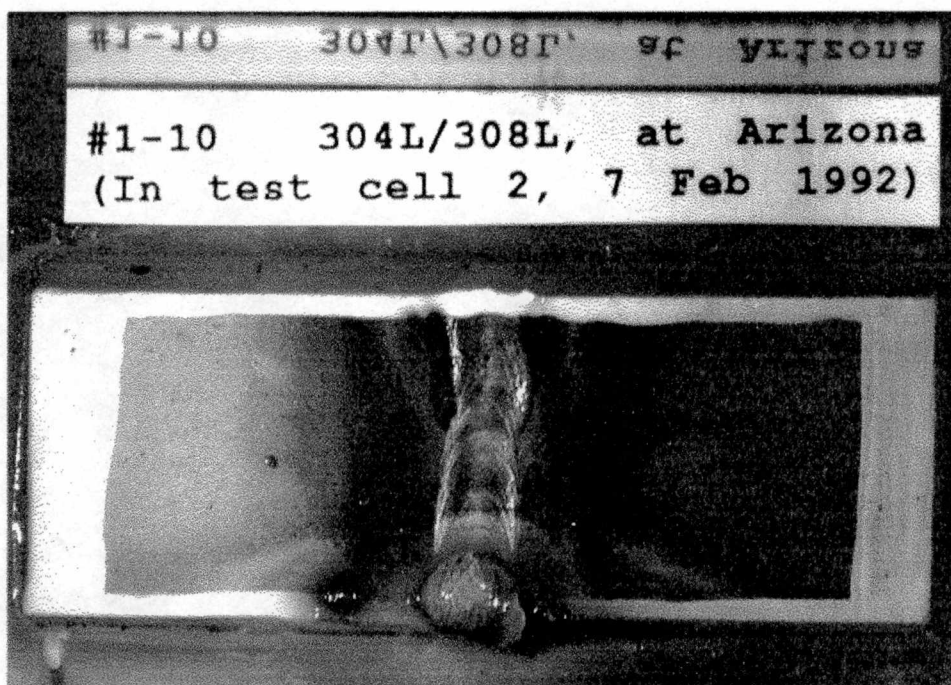


Figure 3-25. Photograph of 304L/308L, no treatment, after 140-day exposure at the Arizona field site.

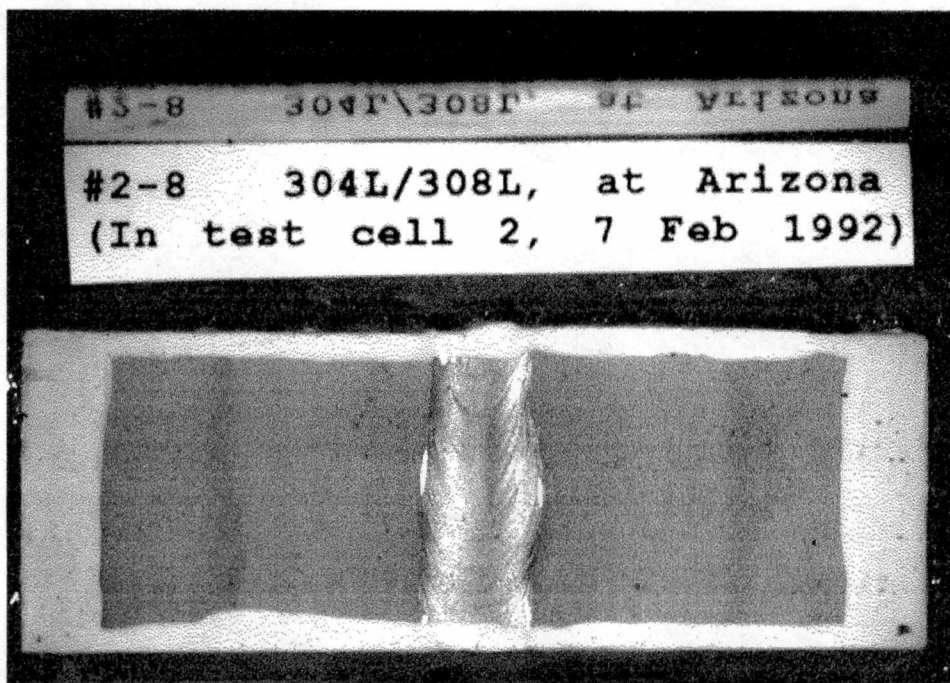


Figure 3-26. Photograph of 304L/308L, pickled, after 140-day exposure at the Arizona field site.

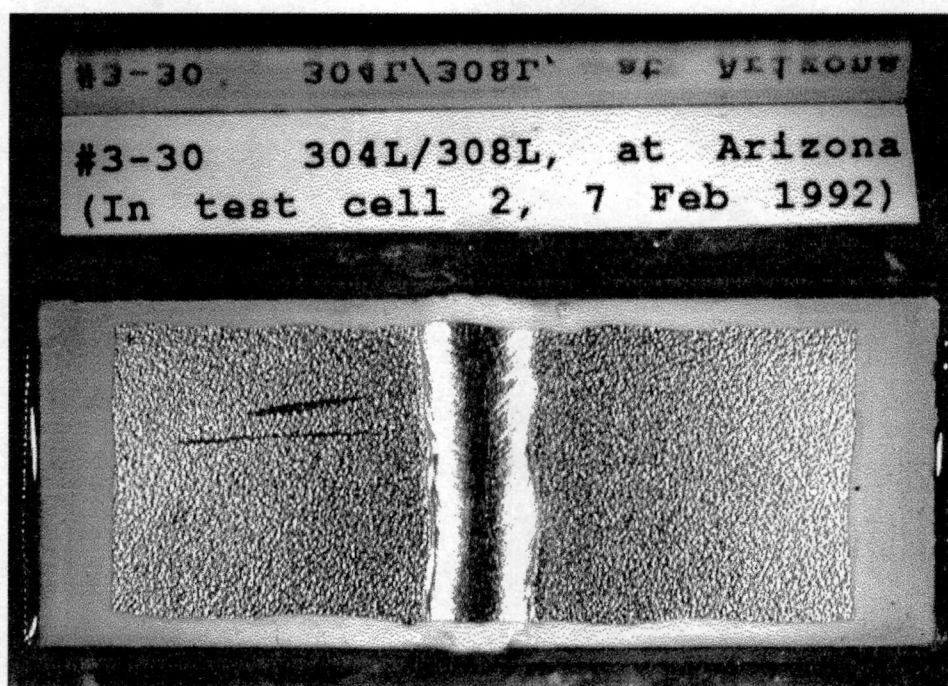


Figure 3-27. Photograph of 304L/308L, electropolished, after 140-day exposure at the Arizona field site.

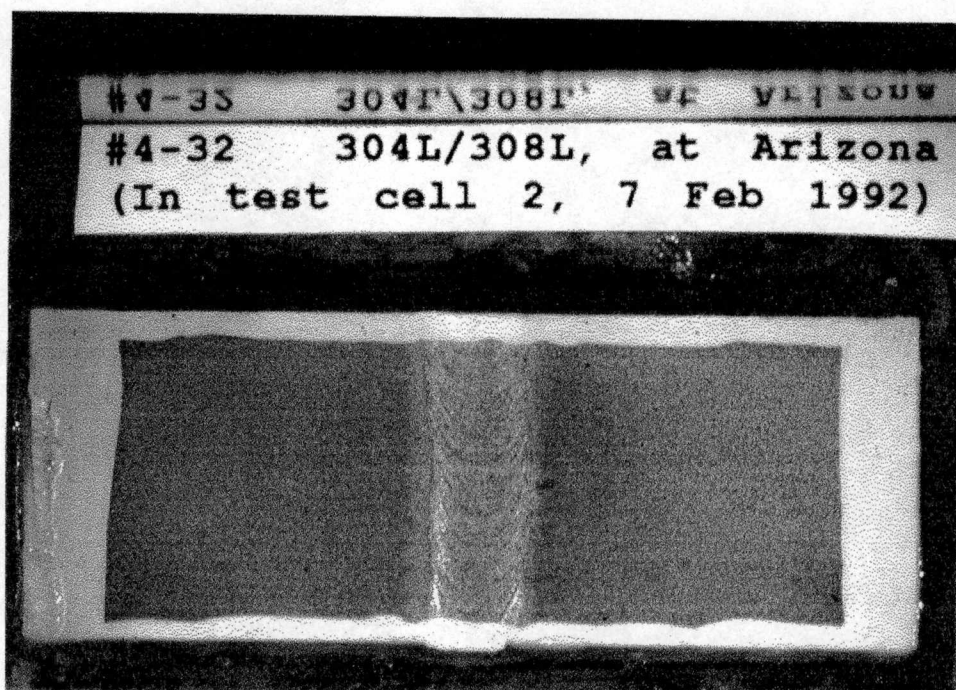


Figure 3-28. Photograph of 304L/308L, SA+WQ+Pickled, after 140-day exposure at the Arizona field site.

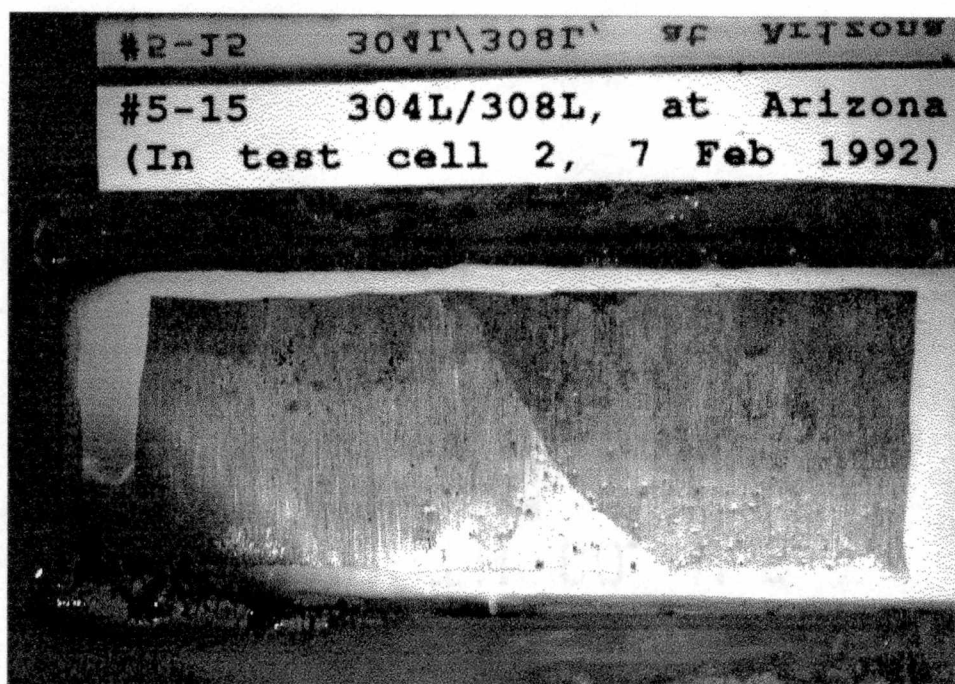


Figure 3-29. Photograph of 304L/308L, ground, after 140-day exposure at the Arizona field site.

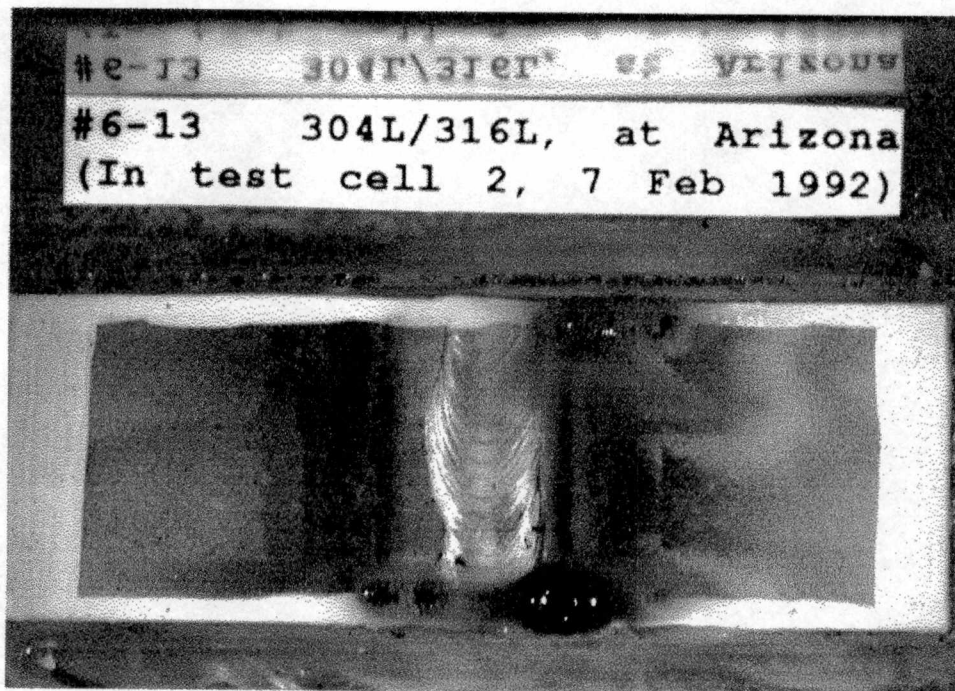


Figure 3-30. Photograph of 304L/316L, no treatment, after 140-day exposure at the Arizona field site.

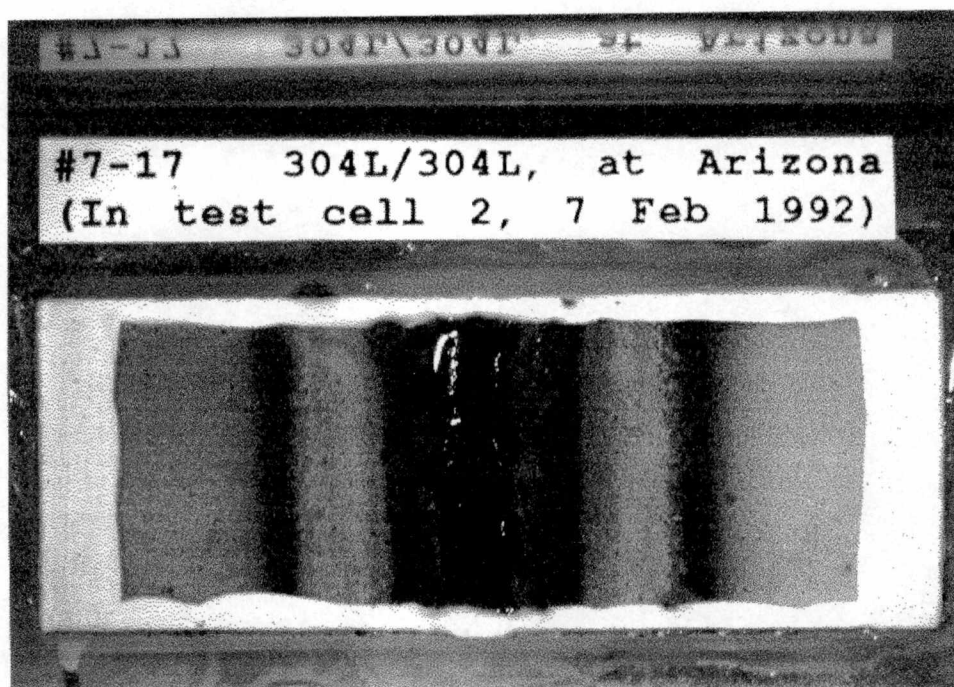


Figure 3-31. Photograph of 304L/308L, purge removal after root pass, after 140-day exposure at the Arizona field site.

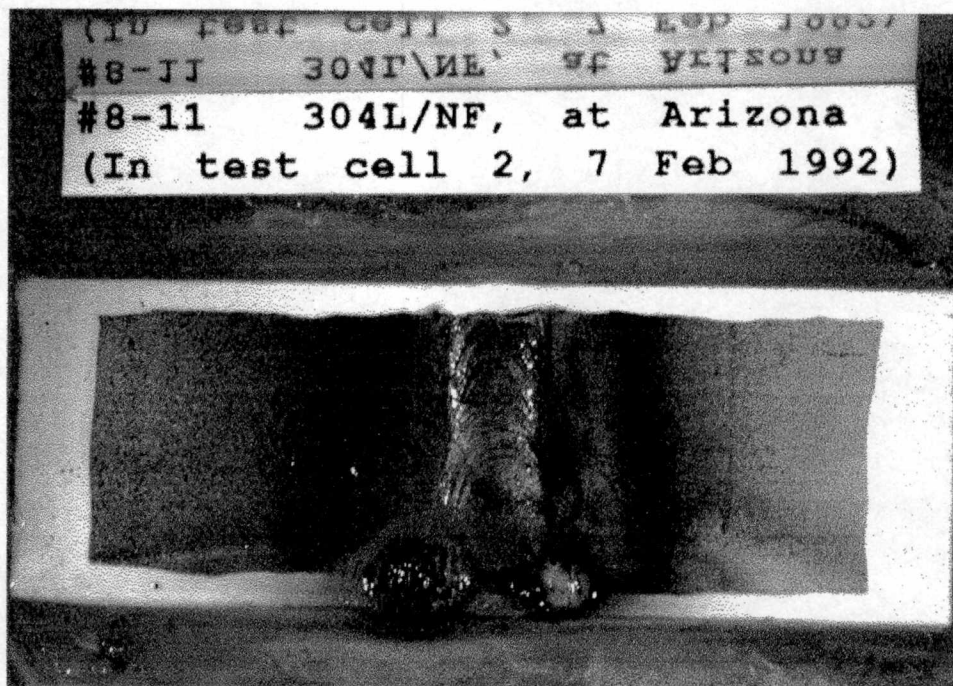


Figure 3-32. Photograph of 304L/None, fuse root pass, after 140-day exposure at the Arizona field site.

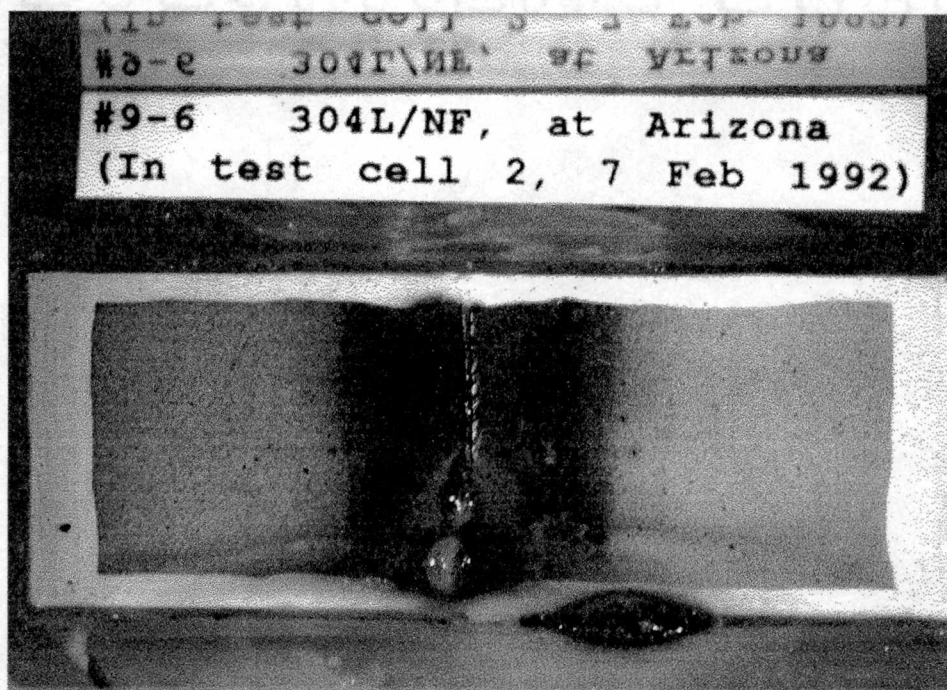


Figure 3-33. Photograph of 304L/None, incomplete penetration, after 140-day exposure at the Arizona field site.

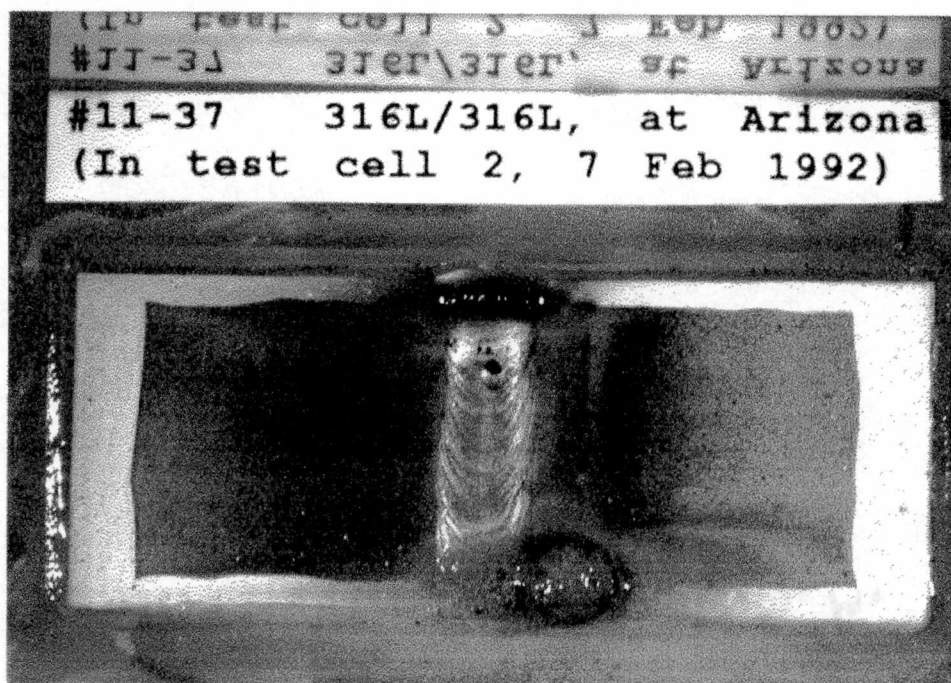


Figure 3-34. Photograph of 316L/316L, no treatment, after 140-day exposure at the Arizona field site.

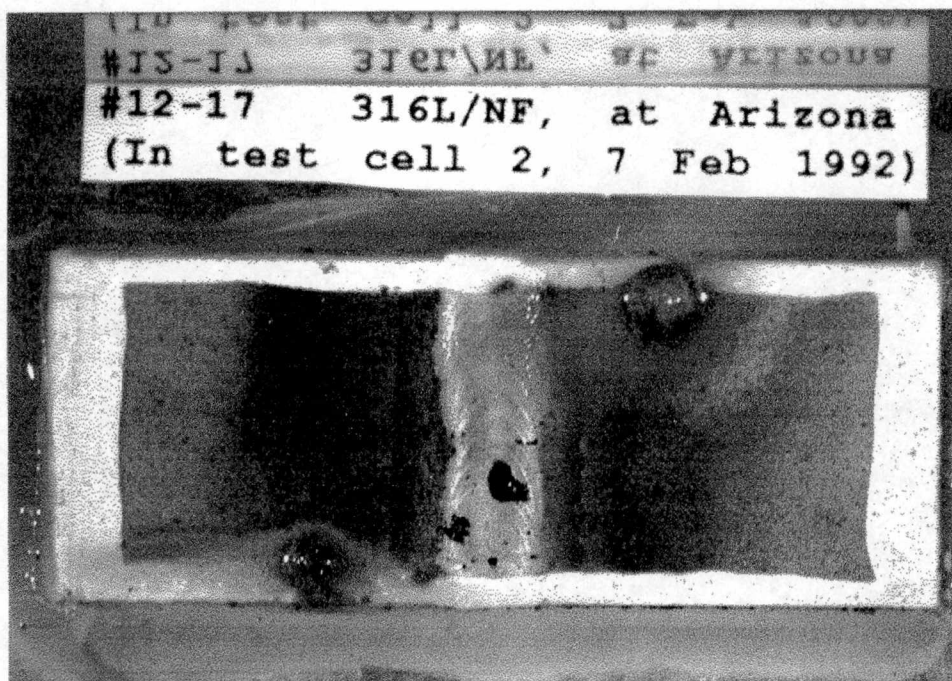


Figure 3-35. Photograph of 316L/None, fuse root pass, after 140-day exposure at the Arizona field site.

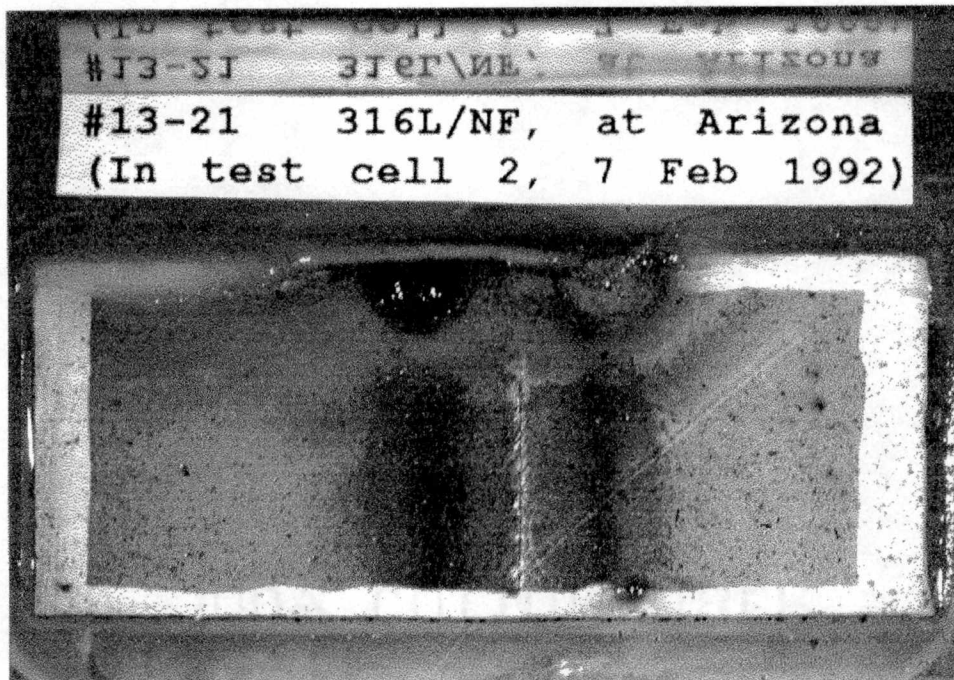


Figure 3-36. Photograph of 316L/None, incomplete penetration, after 140-day exposure at the Arizona field site.

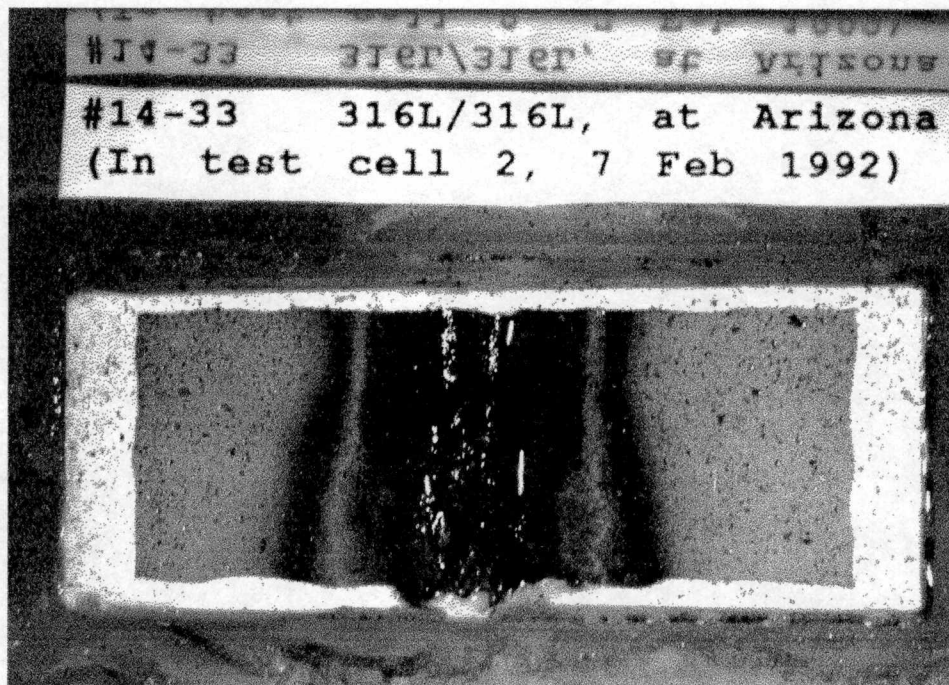


Figure 3-37. Photograph of 316L/316L, purge removal after root pass, after 140-day exposure at the Arizona field site.

electropolished), or mechanically-cleaned surfaces (Figure 3-29, ground), as indicated in Table 3-3. The nodules formed at the interfaces between the coupon and the epoxy coating within the heat-tint area. The nodules had a reddish appearance and were 1-8 mm in diameter. It was difficult to remove the nodules because of relatively hard surfaces and firm attachments. Following removal from the coupon surfaces, the inside of the nodules appeared black. One fluid sample was successfully taken from within one of the nodules before scraping to evaluate the pH. The pH was approximately 4.

Typical open-circuit potential (OCP) variations for the platinum electrodes and the weldment coupons as a function of exposure time are shown in Figure 3-38. The platinum electrodes exhibited a fairly constant redox potential of about +500 mV(SHE) for the well water. The OCPs for most of the weldment coupons began at lower potentials (in the range of 0 to +200 mV(SHE)) and ended at approximately the same value as the platinum electrodes. No OCP decrease for the weldment coupons occurred.

3.2.2. Nodule Analysis

The SEM examination revealed that the nodules were composed of small particles which clustered together to form a material with a porous structure (Figure 3-39). Charging was obviously caused by this non-conducting material which appeared to be corrosion products. EDS showed that the nodule was rich both in metallic elements from the corrosion products and inorganic materials which may be related to the activities of the microorganisms or associated with the surrounding environment. The backscatter images

Table 3-3. Corrosion Characterization on Specimens of Arizona ground water field tests.

Specimens	Corrosion Cell 1		Corrosion Cell 2	
	Nodule Formation	Extent of Corrosion	Nodule Formation	Extent of Corrosion
#1 304L/308L, F, No Treatment	Yes	Metal Loss	Yes	Metal Loss
#2 304L/308L, F, Pickled	No	No	No	No
#3 304L/308L, F, Electropolished	No	No	No	No
#4 304L/308L, F, SA+WQ+Pickled	No	No	No	No
#5 304L/308L, F, Ground	No	No	No	No
#6 304L/316L, F, No Treatment	Yes	Metal Loss	Yes	Incipient
#7 304L/308L, F, Purge Rem. aft. RP	Yes	Incipient	Yes	Incipient
#8 304L/None, F, Fuse Root Pass	Yes	Incipient	Yes	Incipient
#9 304L/None, I, No Treatment	Yes	Incipient	Yes	Incipient
#11 316L/316L, F, No Treatment	Yes	Incipient	Yes	Metal Loss
#12 316L/None, F, Fuse Root Pass	Yes	Metal Loss	Yes	Incipient
#13 316L/None, I, No Treatment	Yes	Incipient	Yes	Incipient
#14 316L/316L, F, Purge Rem. aft. RP	Yes	Incipient	Yes	Incipient

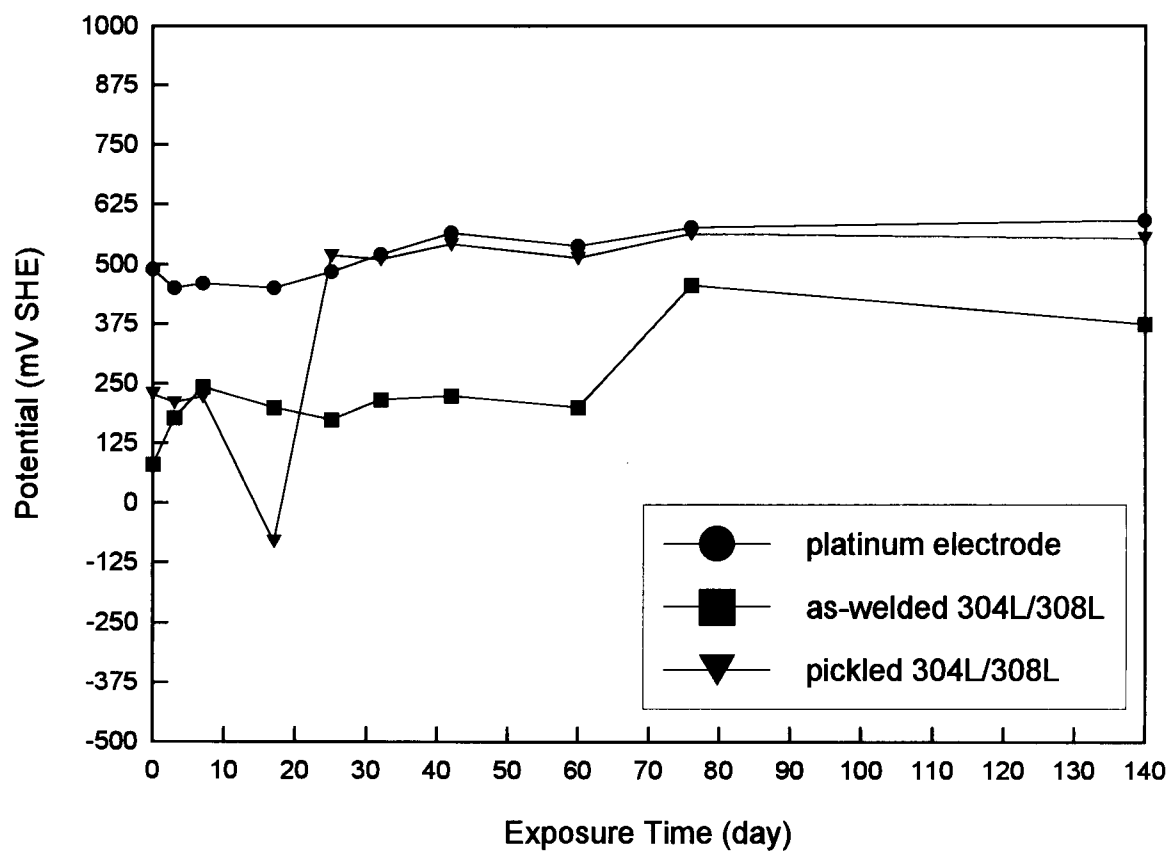


Figure 3-38. Open-circuit potentials of the platinum electrode, and the as-welded and pickled 304L/308L weldment coupons as a function of exposure time at the Arizona field site.

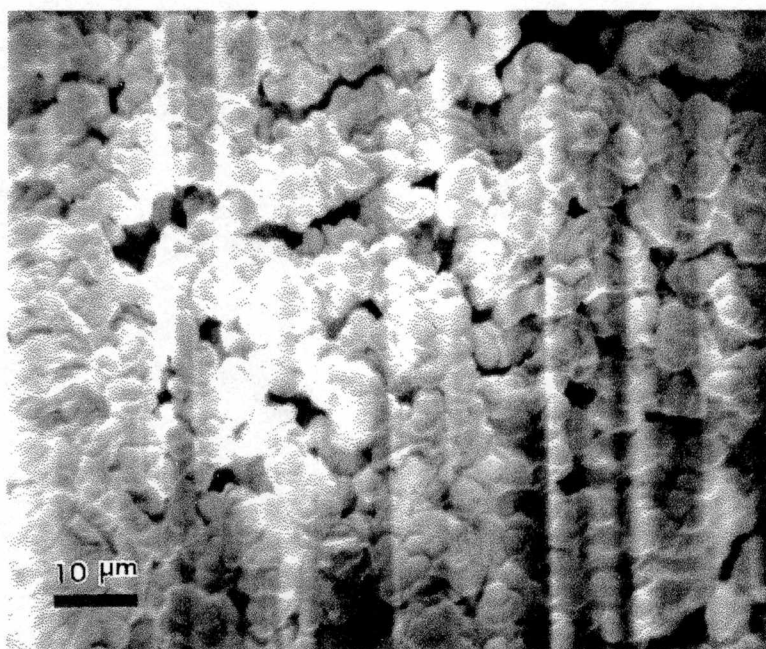


Figure 3-39. SEM micrograph (1000X) showing corrosion products of the nodule.

showed significant differences in contrast compared to the secondary images. Some of the areas in the backscatter images were brighter than in the secondary images. This indicated that the chemical composition in the nodule varied with location. The outer regions of the nodule were rich in light elements such as silicon, while the inner region was rich in heavier elements such as iron and chromium. With regard to the EDS results, the chromium peak from within the nodule was higher than that from the nodule surface, whereas the iron peak was higher at the nodule surface.

After removing the epoxy coating adjacent to the corrosion nodules, bright, shiny surface areas (characterized as "incipient" corrosion) were evident. These bright, shiny surface areas were indicative of areas which were no longer passive and were actively corroding. Furthermore, significant metal loss was observed at several locations (Figure 3-40). These observations indicated that an active corrosion process had taken place under the coating; some of the locations exhibited relatively uniform corrosion, others exhibited very localized corrosion. The overall results are summarized in Table 3-3.

3.2.3. Microbiological Analyses

AODC counts in the water samples showed cell numbers on the order of 10^5 cells/ml. Counts taken from within the nodules ranged from 10^6 to 10^7 cells/nodule. Although slides were examined for the presence of iron bacteria of the species *Gallionella*, none were found. These results are given in Table 3-4.

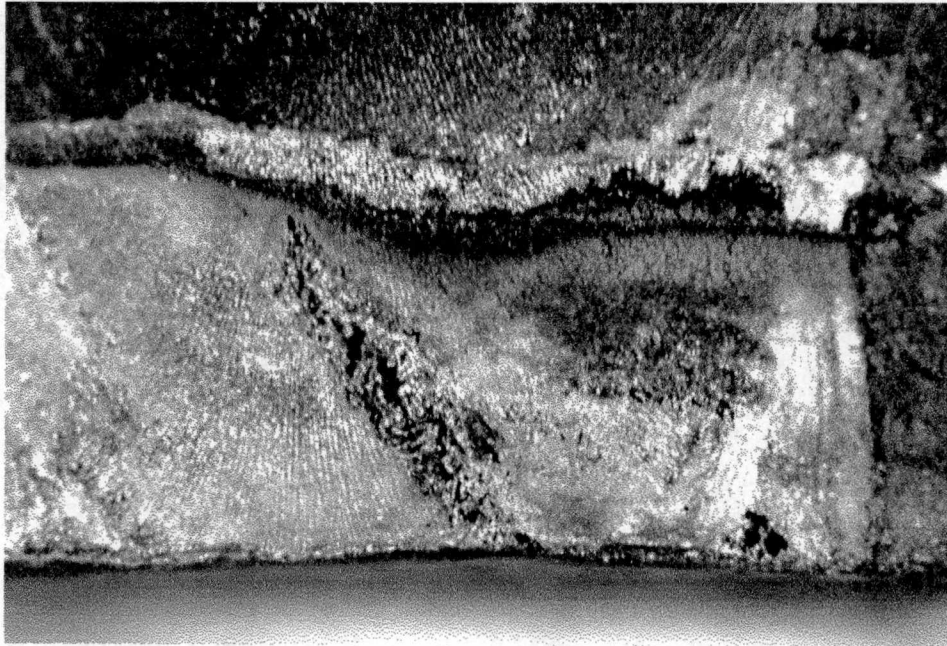


Figure 3-40. Photograph of a close-up view of surface after corrosion nodule and epoxy coating removal showing a metal loss site.

Table 3-4. Total Bacteria from AODC Counts

Sample Number	Origin	Total Cells
Water #1	Water, Test Cell 1	$9.9 \times 10^5/\text{ml}$
Water #2	Water, Test Cell 2	$1.9 \times 10^5/\text{ml}$
Coupon #1	Nodule, Test Cell 1	$2.1 \times 10^7/\text{nodule}$
Coupon #6	Nodule, Test Cell 1	$3.1 \times 10^7/\text{nodule}$
Coupon #13	Nodule, Test Cell 1	$4.3 \times 10^6/\text{nodule}$
Coupon #1	Nodule, Test Cell 2	$1.6 \times 10^7/\text{nodule}$
Coupon #8	Nodule, Test Cell 2	$8.2 \times 10^6/\text{nodule}$
Coupon #12	Nodule, Test Cell 2	$9.2 \times 10^6/\text{nodule}$
Coupon #13	Nodule, Test Cell 2	$1.1 \times 10^7/\text{nodule}$

and Sulfur Oxidizing Bacteria Counts

Sample Number	Origin	Cell Numbers
Water #1	Water, Test Cell 1	Between 10^3 and $10^4/\text{ml}$
Water #2	Water, Test Cell 2	Between 10^2 and $10^3/\text{ml}$
Coupon #1	Nodule, Test Cell 1	None
Coupon #6	Nodule, Test Cell 1	Between 10^1 and $10^2/\text{nodule}$
Coupon #13	Nodule, Test Cell 1	None
Coupon #1	Nodule, Test Cell 2	Between 10^3 and $10^4/\text{nodule}$
Coupon #8	Nodule, Test Cell 2	Between 10^2 and $10^3/\text{nodule}$
Coupon #12	Nodule, Test Cell 2	Between 10^1 and $10^2/\text{nodule}$
Coupon #13	Nodule, Test Cell 2	Between 10^2 and $10^3/\text{nodule}$

SRB cultures from water samples and nodules were all negative. These results were consistent with results from a previous experiment at Palo Verde using the same fire-protection-system well water.

Some evidence was found for the presence of sulfur oxidizing bacteria in low numbers. The pH of the sulfur oxidizing media was initially 4.8. After incubating for one month, those tubes showing turbidity also showed a drop in pH. Results are shown in Table 3-4. The number of sulfur oxidizing bacteria was found to range from 10^2 to 10^4 cells/ml for the water samples taken directly from the test cells. Bacterial counts from nodules were found to range from 0 to 10^4 cells/nodule.

3.2.4. Summary

The results were not conclusive as to the role the bacteria played in nodule formation and the metal loss that occurred under some nodules. Generally, the number of bacterial cells in the nodules (10^7 /nodule) and the number of bacterial cells in the water (10^5 /ml) are considered to be too low to account for MIC. Also, no SRB were present in the well water. The OCPs of the weldment coupons did not show any potential drop even though there were relatively large corrosion nodules on the coupon surfaces. Microscopic examination revealed that incipient corrosion and metal loss occurred beneath the nodules at the areas covered by the epoxy coating. The potential readings and the microscopic examinations indicated that the extent of corrosion was relatively small, i.e., deep pitting had not occurred. It also can be rationalized that since the coupons had a large test area

(12-14 cm²) in comparison to the active corrosion areas, the corrosion current was not high enough to cause a measurable decrease in OCP. Through examination of the nodules and the areas beneath the adjacent epoxy coating, it was found that the nodules possessed the significant characteristic that they always formed at the interface between the coupon surface and epoxy coating, which can be considered a crevice site. Furthermore, the location of the corrosion nodules was always associated with the heat-tint region rather than the base metal. Apparently, the oxide layer created during welding was the least corrosion resistant region of the weldment. More generally, the overall results suggested several possibilities: (a) that the mounting epoxy adhered to the base metal, but did not adhere as well as to the oxide-covered heat-tint region, thus creating crevice sites at the epoxy/metal interface in the heat-tint region but not in the base metal, (b) that crevice regions were formed at the interfaces for both the base metal and heat-tint region, but that the inherent corrosion resistance of the heat-tint region was less than that of the base metal, or (c) a combination of the above possibilities. Therefore, the possibility of, and the nature and extent of, pre-existing crevice configurations at the metal/epoxy interface must be considered important issues with regard to the overall behavior.

3.3. Advanced MIC and Crevice Corrosion Tests

A distinct characteristic of microbially influenced corrosion is that steels and stainless steels are subject to localized corrosion. This lends itself to an acceptance that bacteria, at least one of the causes, initialize localized corrosion due to localized

colonization. As soon as the corrosion starts, bacteria no longer tolerate the corrosion environment and the classic corrosion mechanisms take over. The previous laboratory and field tests did not establish that the localized corrosion in form of the nodule was directly associated with MIC initiation by the bacteria on the stainless steel weldments. What the results indicated was that the bacteria altered the chemical composition of the entire solution in which the weldments were tested. As a result, the weldments were exposed to a homogeneous environment wherein localized corrosion is not likely to occur. Therefore, efforts were put into the advanced MIC tests intended to cause the initiation of localized corrosion by the bacteria. In addition, corrosion behaviors of the weldments were studied by electrochemical polarization. Also, attempts to separate the bacteria influences from the other factors were made in the new control tests. The crevice corrosion issue was resolved in the crevice corrosion tests conducted at the Arizona field site using the Arizona ground water.

In MIC tests, the possible crevice geometry was eliminated by not over-coating the specimen surface to be exposed; strictly speaking, only the backside and edges of the specimen were covered, and the coating and the oxide on the specimen surface were not overlapped. Also, all the specimens used in the tests were as-welded 304L/308L weldment with no further surface treatment.

3.3.1. Immersions at Different Water Level

The experiment was accomplished by exposure of two weldments, one with complete immersion, the other with the specimen surface barely above the water level with the solution being dripped onto the specimen surface. The purpose of this set-up was to attract bacteria onto the specimen surface because of the enriched medium. The open-circuit potentials of the weldments and platinum electrode as a function of exposure time are shown in Figure 3-41. The potentials, of both specimens and platinum which were initially immersed completely into the solution, drop quickly after bacteria inoculation. When the water flow started, the water level was controlled so that one of the specimens had the exposed surface flush with the water level. It is seen that the potential of this specimen rose rapidly to almost the value that the specimen began with and then leveled off for the rest of exposure. The potentials of the other specimen and platinum, both immersed completely in the water, remained at the lower potentials until the end of exposure. During the exposure, a SRB count was made from the water sample, demonstrating a quantity of 10^3 - 10^4 SRB per ml. Visual examination of both specimens after the test did not show any incipient corrosion or nodule formation either at the specimen surface or at the metal/epoxy interface.

Most of the bacteria in the consortium were oxygen-consuming, aerobic bacteria. Since the specimen at water level always received a fresh, oxygen saturated solution, and the specimen immersed into the water was exposed to a bacterial solution, it suggests that there was an oxygen concentration gradient as a function of water depth. The corrosion

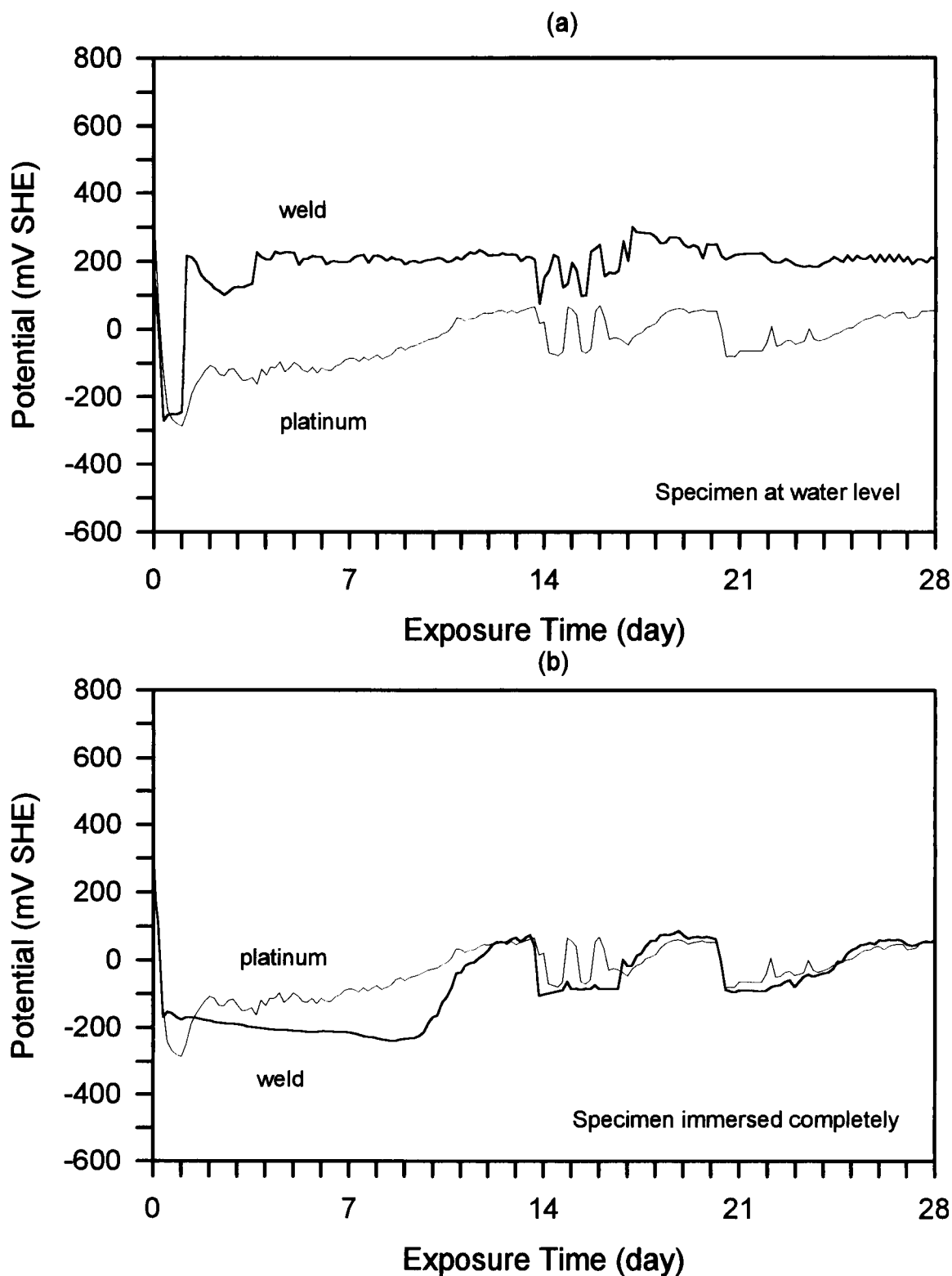


Figure 3-41. Corrosion potentials as a function of exposure time in (a) the specimen at water level, (b) the specimen immersed into water completely.

potential difference between the two specimens reflected the extremes of oxygenated and deoxygenated situations. The purpose to initiate MIC by bacteria aggregation was not achieved. The solution dropping and impacting on the specimen surface by gravity could have affected the bacteria attachment. The experiment did show that the new method of epoxy coating to create the exposed corrosion window was effective in eliminating the crevice related corrosion.

3.3.2. The Consortium with Addition of *Gallionella* sp.

Gallionella sp. is an iron oxidizing bacterium, which oxidizes ferrous ion to ferric ion during metabolism. It is believed by many that MIC in stainless steel alloys is most likely caused by iron bacteria. The test on the as-welded weldments was conducted using *Gallionella* sp. in addition to the bacteria consortium. The corrosion potentials of the specimens as a function of exposure time are shown in Figure 3-42. Again, the potentials dropped rapidly after bacteria inoculation and then stayed in the very negative potentials, which resulted from the deoxygenation. *Gallionella* is an aerobic bacterium, indicating it needs oxygen to survive. The shortage or depletion of oxygen was taken into account whether the bacteria were effective or not. As a result, beginning on the 16th day of the exposure, the corrosion cell was oxygenated by sparging oxygen through the rest of the exposure. It is noted that the potentials (Figure 3-42) rose immediately to positive potentials. During that time a thick biofilm was developed on each specimen surface. Then, the potentials of the specimens decreased with time and finally the negative

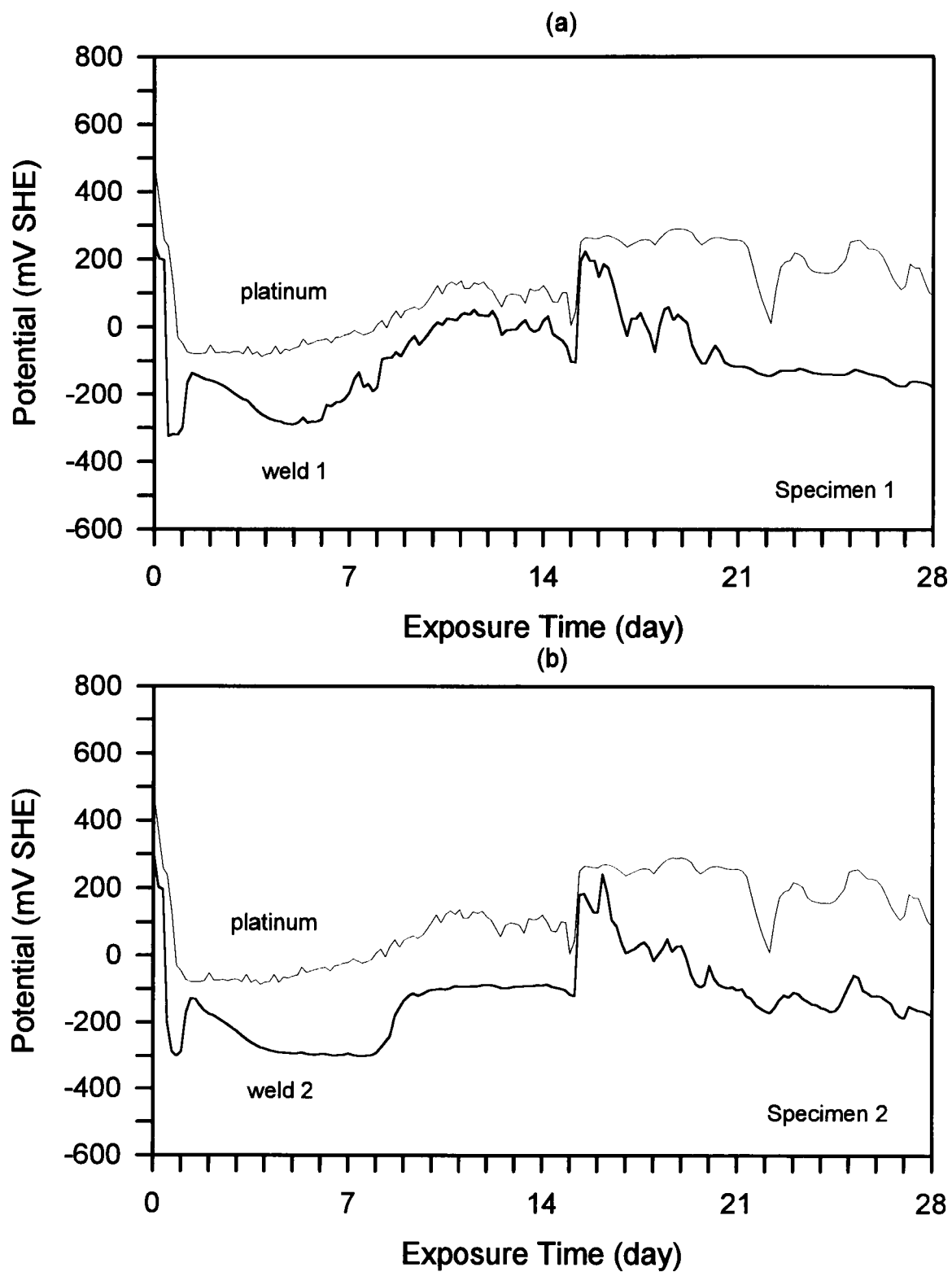


Figure 3-42. Corrosion potentials as a function of exposure time in bacterial solution (Consortium+Gallionella); (a) Specimen 1, (b) Specimen 2.

potentials were restored. The potential rise and then decrease demonstrated that even when the bulk solution is oxygenated, the environment underneath the biofilm can be very well deoxygenated. After the exposure a surface biofilm about 5 mm in thickness was found on each specimen. The film was sticky and viscous but was not adherent to the specimen surface and as such it was easy to flush off. No nodule was observed after removing the thick biofilm.

3.3.3. The Consortium with Addition of Thiobacillus sp.

Thiobacillus sp., a sulfur oxidizing bacterium, is known for oxidizing ferrous ions to ferric ions. The test was run on the as-welded weldments with the addition of Thiobacillus bacteria to the bacteria consortium. The corrosion potentials are depicted in Figure 3-43. As with the Gallionella test, the corrosion cell was oxygenated by sparging oxygen beginning on the 16th day of the exposure time. Surface examination of the specimens after the test did not show nodule formation or any incipient corrosion.

The iron bacterium, Gallionella or Thiobacillus, did not result in any apparent increase in bacterial aggressiveness in the above tests. From a corrosion engineering point of view, iron bacteria require a unique environment. They need oxygen and ferrous ions to survive. Thermodynamically, ferrous ions will be oxidized to ferric ions when oxygen is present in a solution. The argument seems to suggest that iron bacteria live under a condition that ferrous ions and oxygen could co-exist. Such an environment could be

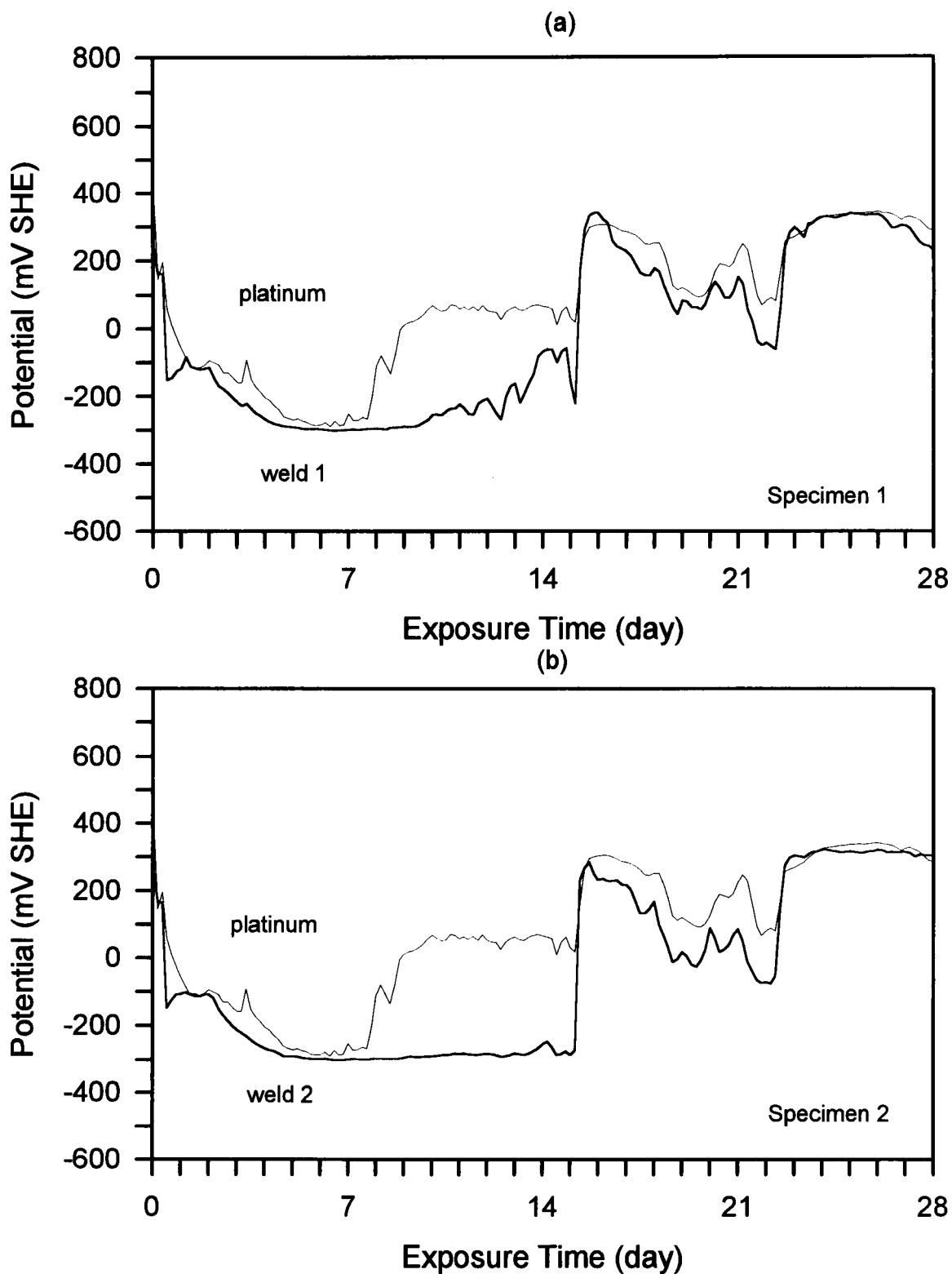


Figure 3-43. Corrosion potentials as a function of exposure time in bacterial solution (Consortium+Thiobacillus); (a) Specimen 1, (b) Specimen 2.

found at an iron surface with an appropriate biofilm, where the iron provides the ferrous ion source and the biofilm creates a situation that a certain amount of oxygen is available to iron bacteria but not enough to oxidize ferrous to ferric. Apparently, this scenario is difficult to achieve under laboratory conditions.

3.3.4. MIC Test with Air Sparging

Oxygen sparging during the tests might suppress the anaerobic bacteria activities. A test on the as-welded weldments was conducted using the bacteria consortium with air sparging. The corrosion potentials as a function of time are illustrated in Figure 3-44. The potential profile was essentially equivalent to those in the previous Tennessee River water laboratory tests, indicating that the solutions with and without air sparging had the similar effect on the cathodic reactions. The decrease in the potentials at day nine was a result of combined effects of the dilution rate and the biofilm coverage. No nodules were found on the specimen surfaces in the 14-day exposure.

3.3.5. MIC Test with A Single Strain of A6F

A6F is a facultatively anaerobic bacterium which demonstrated its aggressiveness in earlier MIC experiments.⁷² A single strain of A6F was selected to run immersion tests on two as-welded weldments. Air was sparged into the corrosion cell throughout the exposure. To further test the previous crevice-related corrosion, one of the specimens

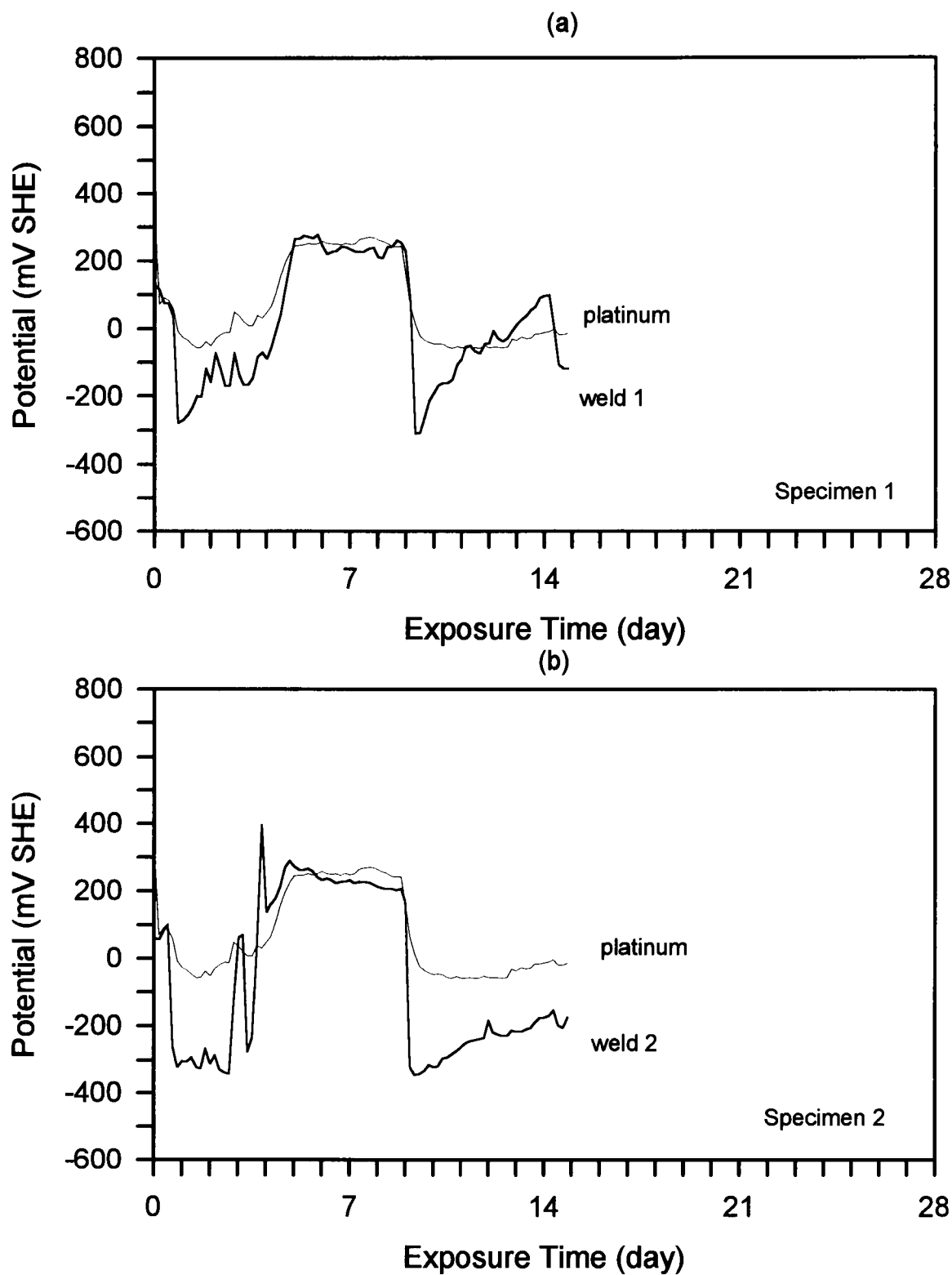


Figure 3-44. Corrosion potentials as a function of exposure time in the bacterial solution with air sparging; (a) Specimen 1, (b) Specimen 2.

was coated with epoxy by overlapping the oxide on the surface, the other one by not coating the oxide on the surface. The corrosion potentials and the platinum potential as a function of exposure time are shown in Figure 3-45. Once again, no potential drop caused by corrosion can be seen from the potential profiles. Post-exposure visual examination on both specimens showed that the one without the epoxy overlapping the oxide exhibited was corrosion free (Figure 3-46), and the one with the epoxy overlapping the oxide had corrosion nodules at the epoxy interface in the weld region (Figure 3-47).

3.3.6. Potentiostatic Constant-Potential Test

As discussed in the literature review, many MIC cases are revealed when a piping system undergoes a hydrostatic water test and then idles under a stagnant condition for a short period of time. It seems that bacteria become so aggressive that a through-wall pipe penetration can take place in as short a time as a few weeks. The reasons for this type of MIC can be rationalized in that the bacteria are effective at some areas inside a pipe where anodic reactions occur, for instance, the areas covered with the residual water, and the surrounding areas support cathodic reactions because moisture condensate exists in the pipe. If such a scenario exists, the galvanic corrosion certainly is taken into account because bacteria are capable of generating the driving force for the galvanic current. As introduced in the early laboratory tests, there exhibited a 500 mV difference in the OCP between the specimens in the bacterial and control solutions. To study this effect, potentiostatic tests were run at an applied potential of 500 mV vs SHE and then the

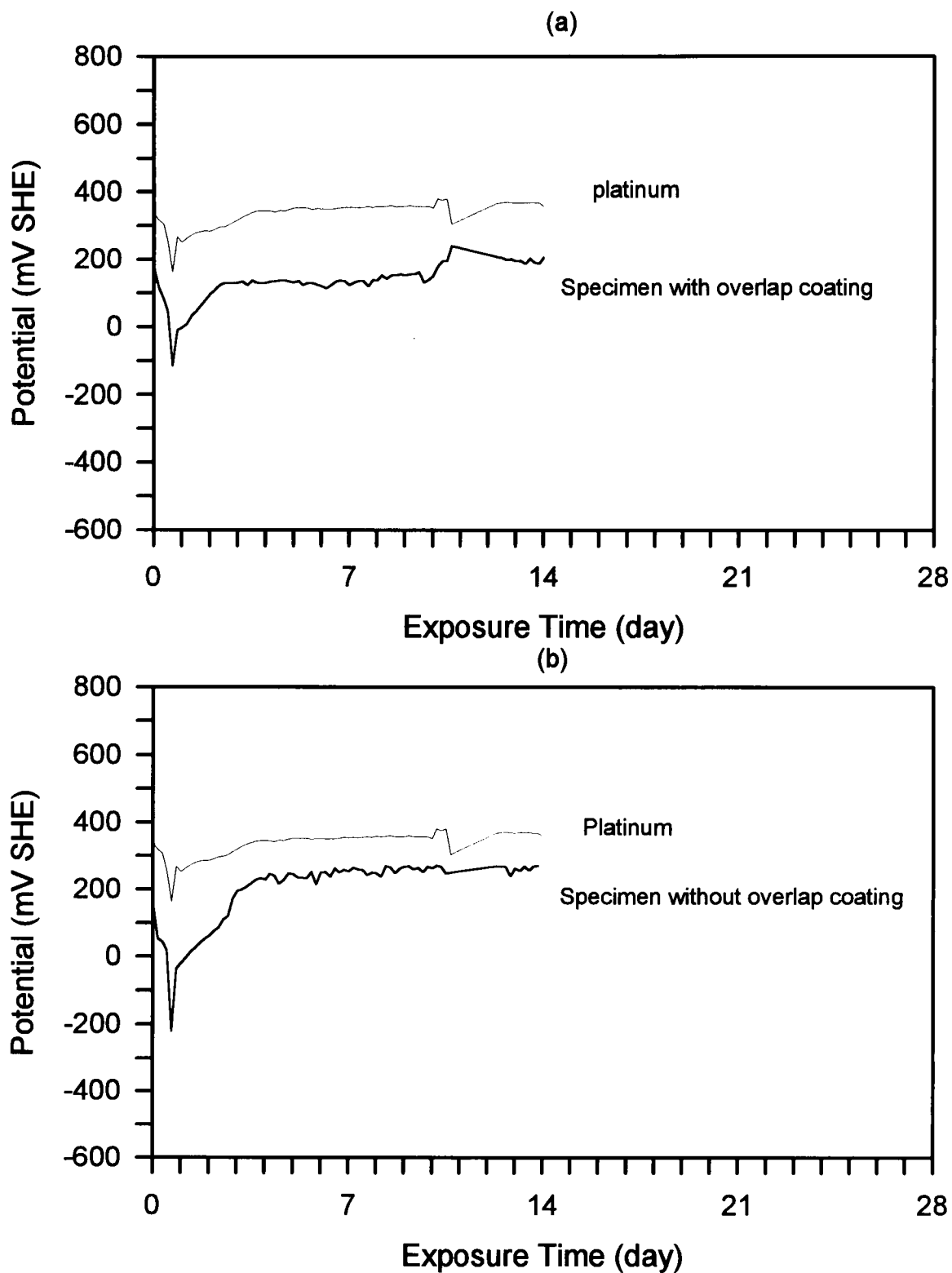
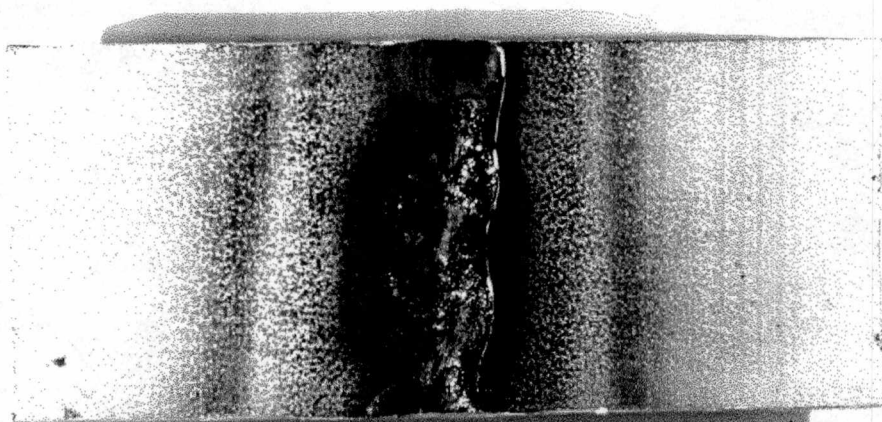
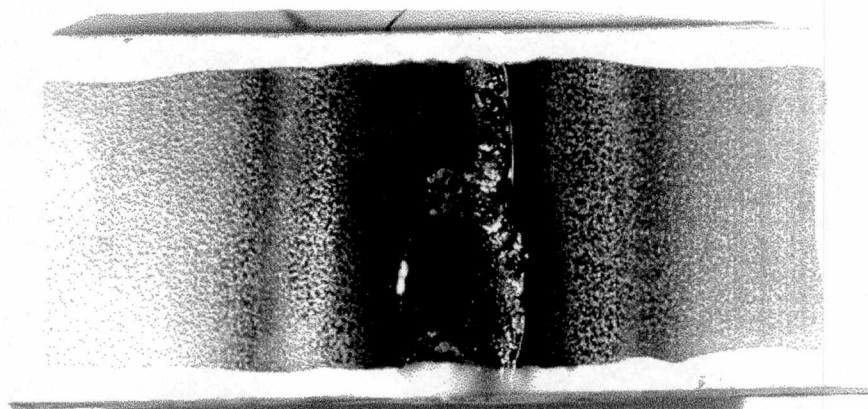


Figure 3-45. Corrosion potentials as a function of exposure time in A6F solution with air sparging; (a) Specimen with overlap coating, (b) Specimen without overlap coating.



#1 304L/308L, F, No Treatment.
Without overlap paint. (Exposure
to the A6F single strain bacteria
for 15 days. 22 Sep 1993)

Figure 3-46. The as-welded specimen without overlap coating showing corrosion free after exposure to the A6F solution.



#1 304L/308L,F,No Treatment.
With overlap paint. (Exposure to
the A6F single strain bacteria
for 15 days. 22 Sep 1993)

Figure 3-47. The as-welded specimen with overlap coating showing corrosion nodules at metal/epoxy interface in the weld region after the exposure to the A6F solution.

resultant currents were examined on the as-welded weldments in the bacterial and control solutions, respectively.

Results of the constant-potential tests (Figure 3-48) showed that, before the constant anodic potential was applied, the OCP of the specimen in the bacterial solution exhibited a negative potential of -300 mV(SHE) and the OCP of the specimen in the control solution exhibited a positive potential of +200 mV(SHE). When the potential of +500 mV(SHE) was applied to the specimens, the resulting current density in the bacterial solution increased rapidly and continued to increase until the experiment was stopped (Figure 3-49). The resulting current density in the control solution increased to a relatively small value and stabilized for the rest of the exposure (Figure 3-49). Pitting occurred on the specimens in both the bacterial and control solutions. Through visual examination (Figure 3-50), however, more pits were found on the bacterial-solution specimen. In contrast, only one pit was found on the control-solution specimen. Most of the pits were concentrated at the transition region between the weld-oxide and base metal.

3.3.7. Anodic Polarization

The anodic polarization results for the as-welded and pickled 304L/308L weldment specimens in the solution without bacteria are shown in Figure 3-51. For comparison, the curve for the pickled and cathodically cleaned specimen also is shown in Figure 3-51. These polarization curves reveal passivation when the bacteria were not inoculated into the corrosion cells. The pickled specimen had a much higher pitting

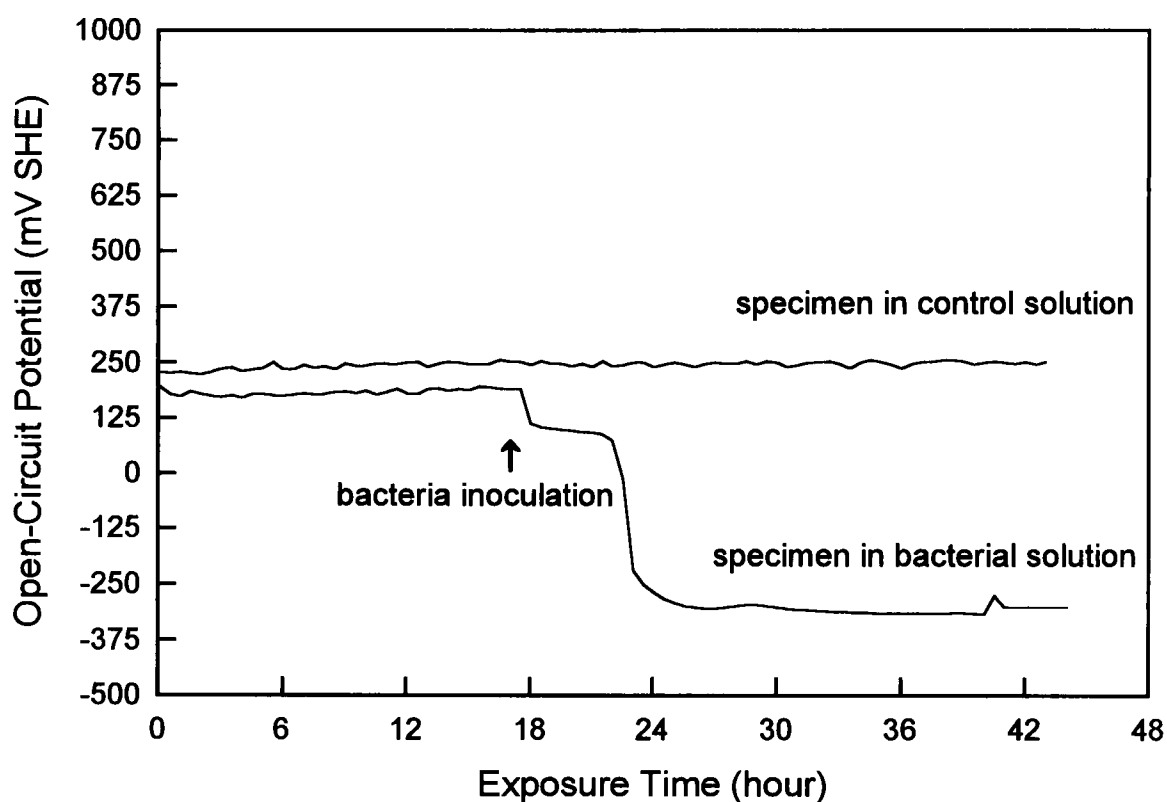


Figure 3-48. Open-circuit corrosion potentials of as-welded 304L/308L weldments in bacterial and control solutions before application of +500 mV (SHE) anodic potential.

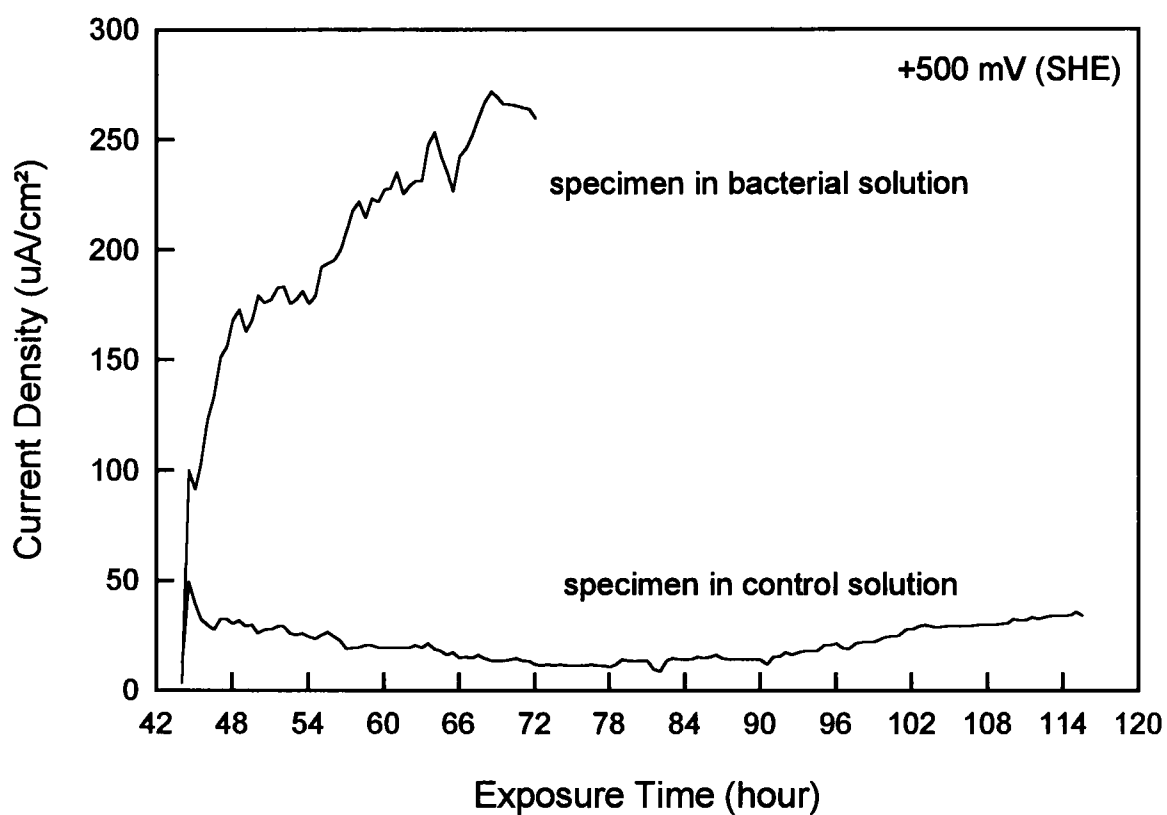


Figure 3-49. Anodic current densities at +500 mV (SHE) for as-welded 304L/308L weldments in bacterial and control solutions.

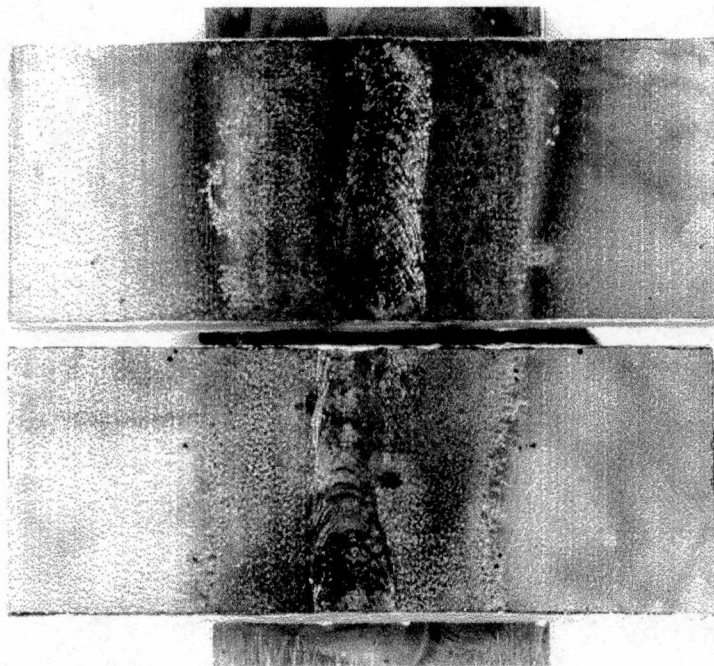


Figure 3-50. Photograph of the specimens after the test showing pits developed in the control solution (top specimen) and in the bacterial solution (bottom specimen).

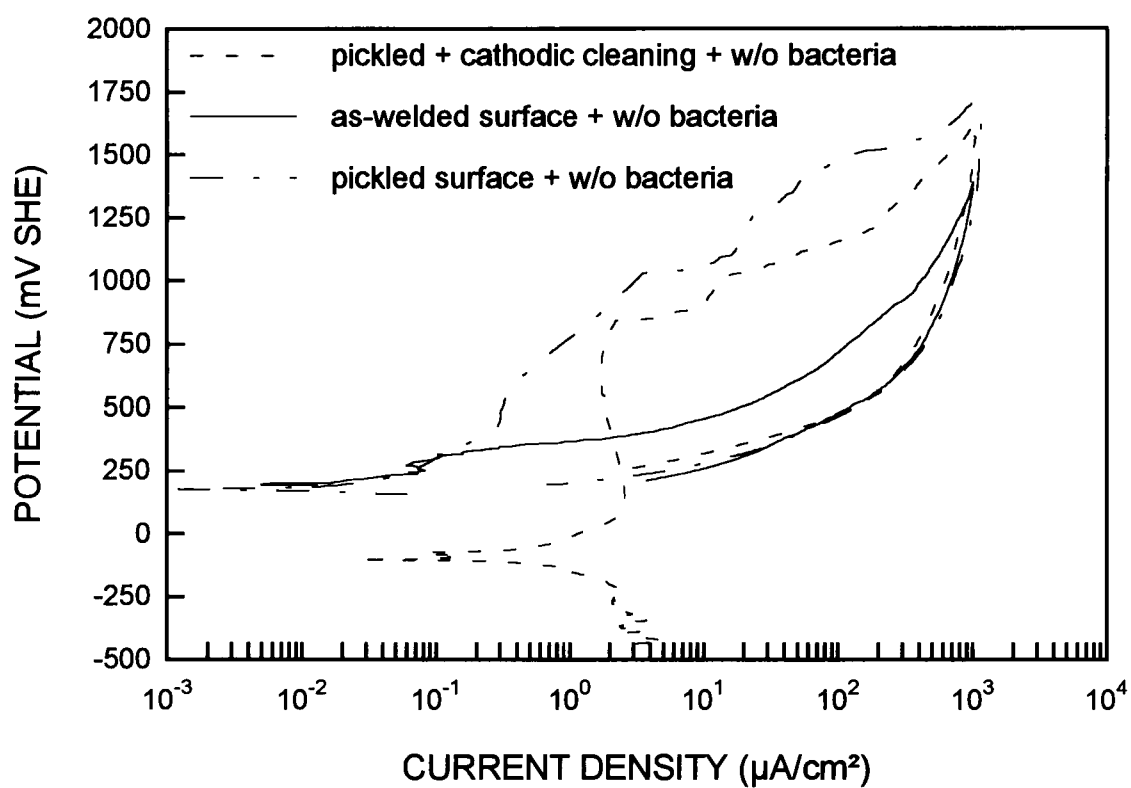


Figure 3-51. Cyclic anodic polarization of the as-welded, pickled and pickled plus cathodically cleaned 304L/308L weldments in the control solution.

potential than the as-welded specimen, implying deterioration caused by the welding oxide. The anodic polarization results in the solution with the bacteria are shown in Figure 3-52. Again, the curve for the pickled and cathodically cleaned specimen is presented in Figure 3-52 as a reference of corrosion behavior for the stainless steel weldment. It is noted that the curve for the pickled specimen showed passivation in the bacterial solution, which is consistent with that in the control solution. However, no passivation was indicated for the as-welded specimen, which demonstrates a striking difference made by the bacteria on the corrosion behavior of the stainless steel weldment. Duplication of the polarization curves on the as-welded specimens in the bacterial and control solutions, respectively, was made to show consistency of the data (Figure 3-53).

When the polarization measurements were made on the stainless steel weldments, it was found that the corrosion products turned black in the bacterial solution and red-brown in the control solution. In the light of the Pourbaix diagram of iron, the corrosion product in a less aerated solution is magnetite at pH of 7, which is black in color. Under an adequate aerated condition, the corrosion product is hematite or ferric hydroxide which is red-brown in color. This again is supportive that deoxygenation by the bacteria accounts for the corrosion behaviors of the stainless steel weldments. Furthermore, polarization on the as-welded specimen depicted in Figure 3-53 was made in the control solution using nitrogen to deaerate the solution. The curve shows passivation more clearly than that without nitrogen deaeration while the breakdown potential remained the same. In comparison to the polarization in the bacterial solution, the curve also shows that the extent of deaeration by the bacteria was more efficient than that by sparging nitrogen.

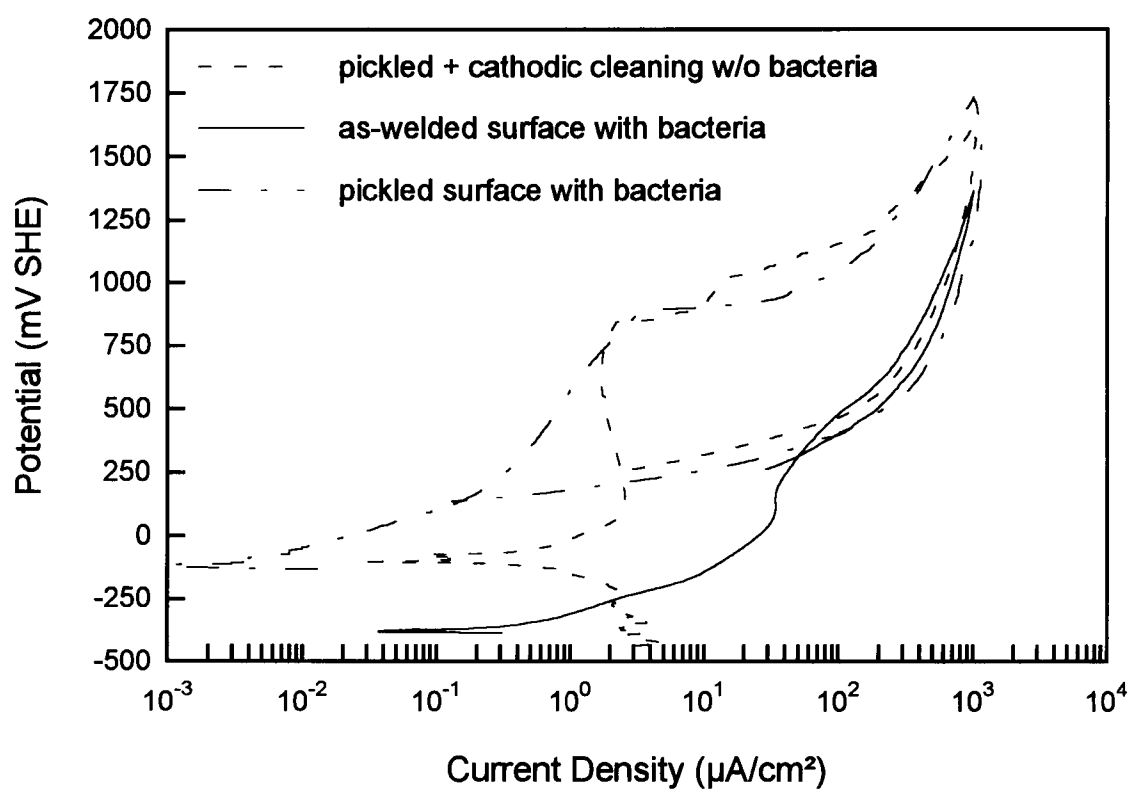


Figure 3-52. Cyclic anodic polarization of the as-welded, pickled and pickled plus cathodically cleaned 304L/308L weldments in the bacterial solution.

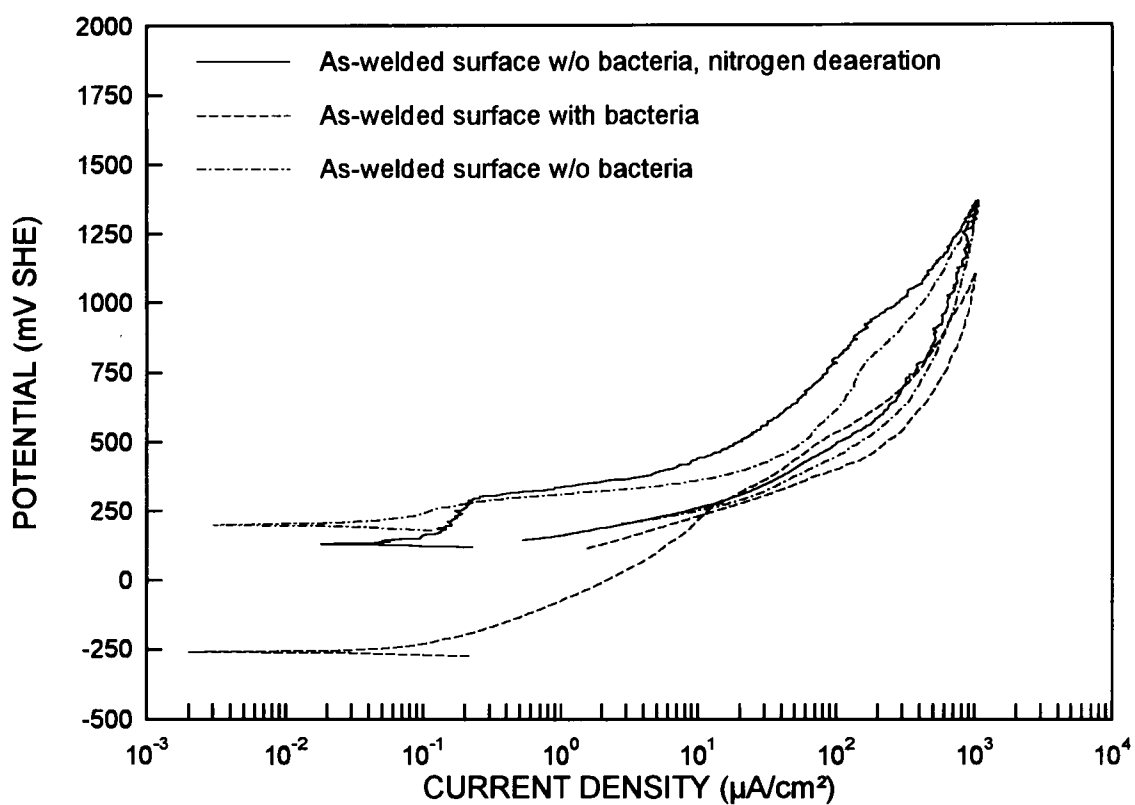


Figure 3-53. Duplication of polarization on the as-welded specimens in the bacterial and control solutions, and the as-welded specimen in the control solution using nitrogen deaeration.

3.3.8. Control Tests

In the additional control tests, the specimens selected were from the #1, #6, #8, and #9 weldments which had the welding oxide on the surfaces. Corrosion nodules were found at the metal/epoxy interface and within the heat tint region after the 90-day exposure. The results of the additional control tests under different possible-contamination conditions are summarized in Table 3-5. The table illustrates that more nodules were found under the "worst contamination" condition and that the "better" control tests led to fewer nodules. Since corrosion nodules are noted under all circumstances, the results suggest that the nodules were initiated by the crevice condition and that corrosion might be accelerated by the microbial activities.

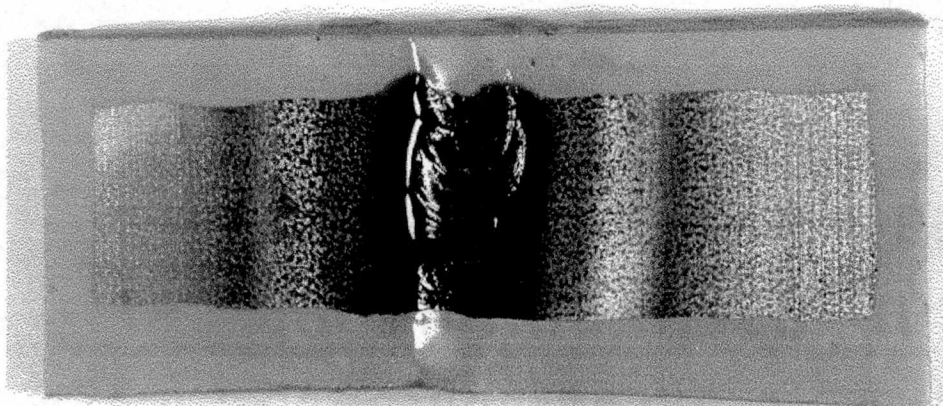
3.3.9. Chloride Tests

The results of the additional control tests, with different chloride concentrations, showed that corrosion nodule formation was found at the metal/epoxy interface in the heat tint area for the specimen in the 100 ppm chloride solution (Figure 3-54). The specimen exposed to the zero-chloride solution was corrosion-nodule free (Figure 3-55). In the 10 ppm chloride solution, which corresponded to the chloride level in the actual Tennessee River water, no corrosion nodules were observed regardless of the weld-oxide and crevice geometry (Figure 3-56). These results indicate that the chloride concentration plays a key role in the initiation of nodules.

Table 3-5. Additional control tests showing corrosion nodule number and size developed under various control circumstances.

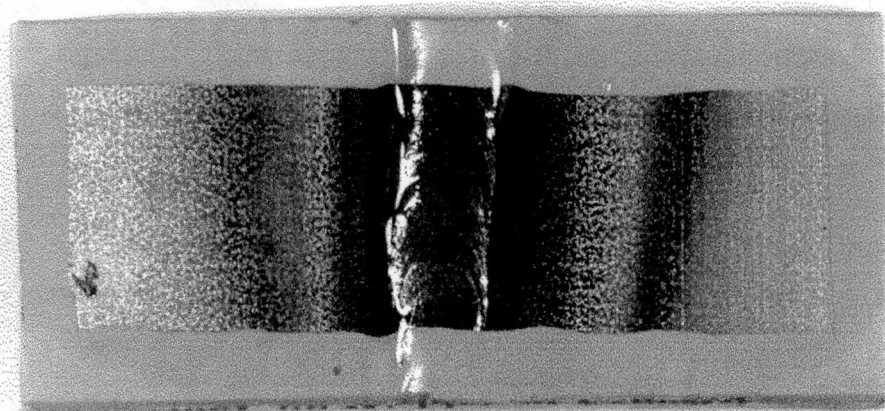
Coupon Number	Cell Open to the Air, with Carbon Sources		Sterilized Cell, with Carbon Sources		Sterilized Cell, without Carbon Sources		Sterilized Cell, without Carbon Sources, with Biocide Addition	
	Number	Size	Number	Size	Number	Size	Number	Size
1	Yes-10	L:1, S:1	Yes-3	L:1, S:1	Yes-9	L:2, S:1	Yes-3 No No	L:1, S:1
6	Yes-2	L:1, S:1	No		Yes-4	L:2, S:1	No	
8	Yes-1	L:1	No		No		No	
9	Yes-2	L:3, S:1	No		No		No	

Size: L (Largest), S (Smallest), 1 (1 mm)



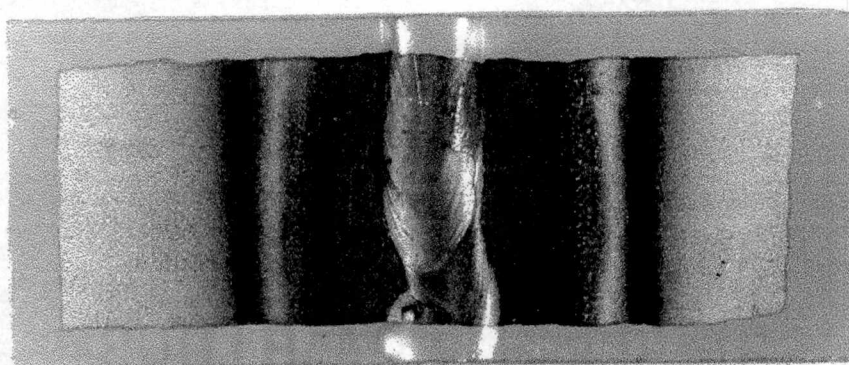
**304L/308L SS Weldment Exposed to a
Sterilized, Simulated Tennessee River
Water with 100 ppm Cl^- for 96 Days**

Figure 3-54. Photograph of the as-welded specimen after the chloride test showing corrosion nodules.



**304L/308L SS Weldment Exposed to a
Sterilized, Simulated Tennessee River
Water without Cl^- for 96 Days**

Figure 3-55. Photograph of the as-welded specimen after the chloride test showing corrosion free surface with the zero-chloride concentration.



304L/308L SS Weldment Exposed to a
Sterilized, Simulated Tennessee River
Water with 10 ppm Cl^- for 113 Days

Figure 3-56. Photograph of the as-welded specimen after the chloride test showing corrosion free surface with 10 ppm chloride concentration.

3.3.10. Crevice Tests

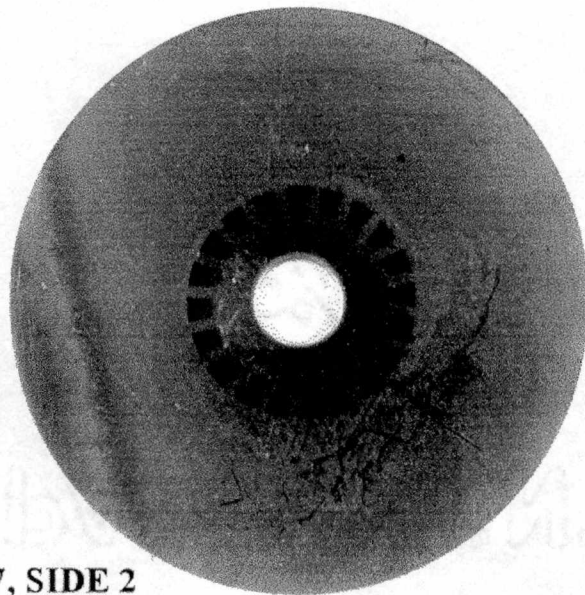
The results of the LaQue crevice-corrosion tests on 304L and 316L base-metal coupons are summarized in Table 3-6. The 304L base-metal plates (4 specimens having 160 crevice sites) exhibited no visible crevice corrosion. The 316L base metal plates (4 specimens having 160 crevice sites) also exhibited no visible crevice corrosion (Figure 3-57), except at two crevice sites which were "etched" (no measurable depth, Figure 3-58).

The UT 304L/308L crevice-corrosion coupons, following the 148-day exposure, are illustrated in Figure 3-59 through Figure 3-62. Corrosion occurred on the creviced coupons with as-welded surfaces (Figure 3-59) but not on the creviced coupons with pickled surfaces (Figure 3-60). The non-creviced coupons with both as-welded surfaces (Figure 3-61) and pickled surfaces (Figure 3-62) were all corrosion free. The creviced coupon with the as-welded surface showed that pitting had occurred along the crevice locations in the heat-tint region. No corrosion was found in the base-metal although the crevice geometry was present over both the base-metal and the heat-tint region. The creviced coupon with the pickled surface showed no visible corrosion at any location. The creviced as-welded coupon and the creviced pickled coupon, after water/soft-brush cleaning, are compared in Figure 3-63. The results are summarized in Table 3-7.

The results of the crevice tests showed that localized corrosion and nodule formation occurred only in the heat-tint regions of the as-welded coupons and only when a crevice geometry existed, i.e., the corrosion did not occur in the base-metal regions of creviced as-welded coupons, nor on creviced base-metal specimens, nor on creviced

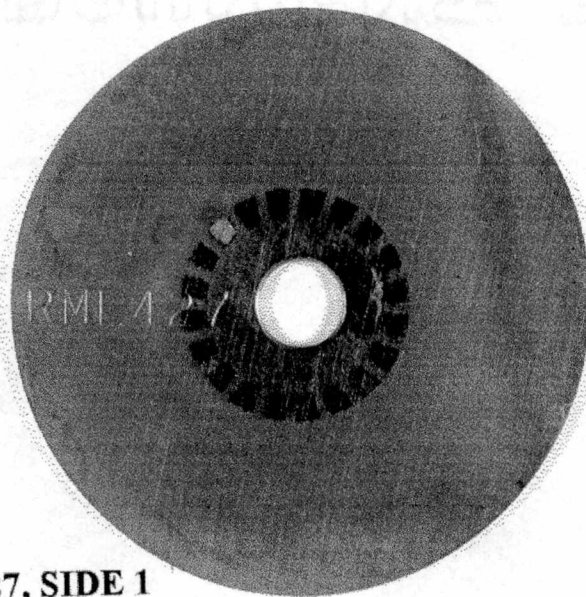
Table 3-6. Type 304L and 316L Crevice Corrosion Tests (Arizona Ground Water)

304L Base Plate Specimen	Depth of Pitting (mils)		
	Boldly Exposed		40 Creviced Sites
	Average	Max	Max
Rack A-1, ULL 861	0	0	0
Rack A-2, ULL 857 ⁽¹⁾	0	0	0
Rack B-1, ULL 860	0	0	0
Rack B-2, ULL 859	0	0	0
316L Base Plate Specimen			
Rack B-1, RML 427	0	0	<1 ⁽²⁾
Rack B-2, RML 429	0	0	<1 ⁽²⁾
Rack A-1, RML 425	0	0	0
Rack A-2, RML 428	0	0	0 ⁽²⁾
⁽¹⁾ Multihued deposit near one edge, not apparently corrosion related.			
⁽²⁾ 1 of 40 creviced sites specimen 427 and 429 was etched over whole area of 1 site to no measurable depth.			



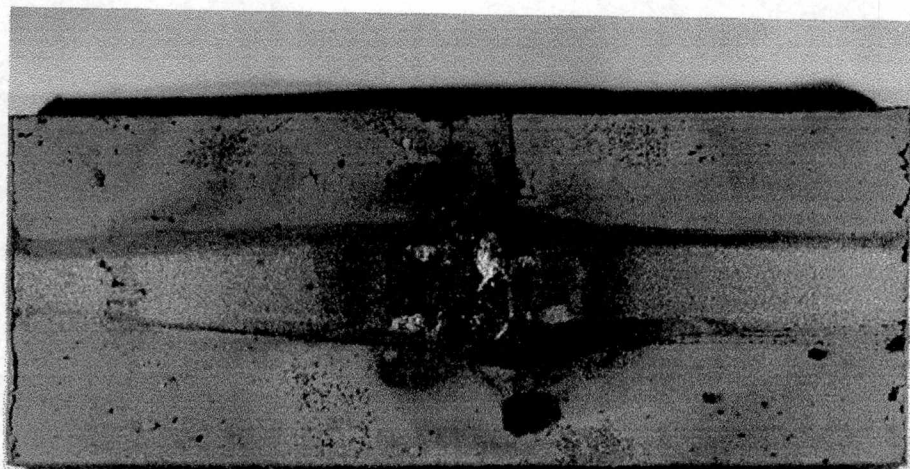
RML 427, SIDE 2

Figure 3-57. Photograph of Type 316L base metal after the crevice test showing a corrosion free surface.



RML 427, SIDE 1

Figure 3-58. Photograph of Type 316L base metal after the crevice test showing one of the crevice sites subject to minus corrosion.



1/24 AS-WELDED, CREVICED

Figure 3-59. Photograph of the as-welded and creviced specimen subject to a crevice corrosion attack in the heat tint region after 148-day exposure.

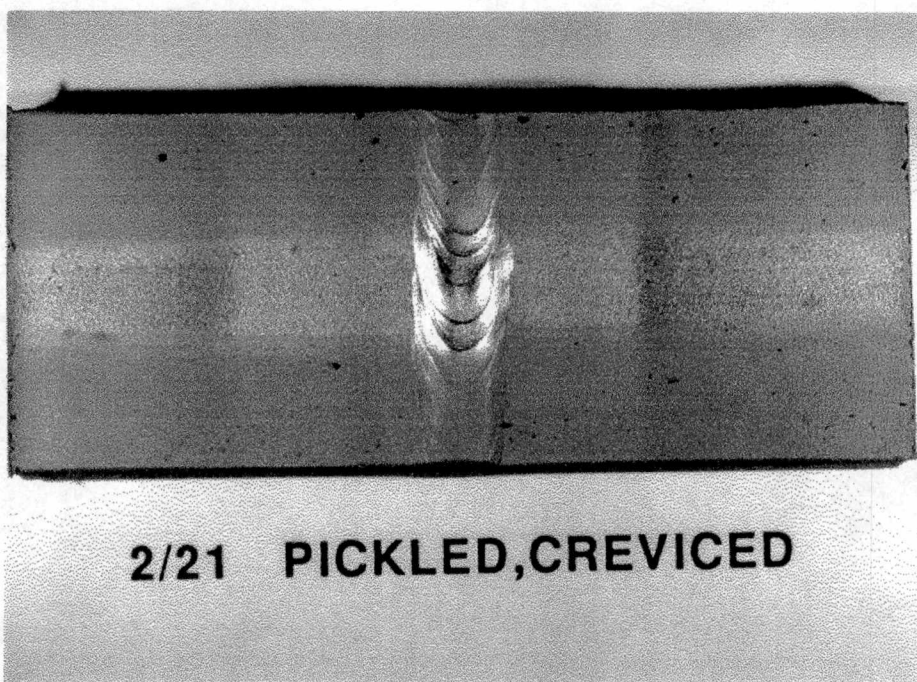


Figure 3-60. Photograph of the pickled and creviced specimen after 148-day exposure showing a corrosion free surface.

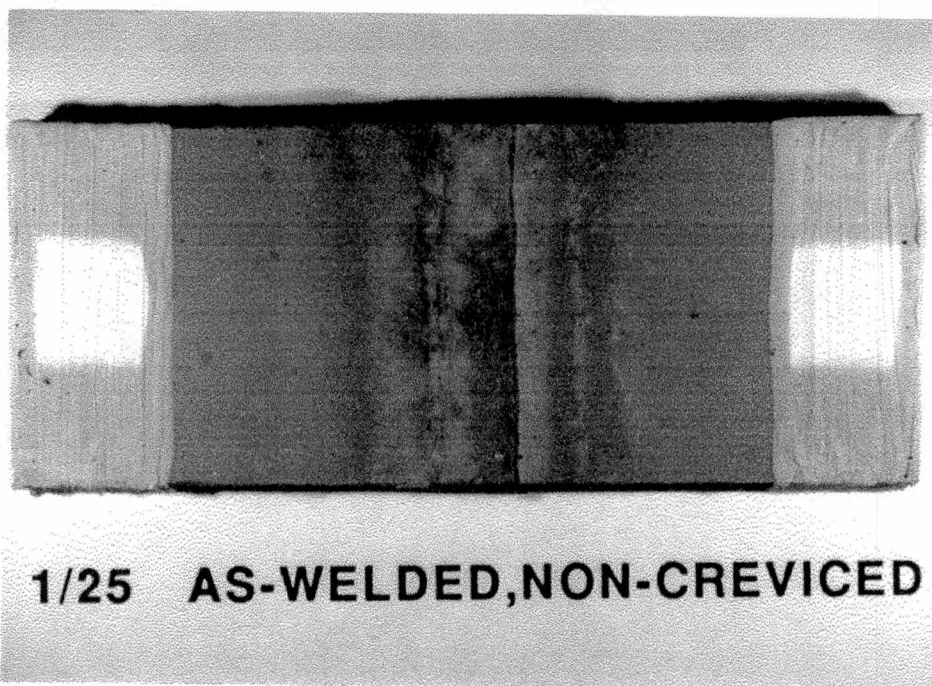


Figure 3-61. Photograph of the as-welded and non-creviced specimen after 148-day exposure showing no visible corrosion.

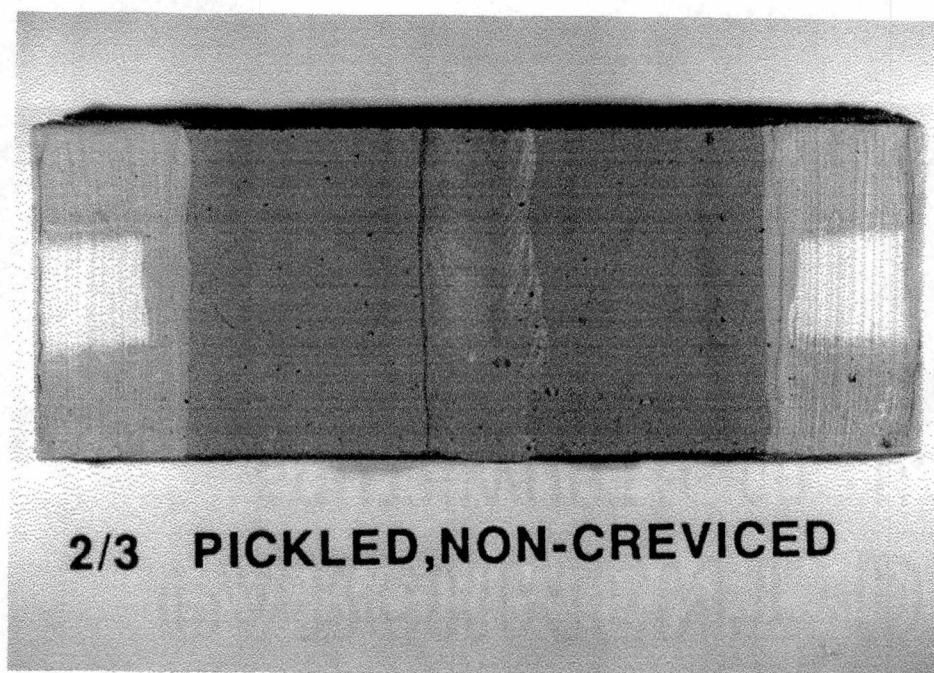


Figure 3-62. Photograph of the pickled and non-creviced specimen after 148-day exposure showing a corrosion free surface.

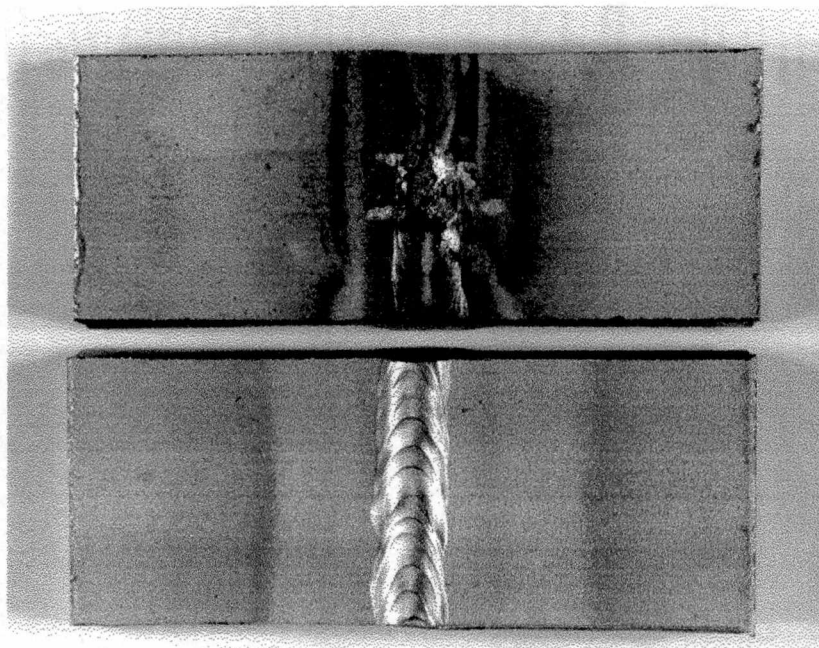


Figure 3-63. Comparison of creviced as-welded (top) and creviced pickled (bottom) 304L/308L specimens after 148-day exposure.

Table 3-7. 304L/308L Weldment UT Crevice Corrosion Tests (3/8" silicone rubber rod formed crevice across weld, HAZs and base metal) Arizona Ground Water

As-welded, Creviced	Max Depth of Crevice Corrosion (mils)		
	Base Metal	HAZs	Weld Metal
#1-24 (ID) Cleaned	0	<5	<5
#1-24 (OD) Cleaned	0	~10	~10
#1-27 (ID) As-exposed	0	Active Sites	Active Sites
#1-27 (OD) As-exposed	0	Active Sites	Active Sites
Pickled, Creviced			
#2-21 (ID) Cleaned	0	0	0
#2-21 (OD) Cleaned	0	0	0
#2-19 (ID) As-exposed	0	0	0
#2-19 (OD) As-exposed	0	0	0
As-welded, Non-creviced			
#1-26 (ID) Cleaned	0	0	0
#1-26 (OD) Cleaned	0	0	0
#1-25 (ID) As-exposed	0	0	0
#1-25 (OD) As-exposed	0	0	0
Pickled, Non-creviced			
#2-3 (ID) Cleaned	0	0	0
#2-3 (OD) Cleaned	0	0	0
#2-18 (ID) As-exposed	0	0	0
#2-18 (OD) As-exposed	0	0	0

pickled weldment coupons, nor on non-creviced as-welded coupons. These results show that the necessary condition for accelerated corrosion and nodule formation in the Arizona ground water is the co-existence of the welding-oxide heat-tint region and the crevice geometry. The results also strongly suggest that, in the Arizona ground water field tests and the Tennessee River water laboratory tests, corrosion-nodule formation in the heat-tint region at the metal/epoxy interface is due to a crevice geometry at the metal/epoxy interface and to a lower crevice-corrosion resistance associated with the heat-tint region.

3.3.11. Summary

In all the laboratory experiments associated with SRB inoculation, it was noted that a black film formed on the as-welded weldment only within the welding oxide region when the corrosion potential was negative. This film appeared smooth and homogeneous and uniformly covered the surface. When the corrosion potential became positive as a result of either imposed aeration or stopped solution supply, the black film disappeared and the oxide discoloration became visible again. If the film is composed of corrosion products such as magnetite, it indicates that the weld oxide region is a weak link in corrosion resistance because that is where the corrosion occurs. In addition, if the film is composed of corrosion products associated with SRB such as iron sulfide, it suggests that the corrosion behavior of the weldment caused by SRB is associated with the corrosion potential.

With regard to the relationship between OCP and the role of SRB in the corrosion process, the SRB metabolic sulfate-reduction reaction is given as $\text{SO}_4^{2-} + 8\text{H} \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O}$ (or $\text{SO}_4^{2-} + 8\text{H} \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} + 2\text{OH}^-$).^{20,21} Thus, in order for SRB to reduce sulfates to sulfides, hydrogen must be available. If the hydrogen comes from the cathodic reaction associated with the corrosion process (in line with the classical SRB corrosion mechanism),²⁵ the open-circuit or corrosion potential must be less than the equilibrium hydrogen-reaction ($2\text{H}^+ + 2\text{e} = 2\text{H}$) or water-reaction ($\text{H}_2\text{O} + \text{e} = \text{H} + \text{OH}^-$) potential. This potential depends on pH and hydrogen partial pressure (hydrogen concentration), and as given by the Nernst equation, is -413 and -354 mV(SHE) for a pH = 7 solution at hydrogen partial pressures of 1 and 10^{-2} atm., respectively. If the biofilm is acidic at, for example, pH = 4, the equilibrium values are -236 and -177 mV(SHE), respectively. Therefore, in order for the SRB to be active and contribute to the corrosion process, the corrosion potential (either widespread or locally) has to be quite low, and less than the general range of values given above. This situation corresponds to a deoxygenated state for the solution at the metal surface (which also is necessary for SRB survival), and also can be associated with the local breakdown of passive films. SRB survive adjacent of the metal surface to obtain the hydrogen, and underneath the biofilm to meet the deaerated condition.²⁰

It became clear during the course of these tests that nodule formation was related to the crevice geometry, the weld-oxide area, and the chloride concentration. The specimens with pickled and electropolished surfaces showed corrosion resistance (no nodules). The crevice effect was only associated with the weldment heat tint area; the

base metal region of the weldment was consistently corrosion free in all runs. The crevice was formed by the overlapped epoxy on the weldment heat tint area. The chloride concentration also was a factor in the initiation of crevice corrosion. Moreover, a major OCP difference exists for the specimens in the bacterial run as compared to the control run. As mentioned in the discussion of the Tennessee River water laboratory tests, deoxygenation by the bacteria can account for this potential difference. It appears that the bacteria are able to reduce the dissolved oxygen to low levels, levels lower than can be achieved in the laboratory by nitrogen sparging. Another microbial effect on corrosion is reflected through comparing the bacterial tests to the control tests. The extent of incipient corrosion in terms of nodule formation is less in the control tests than in the bacterial tests, as determined by measurements of nodule number and size.

The results of the laboratory, the field, and the advanced tests indicate that when the weld-oxide is removed chemically or electrochemically, and the bacteria are not present, the specimen is corrosion resistant regardless of the crevice geometry. When the weld-oxide is removed and the bacteria are present, the specimen also is corrosion resistant. Although the OCP is decreased by activities associated with bacterial metabolism, the specimen is still able to passivate. When the weld-oxide is not removed, and the bacteria are not present, the specimen again indicates corrosion resistance in the absence of the crevice geometry. However, if the crevice geometry is present at the heat-tint area, crevice corrosion develops in the form of corrosion nodules. Thus, the creviced region in the heat tint area is less corrosion resistant than the creviced region in the base metal area. When the weld-oxide is not removed, and the bacteria are present, the

specimen indicates lower corrosion resistance. The anodic polarization test reveals that the specimen is not passivated under these conditions. As described in the laboratory tests, deoxygenation occurs when the bacteria are active. The depletion of the dissolved oxygen lead to a condition for which the specimen can not be passivated.⁷³ The fact that the as-welded 304L/308L stainless steel weldment shows no passivation in the solution with the bacteria added is a significant result. This, along with prior results relative to the heat-tint effect, indicates that both the as-welded surface and the bacteria simultaneously contributed to enhanced corrosion.

3.4. Welding Oxide Tests

When a metal is exposed to an oxidizing gas such as oxygen at elevated temperatures, oxidation occurs at the metal surface. As a result, oxide or scale forms at the surface and oxidation continuously takes place depending on either oxygen diffusing inward or metal diffusing outward through the oxide. It is found that usually metallic ions rather than metal atoms migrate through the oxide along with electrons to react with oxygen at the outer oxide surface. Reaction occurring at the outer rather than the inner oxide surface can be illustrated by observations of Pfeil⁷⁴ or Wagner.⁷⁵ Pfeil noticed that when a sample of iron was painted with a slurry of Cr_2O_3 on the surface, this chromium oxide was served as a marker and was buried in the lower layers of iron oxide after oxidation. Wagner showed that when two weighed pellets of Ag_2S were placed on silver and a molten sulfur pool was added on the top of the Ag_2S pellets (Figure 3-64), after one

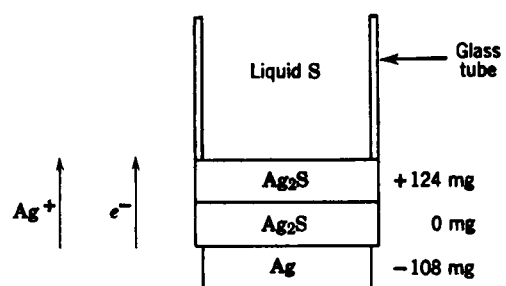
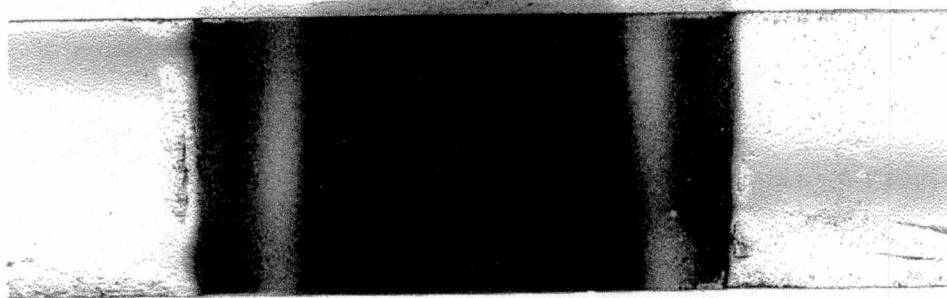


Figure 3-64. Wagner experiment showing the oxidation process.

hour at 220°C the bottom pellet which contacted with the silver did not gain or lose weight; however, the top pellet gained weight which corresponded to the loss of the silver in chemically equivalent weight. In both cases, metallic ions diffused through the compound (oxide or sulfide) to react with the oxidizing agent at the outer compound surface. Therefore, an oxide can be considered an electrolyte. Sometimes, this type of corrosion is called dry corrosion, in contrast to wet corrosion which is electrochemical corrosion in general.

3.4.1. The Gleeble Simulation and The Teat-Tinted Weldment

The specimens from the Gleeble simulations carried out in air at peak temperatures of 2400°F, 1600°F, and 800°F on 304L stainless steel are shown in Figures 3-65 to 3-67. By comparing the specimen appearances, it is seen that oxides were formed homogeneously on the specimens under all circumstances but to different degrees. The specimen that experienced the 2400°F peak temperature appeared to be dark gray in color, which could correspond to the oxide formed adjacent to the weld. The 1600°F specimen had a brownish appearance and the oxide seemed much thinner than that on the 2400°F specimen. The specimen that experienced the 800°F peak temperature appeared to be shiny but had an elusive light yellow colored oxide. This oxide, which is normally neglected when viewed by the naked eye, could correspond to the outer side of the oxide region on a weldment.



The 2400°F Gleeble specimen

Figure 3-65. Photograph of the 2400°F Gleeble specimen.

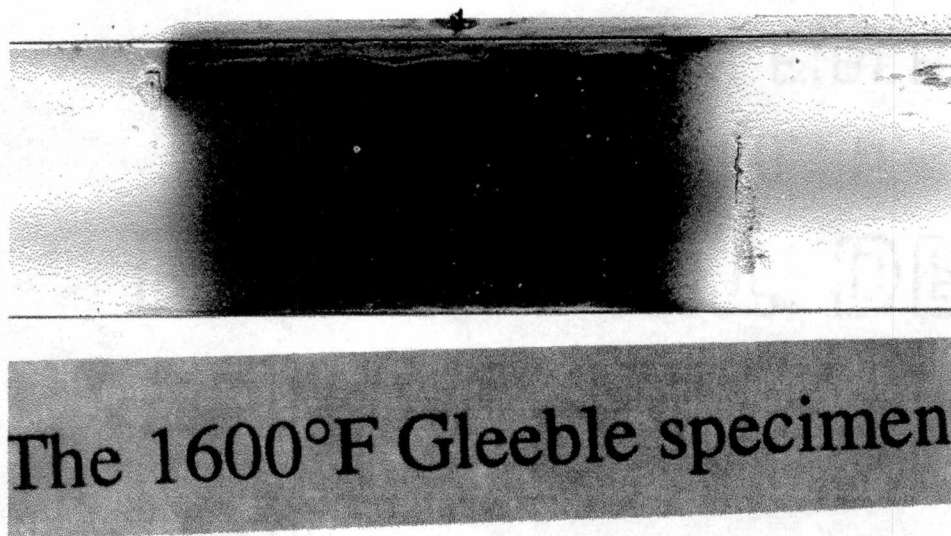


Figure 3-66. Photograph of the 1600°F Gleeble specimen.



The 800°F Gleeble specimen

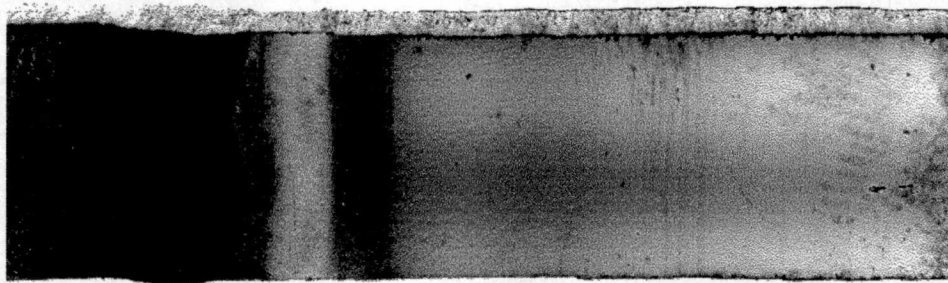
Figure 3-67. Photograph of the 800°F Gleeble specimen.

The heat tinted weldment specimen (Figure 3-68) shows various colored oxides from dark gray adjacent to the weld bead to light yellow at the outer edge of the heat tinted region adjacent to the base metal. A schematic diagram, as shown in Figure 3-69, defines the various oxide colors and their locations in the heat tinted region. A dark gray oxide was formed adjacent and contiguous with the weld bead, which is the highest temperature exposure. As the distance from the weld bead increases brown and then blue oxide colors develop. The color of the oxide out board of the blue oxide is straw-colored, however, a streaky rose color is superimposed at the borderline of the blue and the straw-colored oxides. A light yellow oxide appears at a location closest to the untinted base metal, and this is the region which experiences the lowest temperature for the visible oxides. This oxide classification within the heat tinted region is used in discussions of the oxide microscopic analyses.

It is interesting to point out that a micro-grain structure after the welding was revealed from the surface at the blue and straw-colored oxide regions because of grain boundary movements (Figure 3-70). This grain boundary movements could have caused mechanical strain in the blue and straw-colored oxides.

3.4.2. Crevice Corrosion Tests

Crevice corrosion tests on the 2400°F specimens simulated in air and argon atmospheres, respectively, were conducted in the bacterial solution. Open-circuit potential measurements were made during the exposure, as shown in Figure 3-71. The



The heat-tinted specimen

Figure 3-68. Photograph of the heat-tinted specimen showing oxide discoloration.

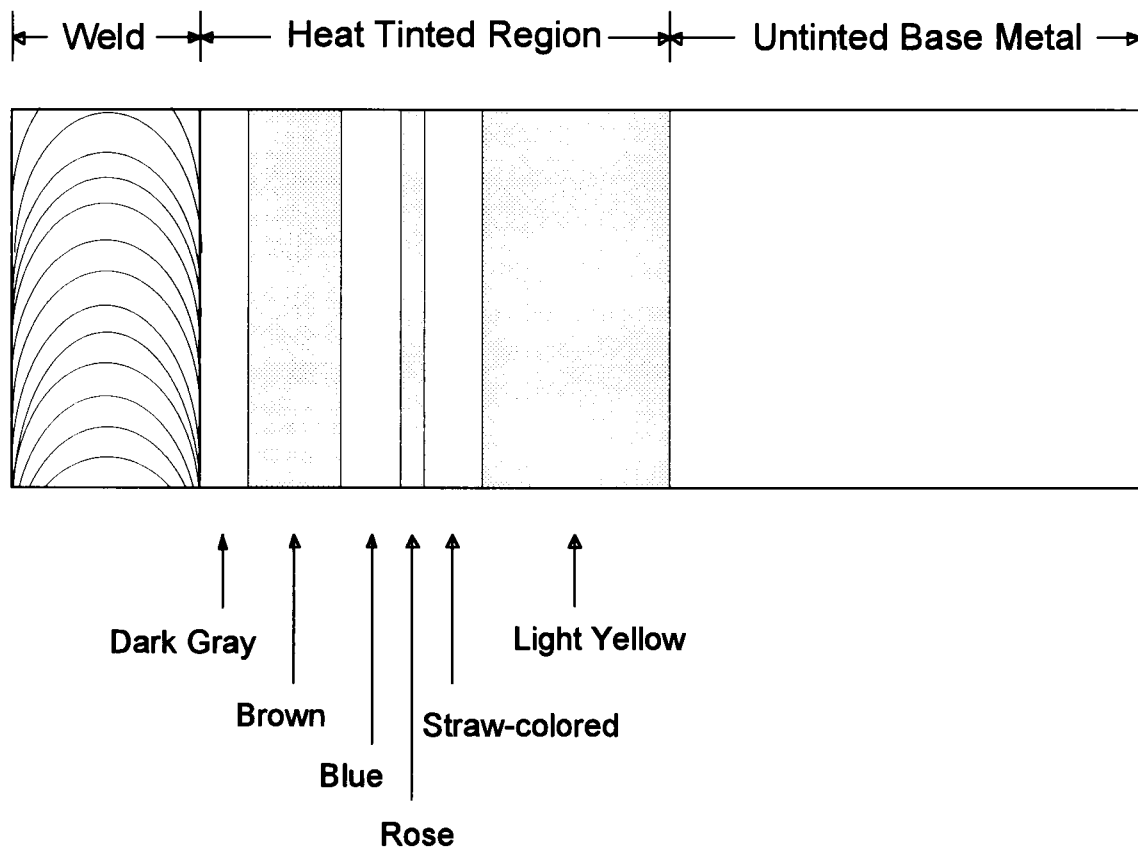


Figure 3-69. Schematic diagram of a heat tinted weldment specimen surface showing the oxide extent and coloration.



Figure 3-70. Photograph (30x) of the heat-tinted specimen showing grain boundaries at blue and straw-colored oxide regions after welding.

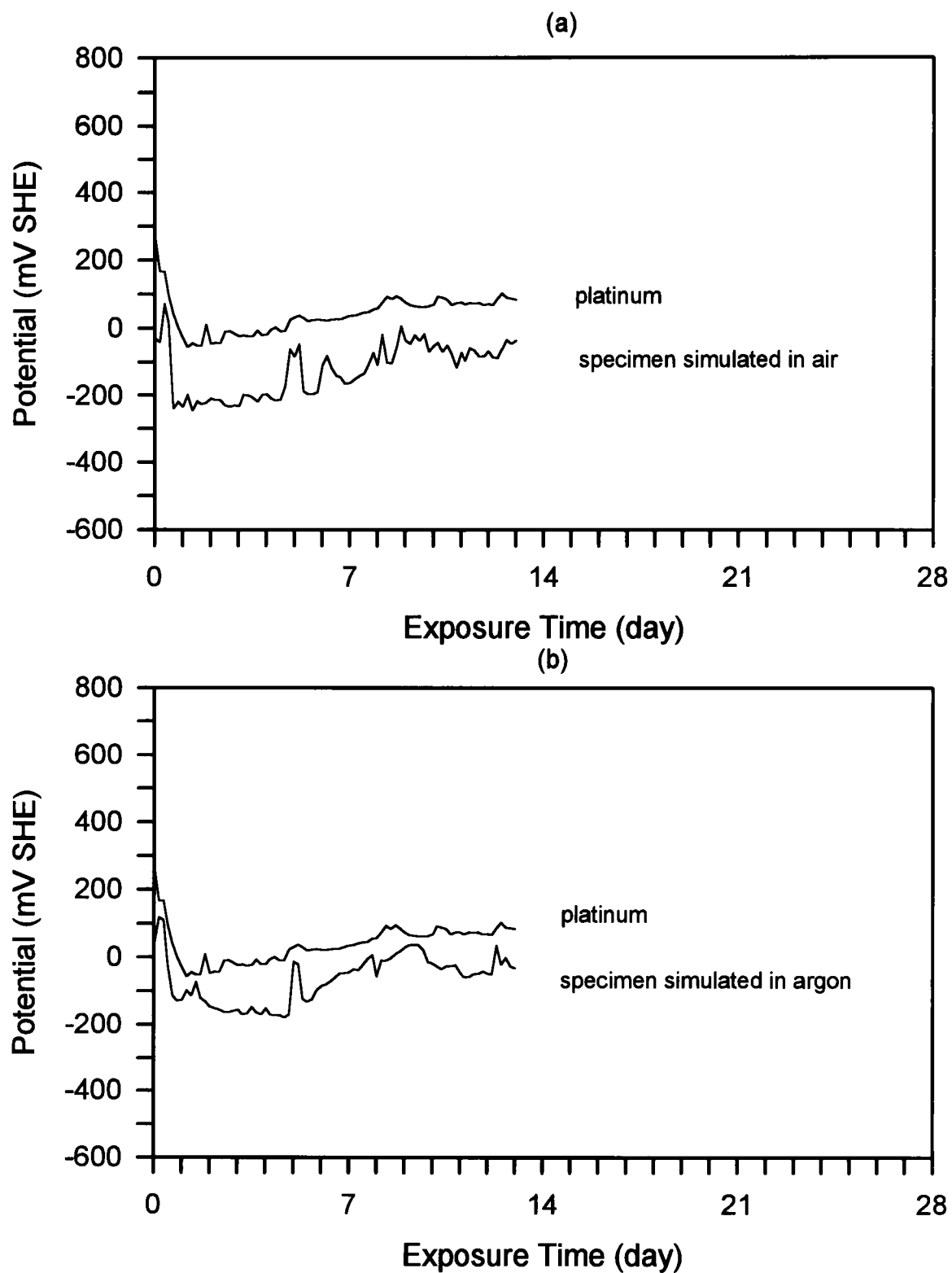
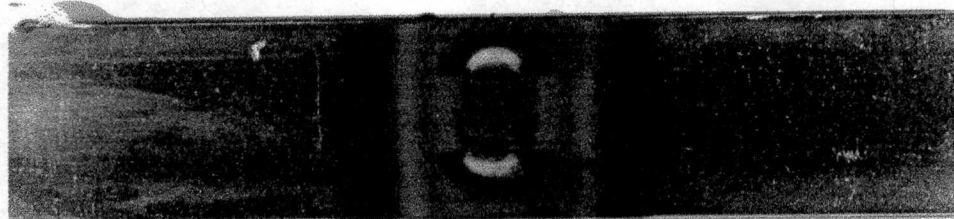


Figure 3-71. Open-circuit potentials of the Gleeble specimens simulated in air (a) and argon (b) in the bacterial solution.

two specimens almost had an identical potential profile although one specimen had oxide on the surface and the other one did not. The oxide specimen (Figure 3-72) experienced crevice corrosion attack at the oxide region while the non-oxide specimen (Figure 3-73) did not experienced crevice corrosion attack, indicating that the crevice corrosion was attributed to both the bacterial solution and the oxide.

A series of crevice corrosion tests on the Gleeble specimens with the different peak temperatures was conducted in the bacterial and control solutions, respectively. Open-circuit potentials of the specimens and platinum electrodes are shown in Figure 3-74 for the bacterial run, and in Figure 3-75 for the control run. The potential profiles are essentially in an agreement with that in the Tennessee River water laboratory tests. It appears that the presence of the crevice geometry had few influences on corrosion potential for the bacterial run. The bacterial effect on open-circuit potential was still a dominating factor and consequently made the open-circuit potentials decrease. In the control run, the corrosion potentials diverged to more active values relative to the platinum potential, indicating that an IR drop was caused by the presence of the crevice geometry. Although the corrosion potential did not distinguish the different peak temperature oxides, post-exposure observations on the specimens indicated that the 2400°F oxide specimens both in the bacterial and control solutions experienced incipient crevice corrosion. The rest specimens exposed to 1600°F and 800°F peak temperatures showed crevice corrosion resistance in the bacterial and control solutions for the 14-day exposure. In other words, the specimens with the highest temperature oxide were more susceptible to crevice corrosion than the specimens with lower temperature oxides.



**SS GLEEBLE WELD SIMULATED
IN AIR, CREVICE SAMPLE IN
BACTERIAL SOLN. (10-27-93)**

Figure 3-72. Photograph of the Gleeble specimen simulated in air after the crevice corrosion test showing crevice corrosion at the oxide region.



**SS GLEEBLE WELD SIMULATED
IN ARGON , CREVICE SAMPLE IN
BACTERIAL SOLN. (10-27-93)**

Figure 3-73. Photograph of the Gleeble specimen simulated in argon after the crevice corrosion test showing corrosion free surface.

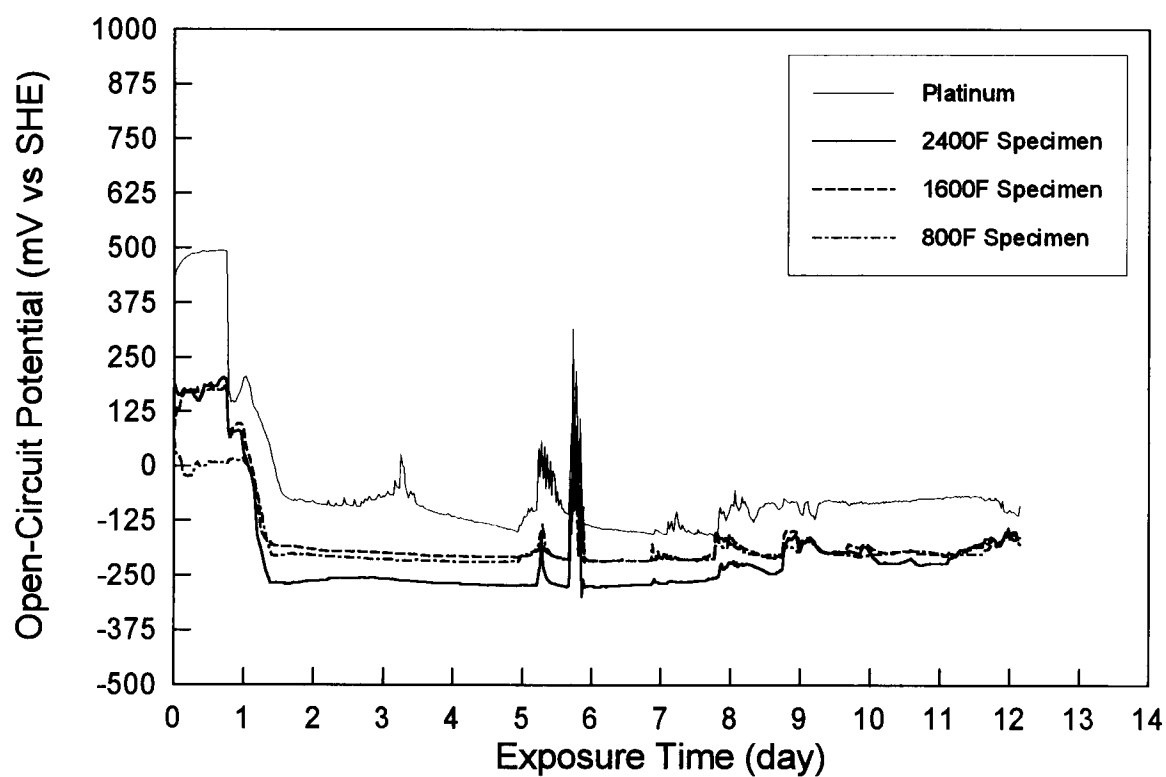


Figure 3-74. Open-circuit potentials of the various Gleeble specimens in the bacterial solution from the crevice test.

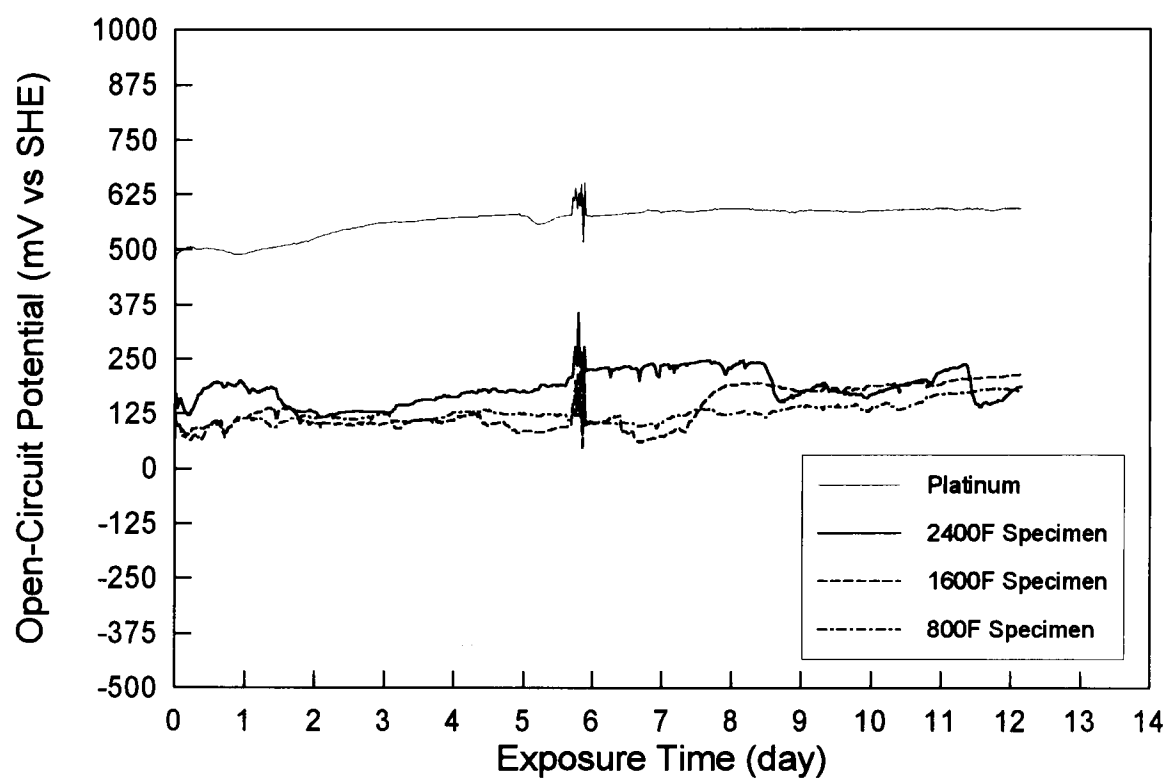


Figure 3-75. Open-circuit potentials of the various Gleeble specimens in the control solution from the crevice test.

In order to further confirm the fact that high temperature oxide is susceptible to crevice corrosion attack, a heat-tinted weldment specimen, in the crevice assembly, was exposed to a 6% ferric chloride solution for one hour at room temperature. It is seen in Figure 3-76 that crevice corrosion occurred in the heat tinted region that experienced the high temperature and did not occur where no visible oxide was observed.

As discussed in the literature review, Kearns⁶⁷ prepared heat tinted and untinted (shielded by argon) specimens (317LX and AL-904L) by making bead-on-plate GTAW welds. Weld oxide was produced on the root side of the weld and the maximum temperature (heat tint temperature) was measured by an attached thermocouple. The heat tinted and untinted (with argon back shielding) specimens were made using different heat energy inputs, and designated by the heat tint temperatures. They were 445°F (229°C), 709°F (376°C), 972°F (522°C), 1232°F (667°C), and 1499°F (815°C). Crevice corrosion tests on the heat tinted and untinted specimens were conducted according to ASTM G-48. It was found that the crevice corrosion resistance tended to decrease as the heat tint temperature was increased. This is in agreement with the current results in that the higher temperature oxide is more susceptible to crevice corrosion in both oxygenated and ferric chloride solutions.



The heat-tinted specimen
after crevice corrosion test

Figure 3-76. The heat-tinted specimen after crevice corrosion test in ferric chloride solution.

3.4.3. Pitting Corrosion Tests

An immersion test on the stainless steel weldments in Table 2-1 was carried out according to the ASTM G48 specification for the purpose of examining pitting resistance. The test was conducted in 6% ferric chloride solution at 50°C for 72 hours. After the test, it was found that pits were concentrated on the area away from weld bead, as shown in Figure 3-77 for the as-welded 304L/308L weldment. This area experienced lower temperatures during welding and was more susceptible to pitting corrosion. When the oxide was removed by pickling the 304L/308L weldment (Figure 3-78), pits tended to be more spread out and also fewer pits were observed.

To further investigate how pitting corrosion resistance varied with different temperature oxides, tests were conducted on the Gleeble specimens and also on the heat-tinted weldment specimen. The specimens were exposed to a 6% ferric chloride solution at room temperature for 24 hours. After exposure, the Gleeble specimens were photographed, and are shown in Figures 3-79 to 3-81, corresponding to the 2400°F, 1600°F, and 800°F specimens, respectively. Pitting associated with the presence of oxide occurred on the all three specimens. It is noted that a few pits were found on the 2400°F and 1600°F specimens, and that the pits occurred at the transition region between the oxide and the metal. A striking pitting result was found for the 800°F specimen, on which not only more pits were noticed but also they were uniformly distributed on the oxide region. One 800°F Gleeble specimen was tested in the same solution after grinding off the oxide formed during the Gleeble simulation. In this case, pitting did not occur, indicating



The as-welded 304L/308L weldment
after pitting test

Figure 3-77. The as-welded 304L/308L weldment after pitting corrosion test per ASTM G48 specification.



The pickled 304L/308L weldment after pitting test

Figure 3-78. The pickled 304L/308L weldment after pitting corrosion test per ASTM G48 specification.

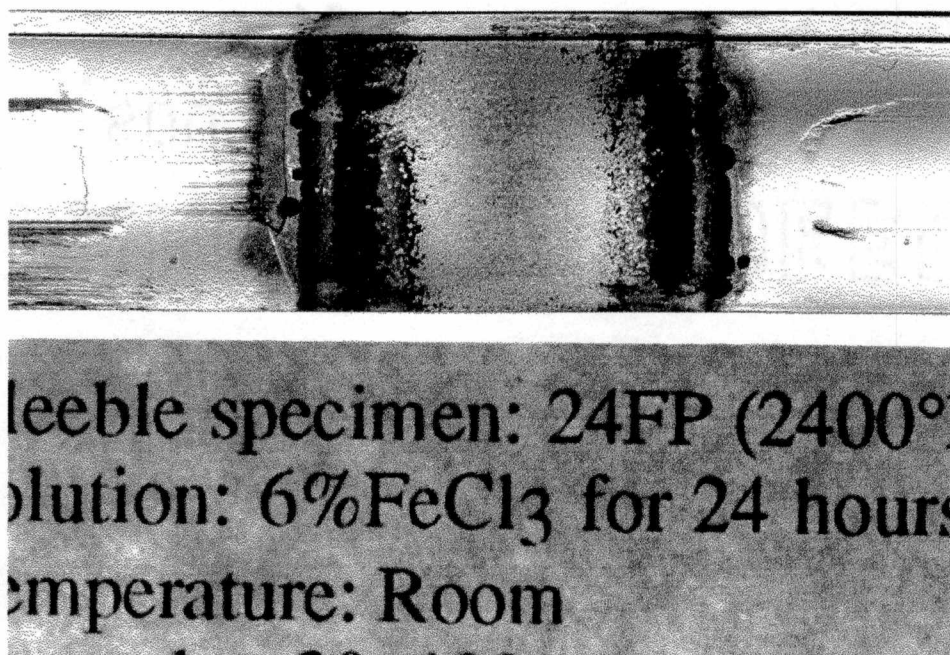
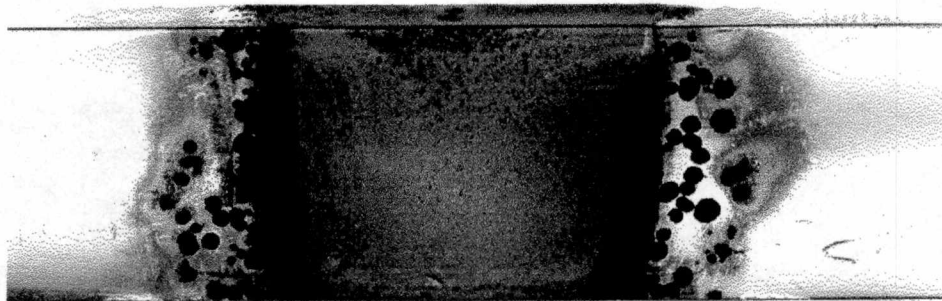


Figure 3-79. The 2400°F Gleeble specimen after pitting corrosion test.



ble specimen: 16FP (1600°F)
tion: 6%FeCl₃ for 24 hours
perature: Room

Figure 3-80. The 1600°F Gleeble specimen after pitting corrosion test.

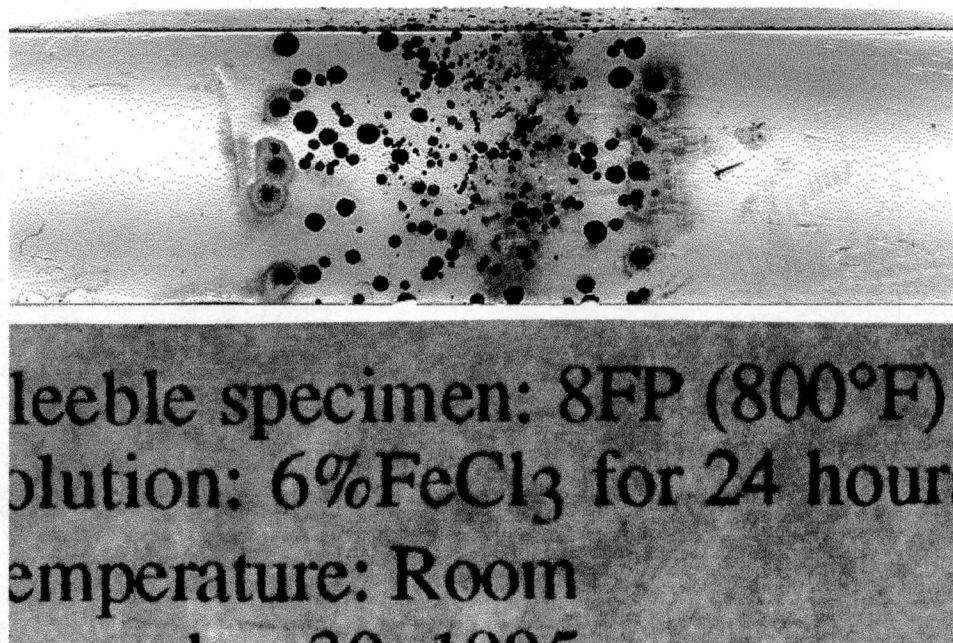


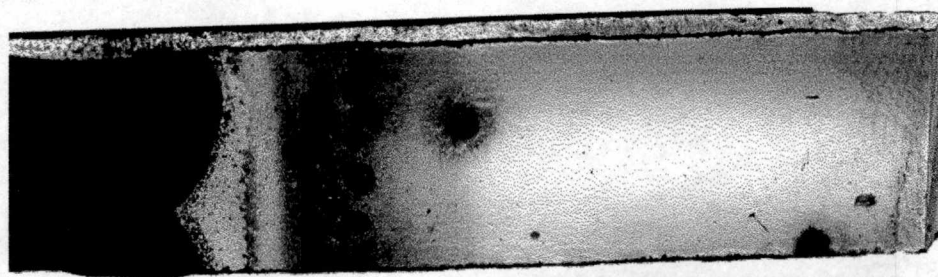
Figure 3-81. The 800°F Gleeble specimen after pitting corrosion test.

that any microstructural changes due to the thermal cycle were not associated with the pitting on the 800°F specimen. A pitting test was conducted on the heat-tinted weldment specimen. The result (Figure 3-82) showed agreement with the previous observation that the lower temperature oxides were most susceptible to pitting corrosion.

As mentioned in the above section, Kearns performed crevice tests according to ASTM G-48. It was found generally that the severity of pitting attack increased with the heat tint temperature of the heat tinted specimen. However, he did mention that the heat tinted specimen with the highest temperature appeared to be relatively corrosion resistant. It is to be noted that the highest heat tint temperature was only 1499°F. Therefore, most of the heat tinted specimens used in Kearns' tests were ones having low temperature oxides, compared to the 1600°F and 2400°F Gleeble simulated oxides used in the current tests. Based on this discussion, Kearns' results again show agreement with the current pitting test results in that the low temperature oxide (800°F Gleeble simulated oxide) is most subject to pitting corrosion.

3.4.4. XPS and AES Analyses

XPS analysis was conducted on the passive film on a 304L stainless steel specimen after a passivation treatment in 20% HNO₃ solution for 30 mins at room temperature. Atomic concentration of the elements as a function of penetration depth is shown in Figure 3-83. It is seen that the passive film is less than about 4 nanometers in thickness. The concentrations of iron and nickel in the passive film are less than those in the matrix.



The heat-tinted specimen
after pitting corrosion test

Figure 3-82. The heat-tinted specimen after the pitting corrosion test.

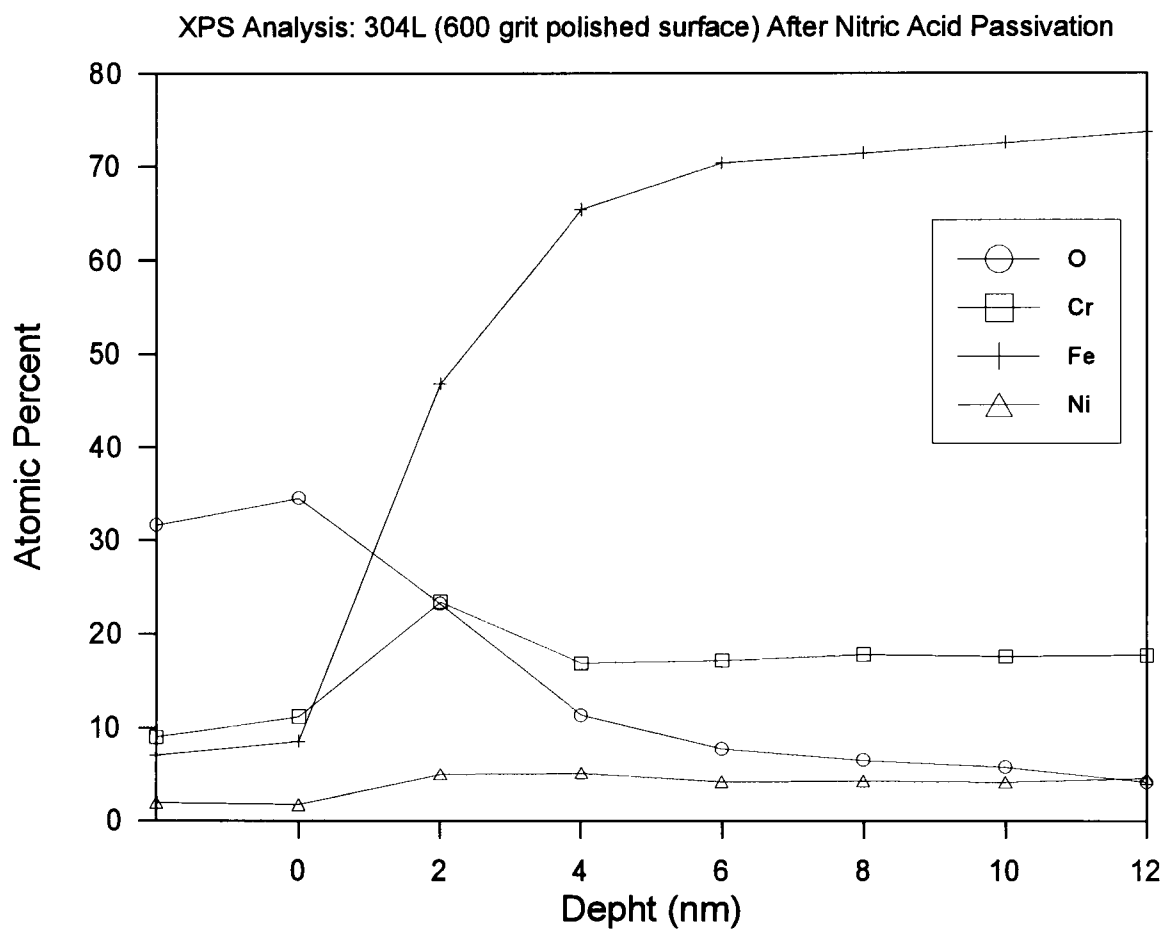


Figure 3-83. XPS depth profile of 304L specimen after a passivation treatment.

However, the depth profile of chromium clearly shows chromium enrichment in the passive film, compared to that in the base material. The photoelectron peaks from chromium as a function of the cycle which is directly related to the depth (Figure 3-84) show that chromium at the surface (the first 2 cycles) exists as a form of chromium oxide rather than metal, which is observed by the chemical shift in binding energy. As the film was sputtered, metallic chromium gradually was revealed, as shown in the peaks of cycle three where the oxide and metal peaks overlap one another. Further penetration gave rise to complete metallic chromium peaks. The photoelectron peaks from iron (Figure 3-85) show that no iron or iron oxide is found at the surface and iron exists as metallic iron as the film was penetrated. The results are in agreement with the classic argument involving passive film formation, in that iron and nickel are dissolved into solution and chromium is left on the surface and transformed to chromium oxide.⁷⁶⁻⁷⁸ This explanation also implies that a certain level of chromium composition in the alloy is necessary to form a complete protective chromium oxide film.

Typical photoelectron peaks for Cr, Fe, Ni, and O collected from the 800°F Gleeble specimen are demonstrated in Figures 3-86, 3-87, 3-88, and 3-89, respectively. Depth profiles of the 800°F, 1600°F, and 2400°F specimens are shown in Figures 3-90, 3-91, and 3-92, respectively. To examine the oxide, a definition of the oxide thickness lends itself to explanations of the data. Unfortunately, no oxide/metal interface can be defined at a specific thickness because of the nature of diffusion. As a general rule of thumb, the interface usually is defined at 50% of oxygen concentration reduction, which leads to a reasonable approximation of the oxide thickness. The depth profiles of the 800°F and

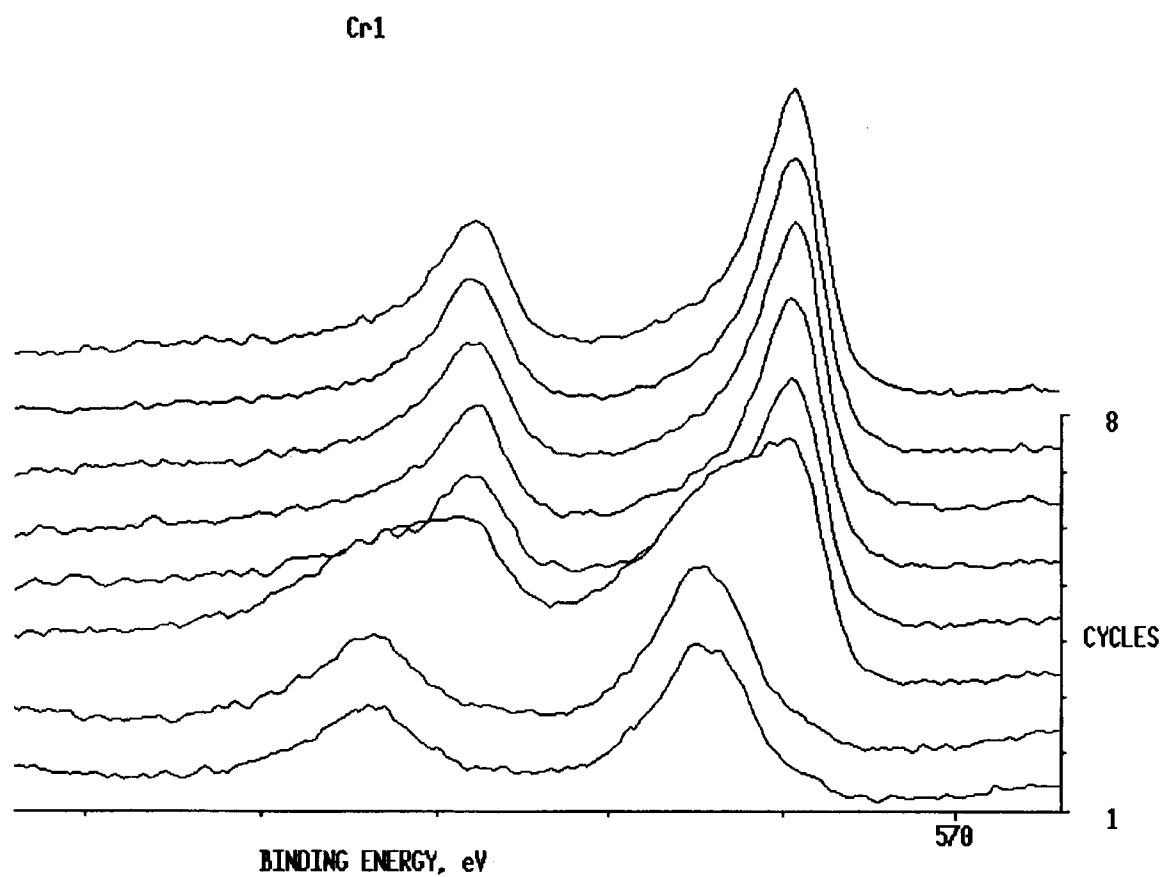


Figure 3-84. Photoelectron peaks of chromium of 304L specimen after passivation treatment showing chromium oxide in the first three cycles (where cycle number corresponds to data point number and corresponding sputter depth as shown in Figure 3-83).

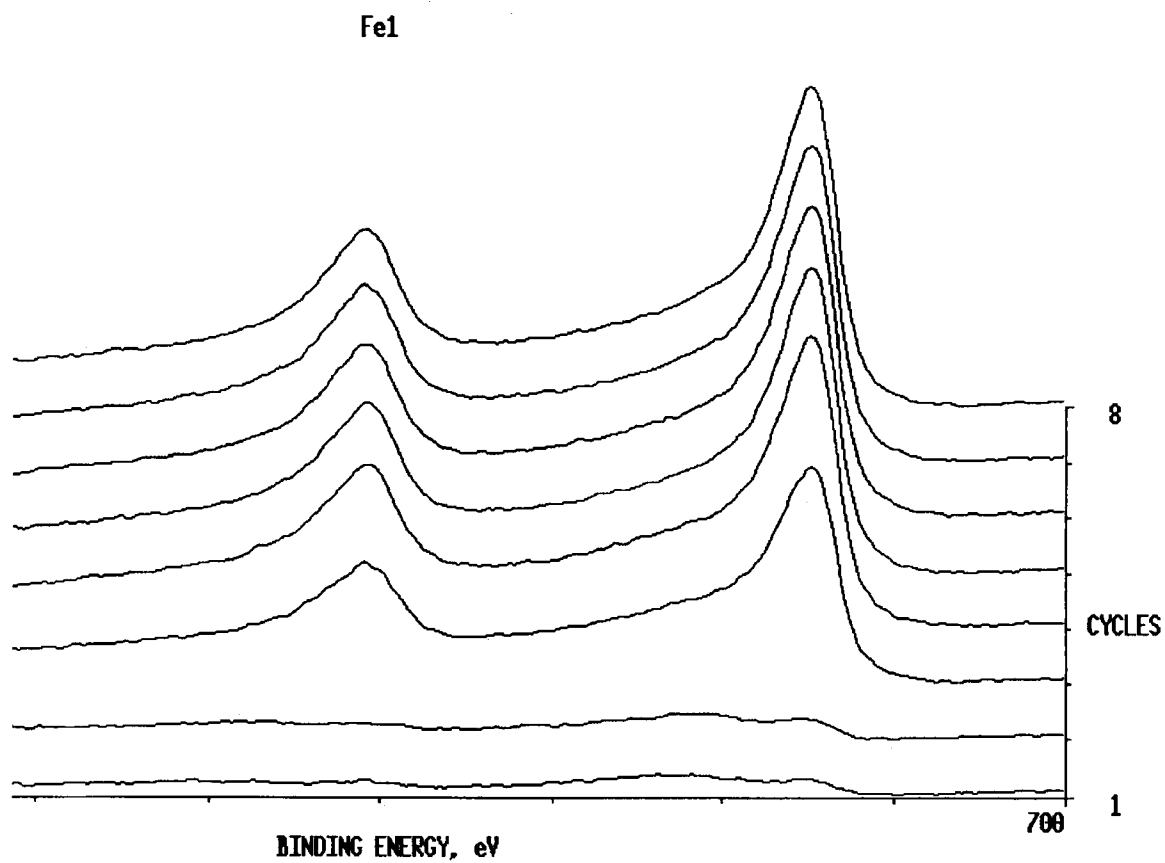


Figure 3-85. Photoelectron peaks of iron of 304L specimen after passivation treatment showing iron metal rather than oxide (where cycle number corresponds to data point number and corresponding sputter depth as shown in Figure 3-83).

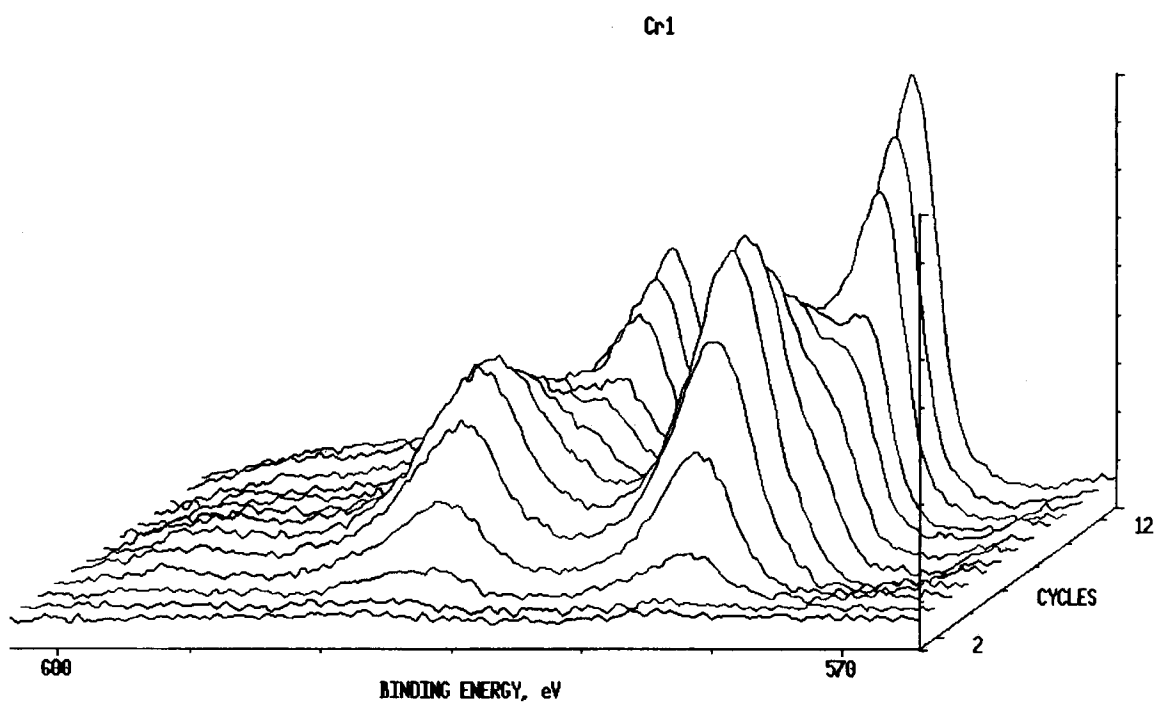


Figure 3-86. Photoelectron peaks of chromium for the 800°F Gleeble specimen as a function of analysis cycle (where cycle number corresponds to data point number and corresponding sputter depth as shown in Figure 3-90).

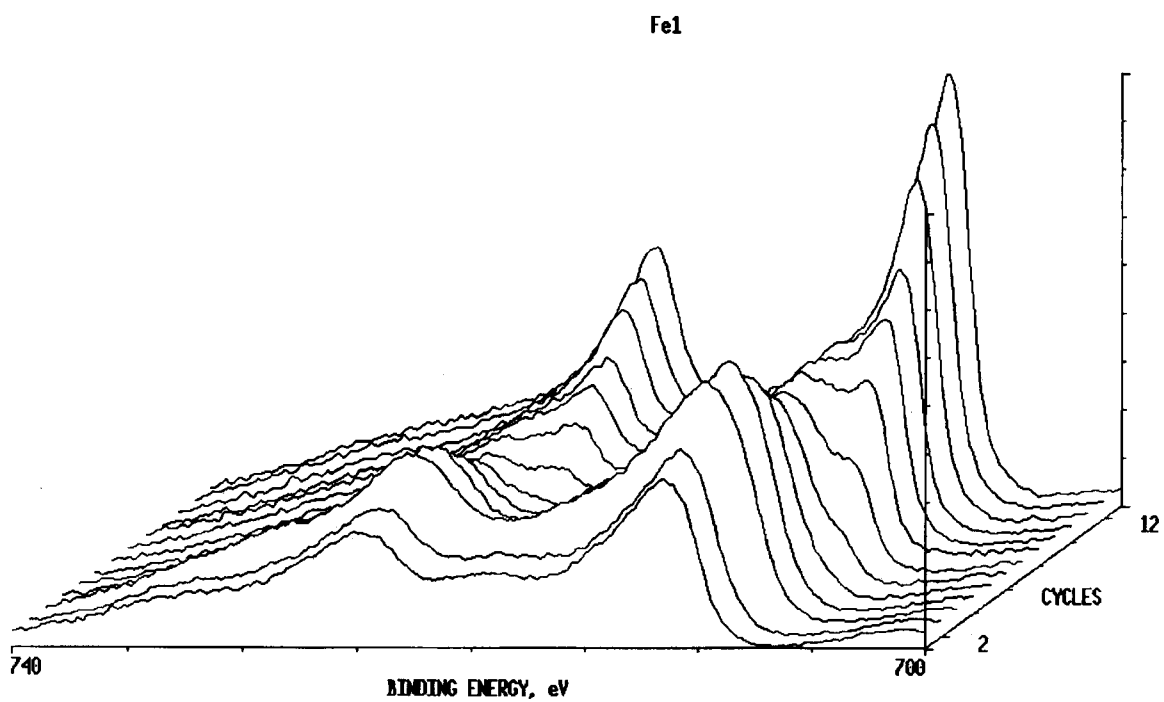


Figure 3-87. Photoelectron peaks of iron for the 800°F Gleeble specimen as a function of analysis cycle (where cycle number corresponds to data point number and corresponding sputter depth as shown in Figure 3-90).

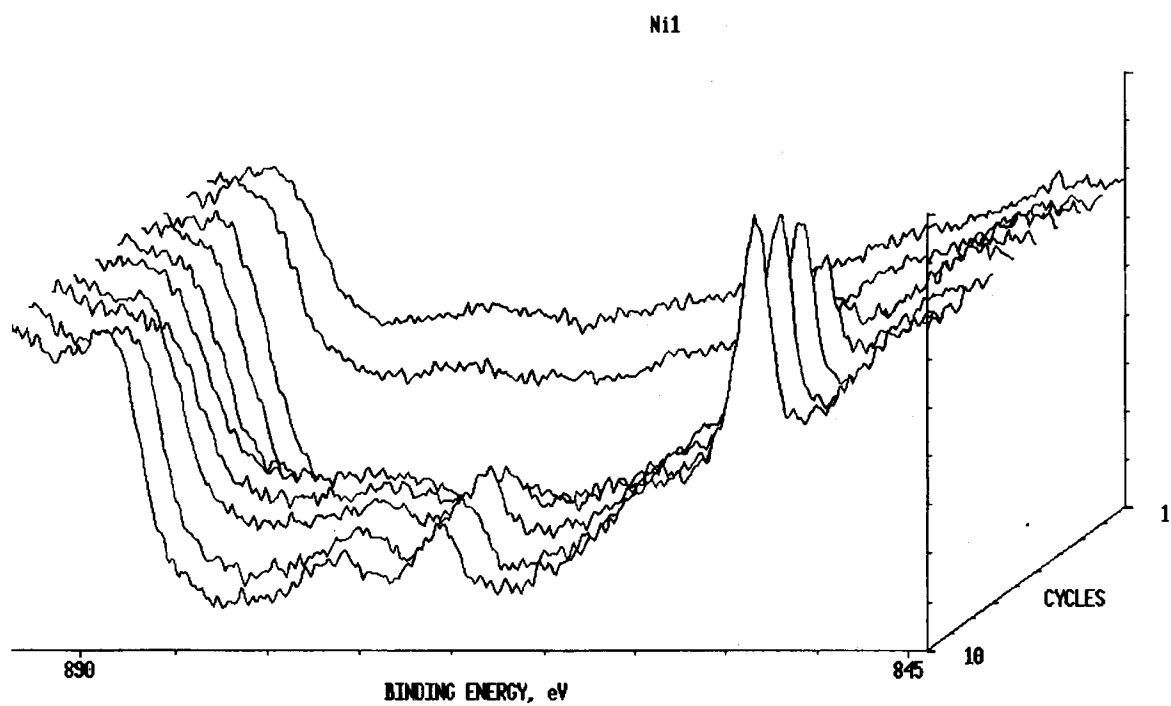


Figure 3-88. Photoelectron peaks of nickel for the 800°F Gleeble specimen as a function of reversed analysis cycle (where cycle number corresponds to data point number and corresponding sputter depth as shown in Figure 3-90).

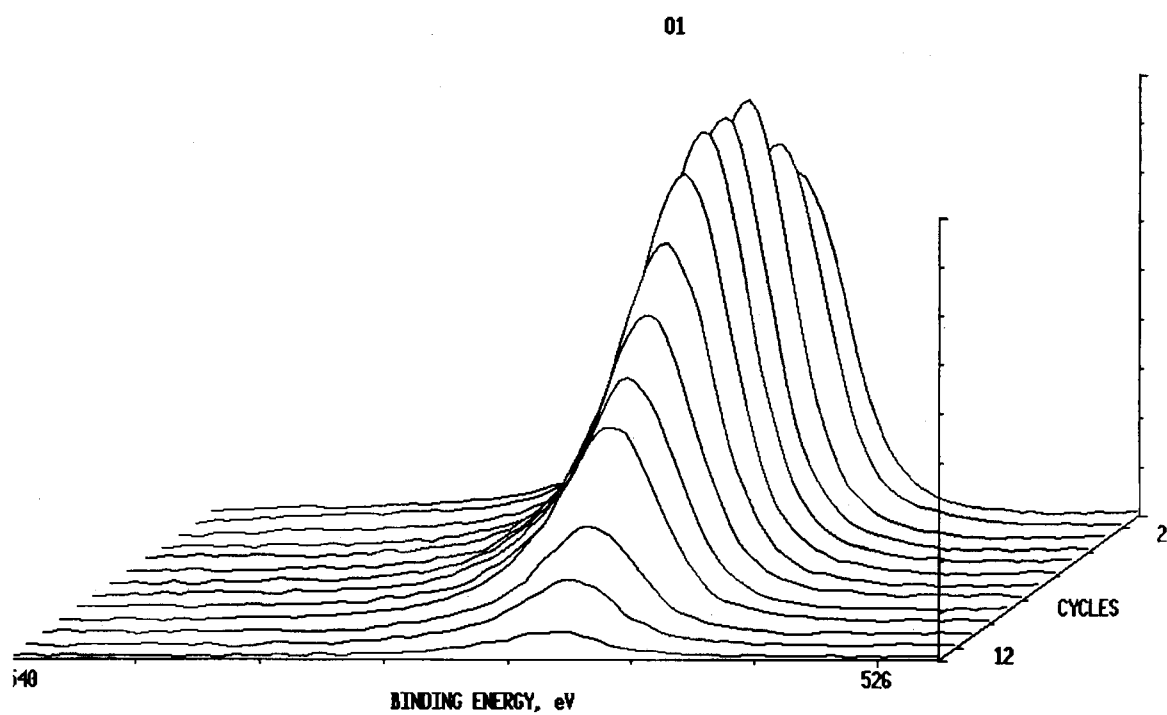


Figure 3-89. Photoelectron peaks of oxygen for the 800°F Gleeble specimen as a function of reversed analysis cycle (where cycle number corresponds to data point number and corresponding sputter depth as shown in Figure 3-90).

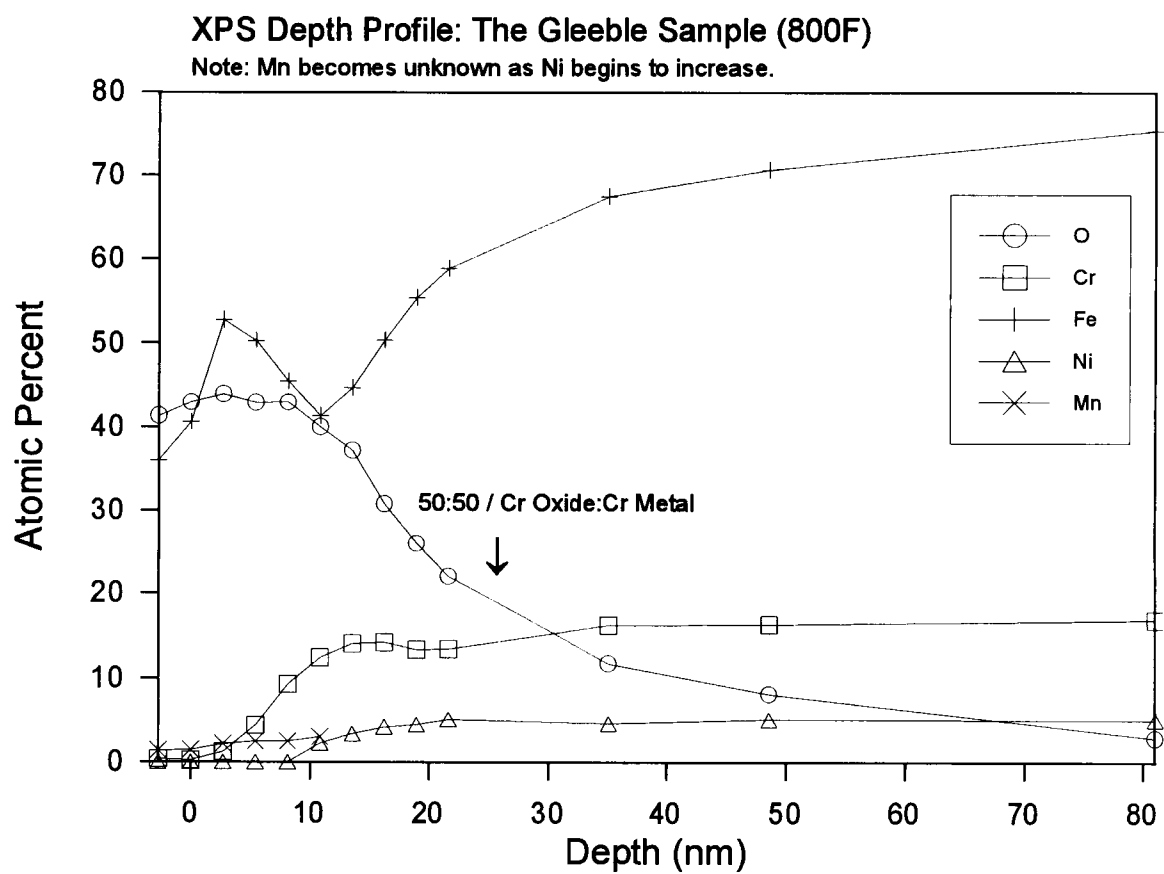


Figure 3-90. Depth profiles of the 800°F Gleeble specimen.

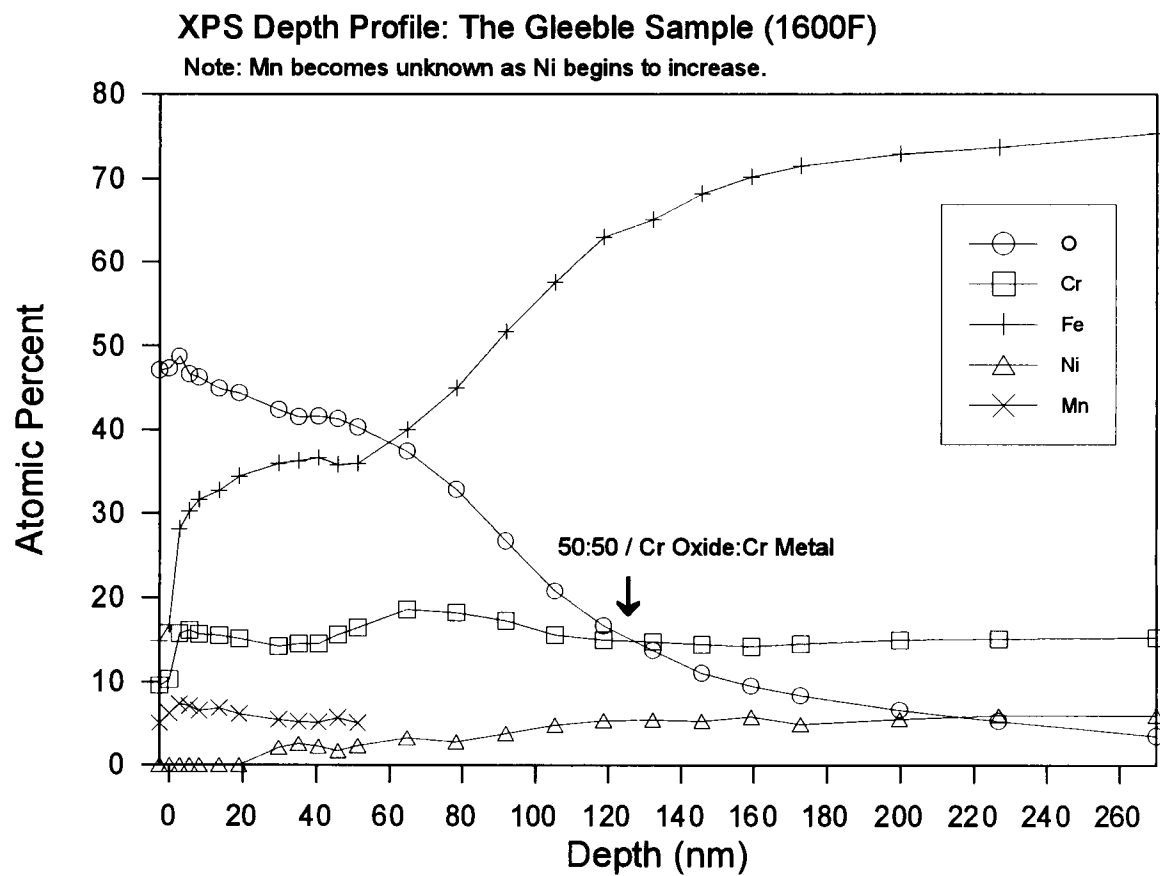


Figure 3-91. Depth profiles of the 1600°F Gleeble specimen.

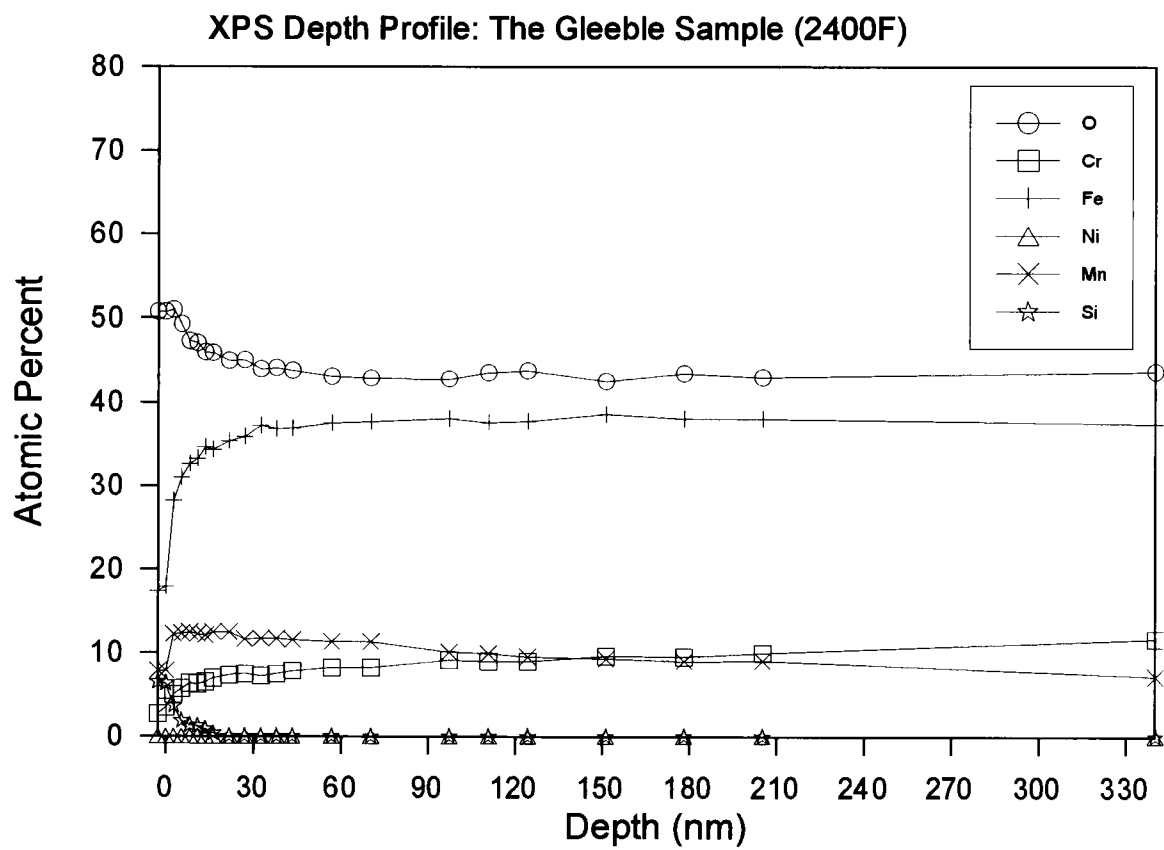


Figure 3-92. Depth profiles of the 2400°F Gleeble specimen.

1600°F oxides show that iron, chromium and nickel, in general, are deficient at the surface and inside the oxide near the surface, compared to the composition of the matrix.

Actually, nickel content is zero within that range. An exception is manganese which appears to be enriched corresponding to that in the matrix. As the oxide was removed layer by layer by sputtering, it is seen that the chromium profile exhibits some chromium enrichment in the oxide near the oxide/metal interface (Figure 3-91) and iron and nickel show increases in concentration. Further sputtering reveals that all the concentration curves reach constant values, indicating that base metal was disclosed. A uniform oxide composition was reached for the 2400°F oxide, as seen in Figure 3-92, indicating that the oxide itself is homogeneous in chemistry. An attempt to sputter completely through the 2400°F oxide was not made since the oxide was so thick and the results obtained from other 2400°F specimens were similar to those of the 800°F and 1600°F specimens.

The heat-tinted weldment specimen has the as-welded surface on which a variety of oxides in terms of discoloration was produced by welding. XPS depth profiles on the heat-tinted weldment specimen at different surface locations are given in Figures 3-93, 3-94, 3-95, and 3-96, which are representative of the invisible oxide (base metal area), the light yellow oxide, the straw-colored or blue oxide, and the dark gray oxide, respectively. The results are consistent with those of the Gleeble specimens in general. Moreover, remarkable chromium enrichments in the oxides were found on the invisible oxide, the light yellow oxide, and the straw-colored or blue oxide.

The analyzing spot for the XPS technique is about 0.8 mm in diameter. The AES technique has a much better spatial resolution than XPS, and is normally able to obtain

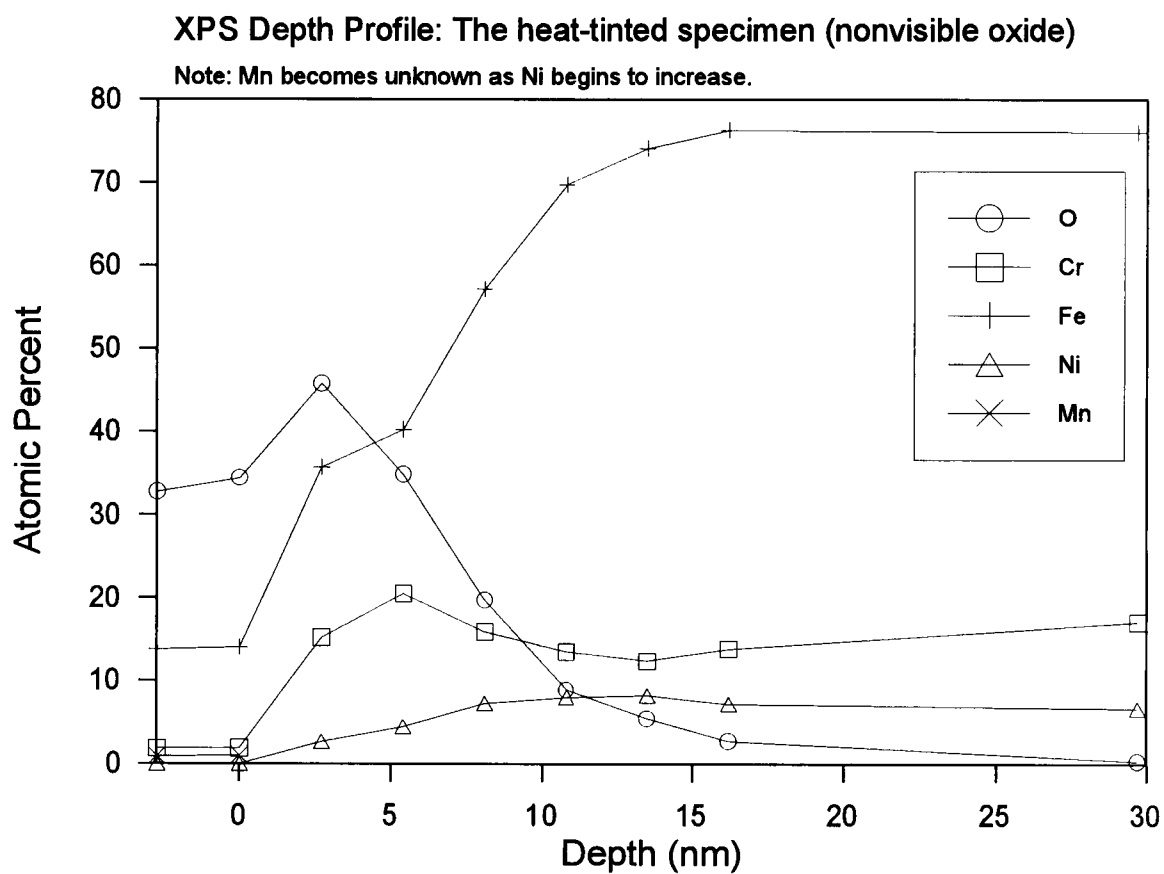


Figure 3-93. Depth profiles of the heat-tinted weldment specimen at a location where no oxide was visible.

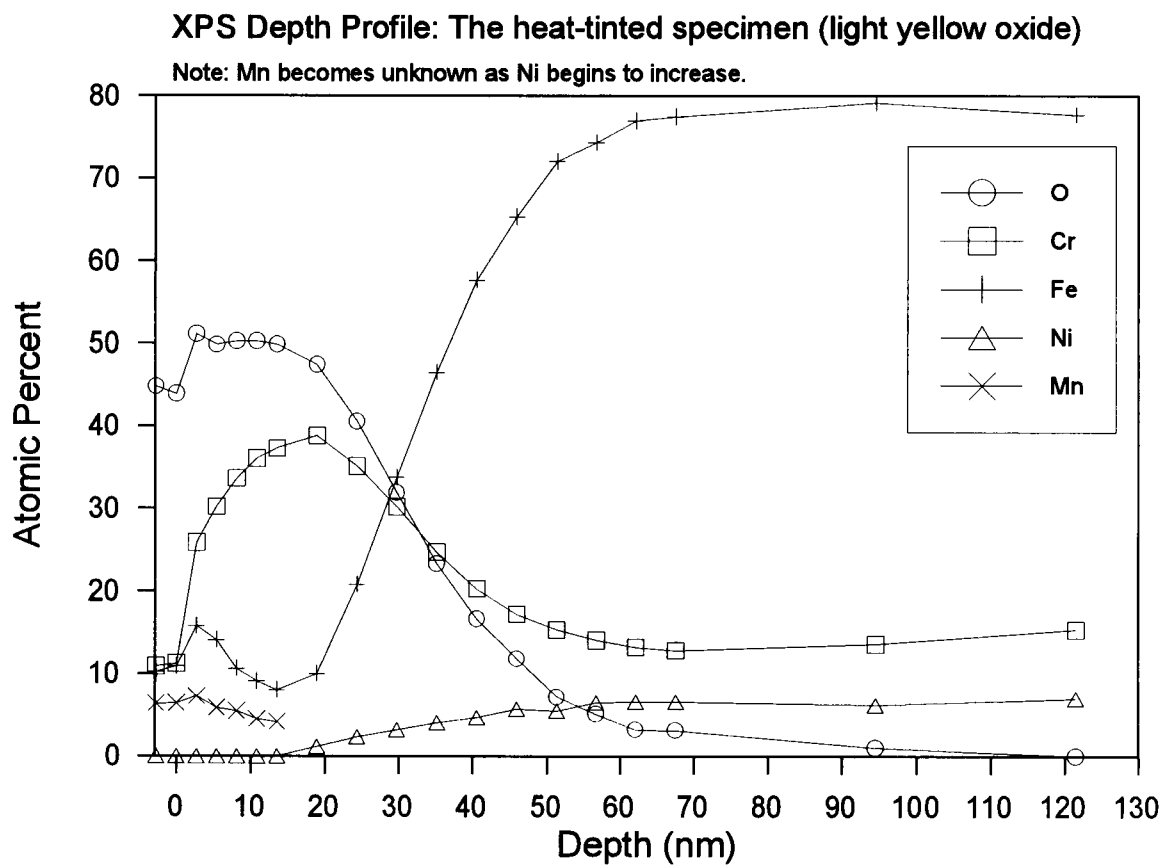


Figure 3-94. Depth profiles of the heat-tinted weldment specimen at a location where the light yellow oxide was observed.

XPS Depth Profile: The heat-tinted specimen (blue or straw-colored oxide)

Note: Mn becomes unknown as Ni begins to increase.

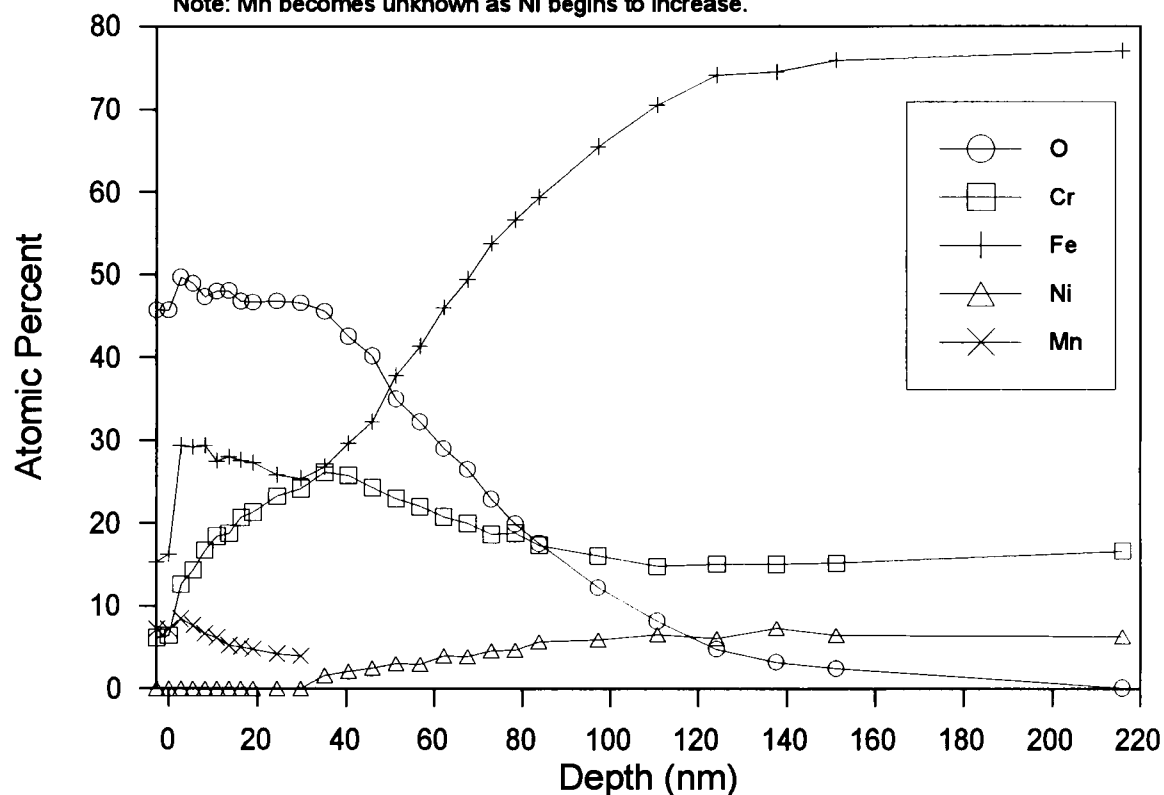


Figure 3-95. Depth profiles of the heat-tinted weldment specimen at a location where the blue or straw-colored oxide was observed.

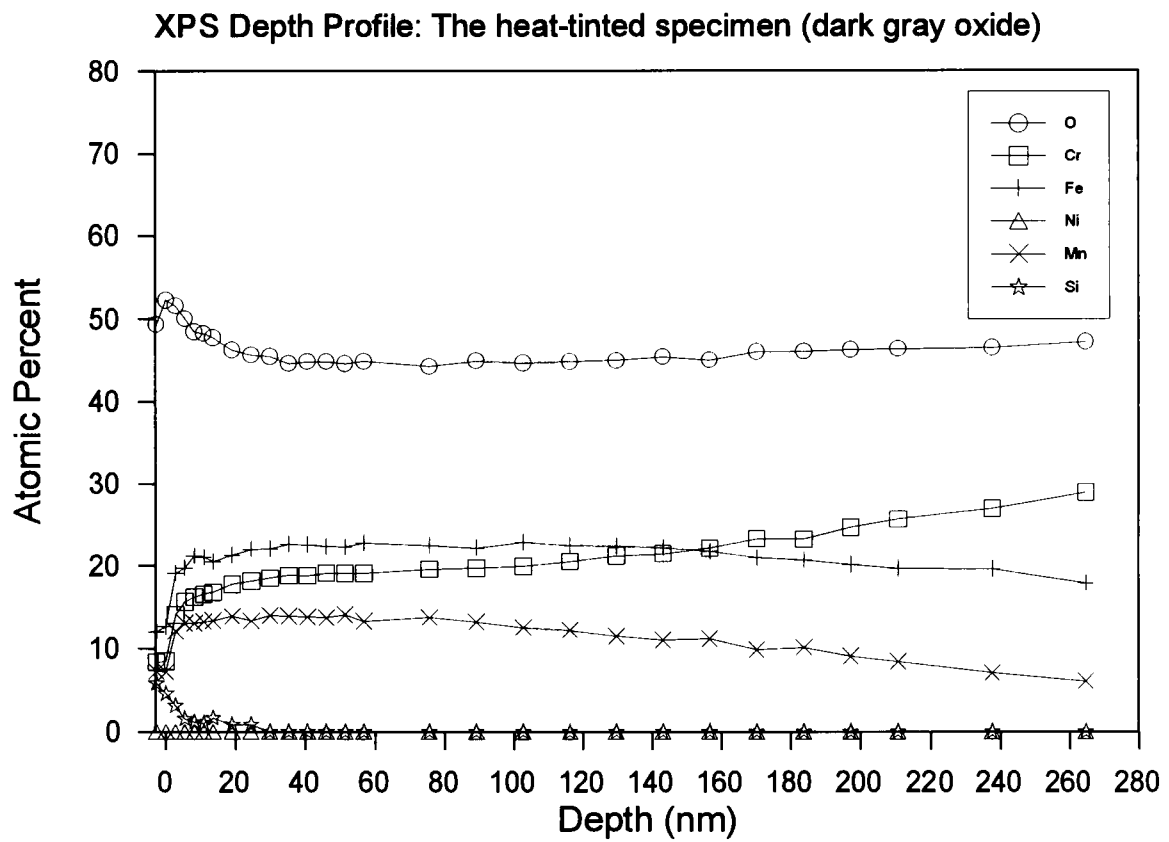


Figure 3-96. Depth profiles of the heat-tinted weldment specimen at a location where the dark gray oxide was observed.

chemical information over an area of $0.25\ \mu\text{m}$ in diameter. This superior spatial resolution makes AES more suitable for analyzing chemically nonuniform material. Typical Auger electron peaks obtained from the heat-tinted weldment specimen on the dark gray oxide are illustrated in Figure 3-97. Since the as-welded 304L/308L weldment has an as-received and relatively rough surface, AES is best to analyze this type of specimen. Several spots on the dark gray and the straw-colored oxides were selected for depth profile measurement. Two of them, one from the dark gray oxide and the other from the straw-colored oxide, are shown in Figures 3-98 and 3-99, respectively. The profiles in general are in agreement with those made by XPS. Since the chemistry information given by AES is very localized and consistent with the XPS analysis, the overall results suggest that the oxide produced either by Gleeble simulation or by welding is chemically homogeneous along the surface dimensions. There are concentration gradients in the depth dimension, which are reflected in the depth profiles.

The oxide chemistry analyses either macroscopically (XPS) or microscopically (AES) revealed that no obvious chromium depletion occurred underneath the oxide in the metal matrix. There were some specimens showing chromium depletion to some extent at the oxide surface. Actually, almost all the specimens showed that chromium was enriched in the oxide near the oxide/metal interface. This enrichment was also observed in that when the depth profile was near the oxide/metal interface, the oxide photoelectron peaks kept constant while the metal photoelectron peaks began to increase, implying that the overall chromium content was increasing. Iron was depleted in the oxide under all circumstances. It appeared that iron and chromium complemented each other, always

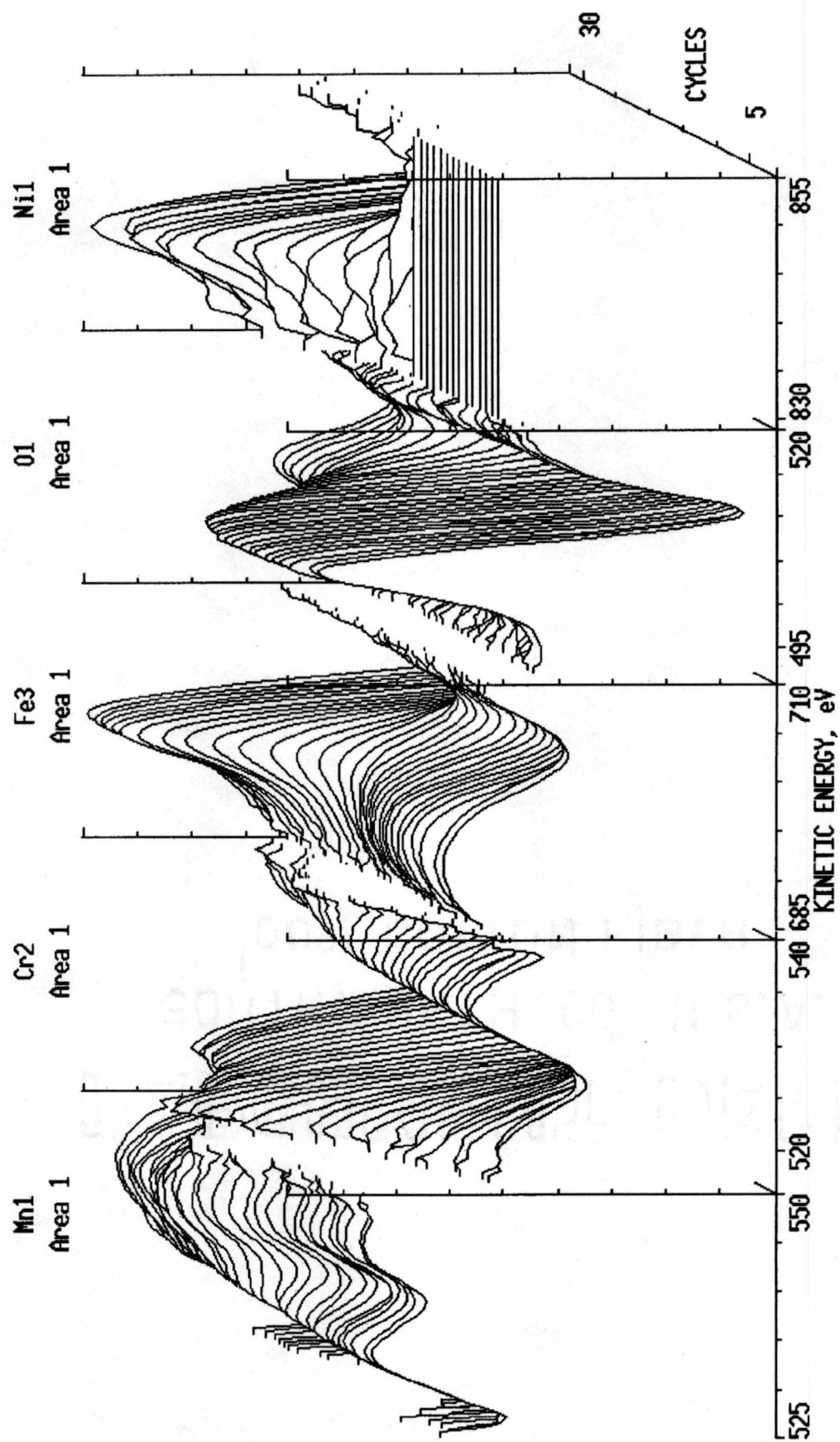


Figure 3-97. Auger electron peaks of the heat-tinted weldment specimen as a function of the data cycle.

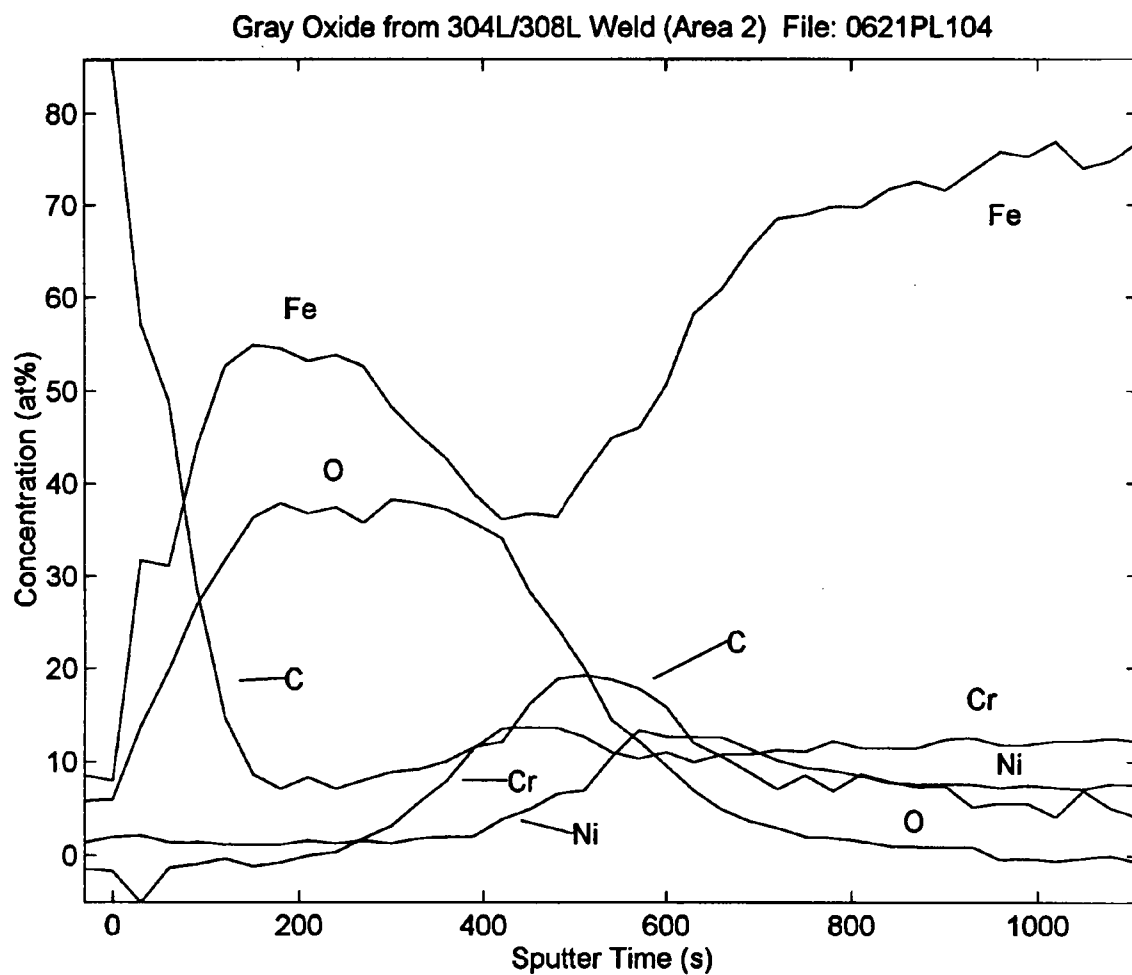


Figure 3-98. AES depth profiles of the dark gray oxide of the as-welded 304L/308L weldment (sputter rate = 200 nm/min).

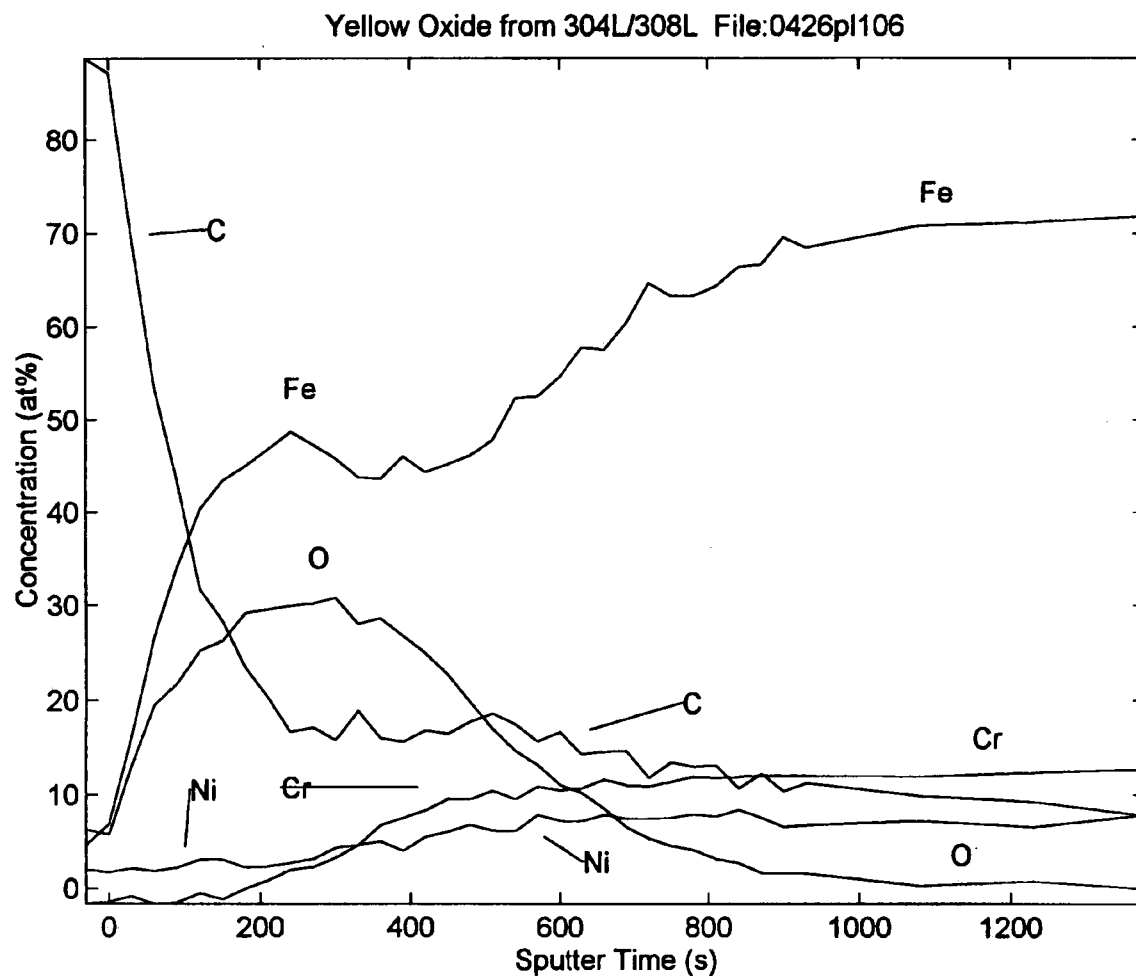


Figure 3-99. AES depth profiles of the straw-colored oxide of the as-welded 304L/308L weldment (sputter rate = 40 nm/min).

making up about 50% of the composition of the oxide. The metallic elements inside the oxide existed in the form of the corresponding oxide. Specifically, the oxide mainly consisted of iron oxide, chromium oxide, and sometimes a little manganese oxide. Nickel was not found inside the oxide near the surface and very little could be found near the oxide/metal interface.

The AES results reported by Turner⁶⁶ and Kearns⁶⁷ showed chromium depletion near the oxide/metal interface. However, because of the limited data presented in both papers, it is difficult to make a comparison to the current XPS and AES results for the oxide analyses. For instance, Turner did not show the oxygen concentration in the oxide so that it was not clear where the oxide/metal interface was located. Kearns showed the depth profiles of an oxide using AES peak to peak height which is not directly related to atomic concentration. In both studies, the authors did not mention that an appropriate separation of oxygen and chromium peaks was made. In the current XPS and AES analyses of the various oxides, the results showed consistently that no apparent chromium depletion was observed near the oxide/metal interface.

3.4.5. SEM Examinations

The oxide morphology was evaluated by SEM. Surface morphologies of the heat-tinted weldment oxide, as shown in Figures 3-100, 3-101, 3-102, and 3-103, were obtained using a LEICA Stereoscan 440 microscope. Different surface locations which correspond to the dark gray, brown, blue or straw-colored, and light yellow oxides were

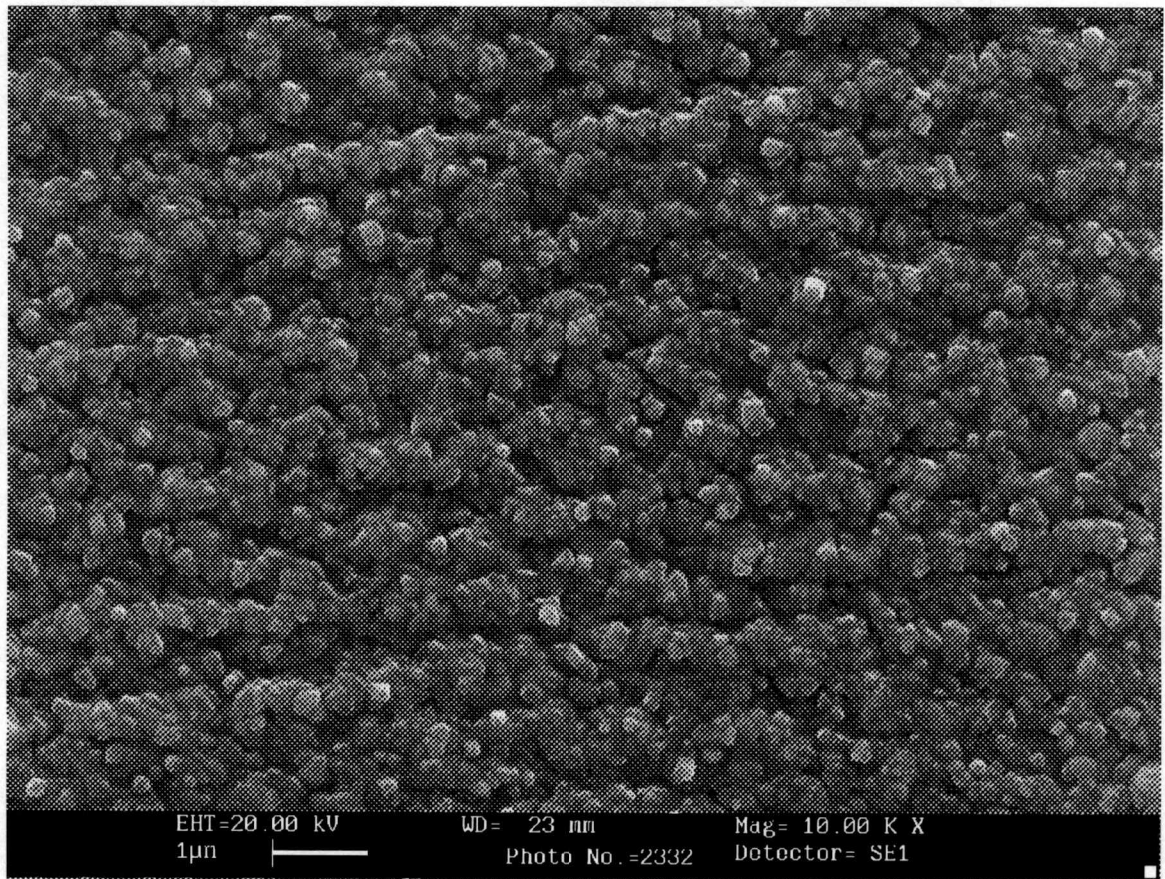


Figure 3-100. SEM micrograph of dark gray oxide on the heat-tinted weldment specimen showing oxide morphology.

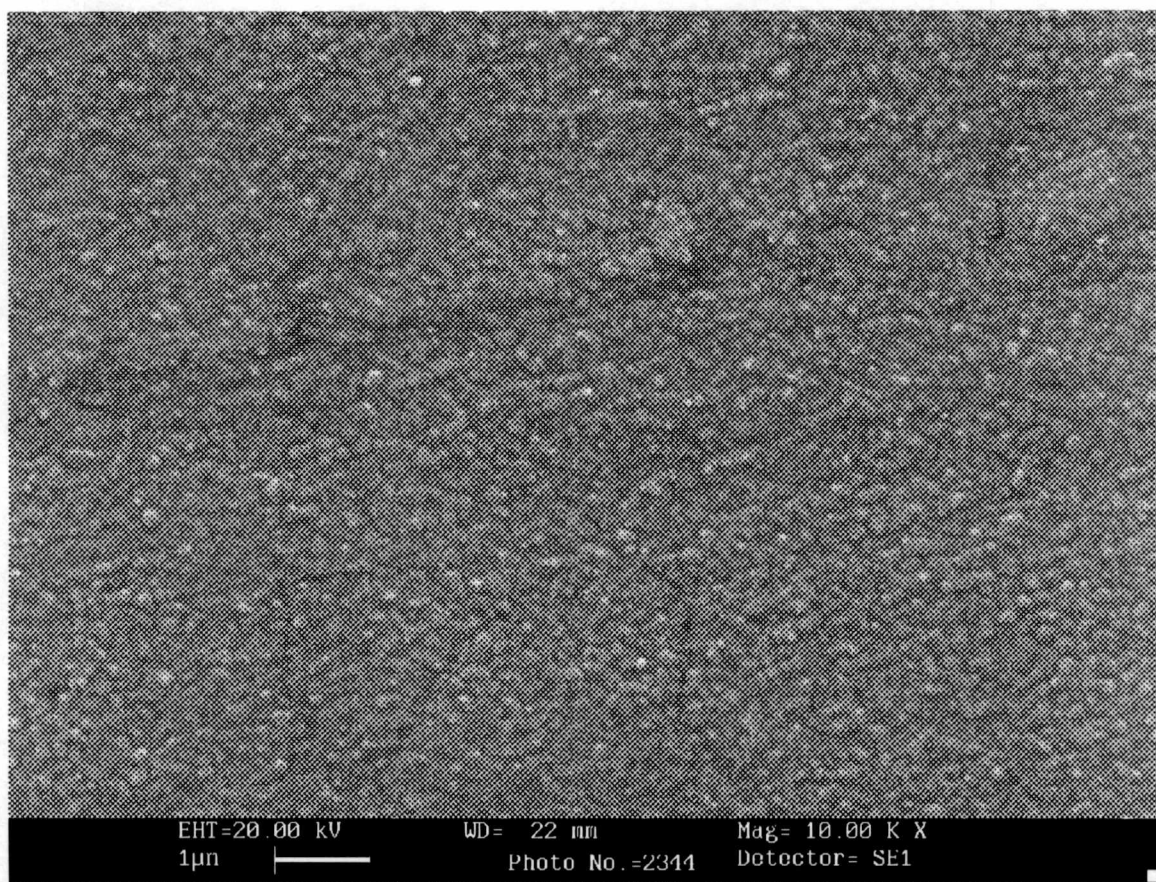


Figure 3-101. SEM micrograph of brown oxide on the heat-tinted weldment specimen showing oxide morphology.

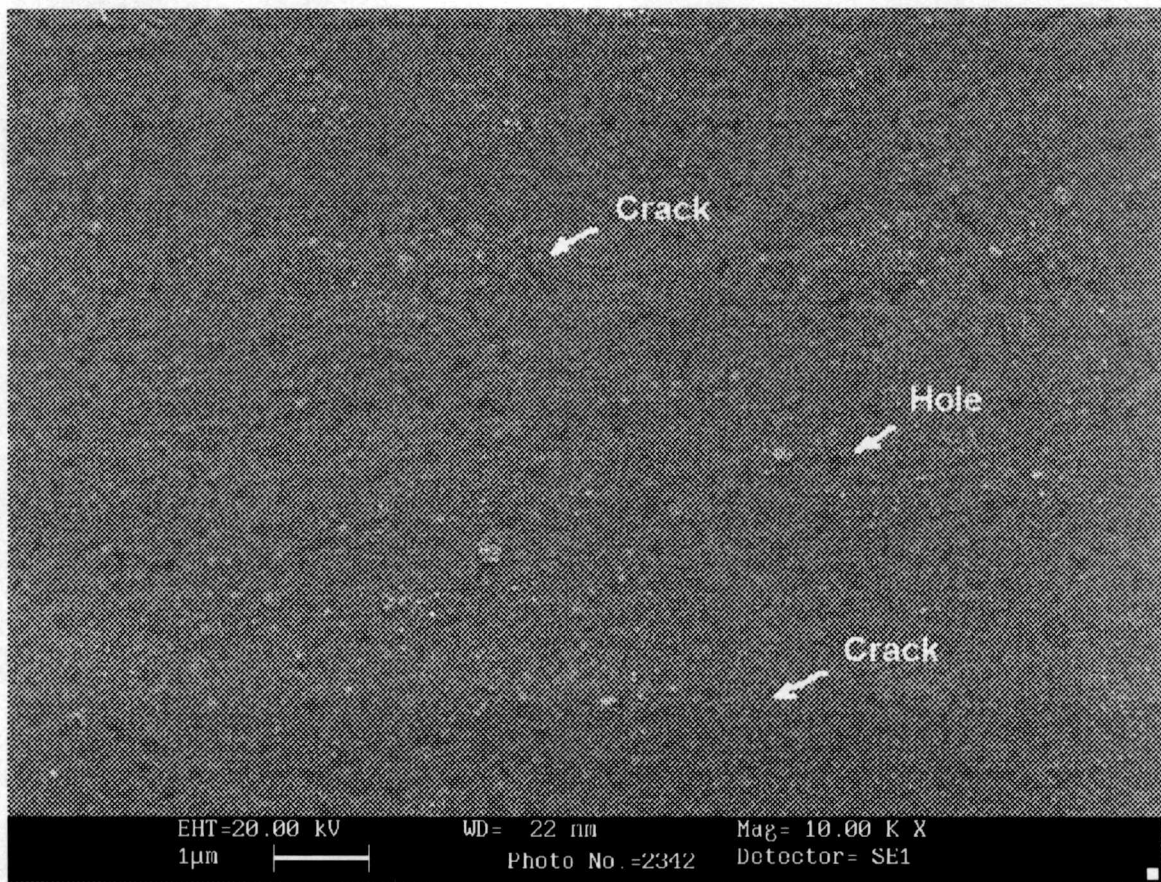


Figure 3-102. SEM micrograph of straw-colored or blue oxide on the heat-tinted weldment specimen showing oxide morphology.

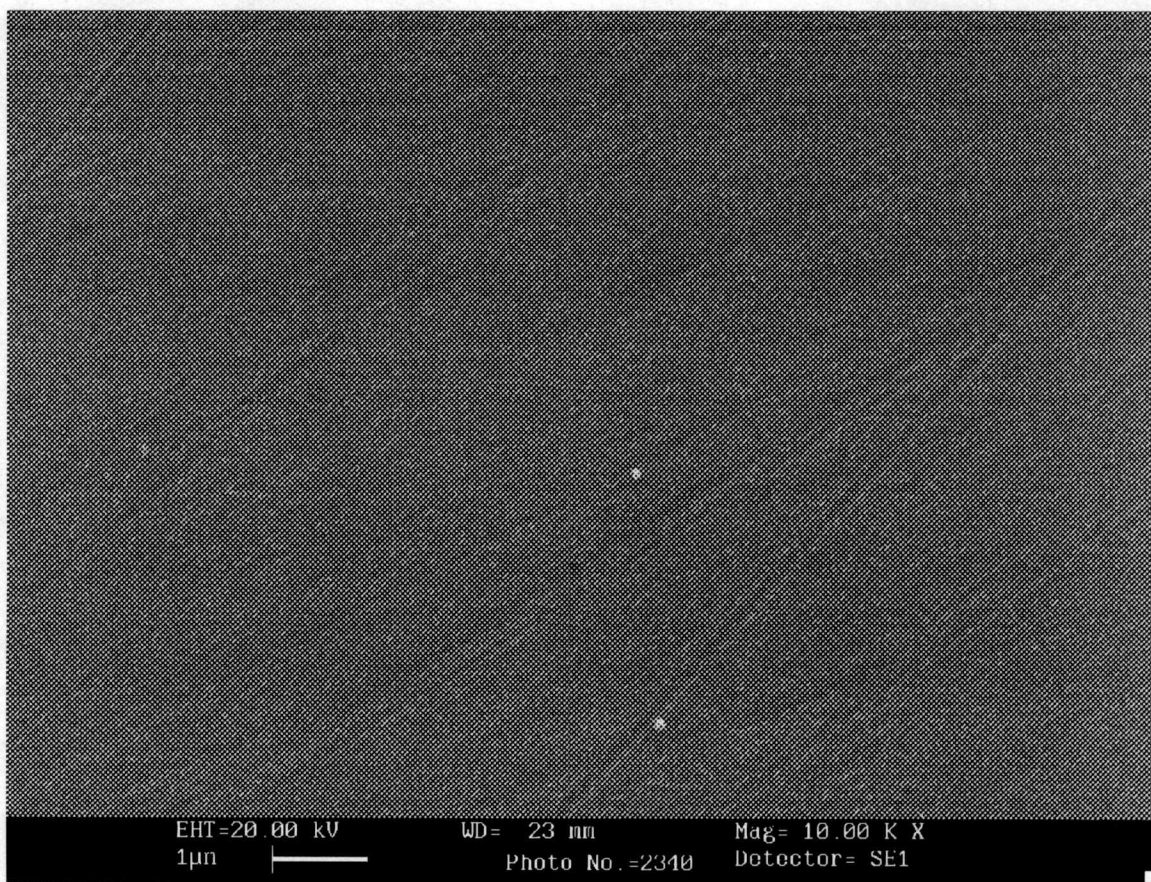


Figure 3-103. SEM micrograph of light yellow oxide on the heat-tinted weldment specimen showing oxide morphology.

characterized. The dark gray oxide (Figure 3-100) appears to consist of small granules which are clustered forming a porous material. This indicates that the dark gray oxide can be penetrated when the oxide surface is exposed to an aqueous environment. The brown oxide (Figure 3-101) appears to be less porous than the gray oxide. However, the oxide appears to be cracked at some locations, suggesting that the oxide is not continuous and can allow penetration of aqueous environments. The blue or straw-colored oxide (Figure 3-102) reveals several features. First, there are cracks in the oxide. Because the straw-colored oxide is thinner than the gray oxide, it apparently can be easily fractured by thermal or mechanical stress. The cracks appear to be aligned in a similar direction, implying that the cracks probably are caused by mechanical strain on weldment cool-down. In addition, the oxide appears to have open holes (dark spots), suggesting that the straw-colored oxide does not form a complete oxide film covering the metal surface. The light yellow oxide (Figure 3-103) reveals features similar to the base metal surface. This oxide, which appears to be smooth and uniform in coverage, is thinner than the straw-colored oxide. The surface morphology of the Gleeble oxides was evaluated using a Cambridge HS360 microscope. The Gleeble oxides for 2400°F, 1600°F, and 800°F peak temperatures, are illustrated in Figures 3-104, 3-105, and 3-106, respectively. The 2400°F Gleeble specimen, which exhibits a dark gray oxide, shows a granular-like porous oxide structure. The 1600°F Gleeble specimen illustrates an apparent nodule-like oxide surface (Figure 3-105). The 800°F Gleeble specimen, which shows a light yellow oxide, reveals a smooth oxide surface (Figure 3-106). The overall observations on the Gleeble oxides were quite consistent with those of the heat-tinted oxides.

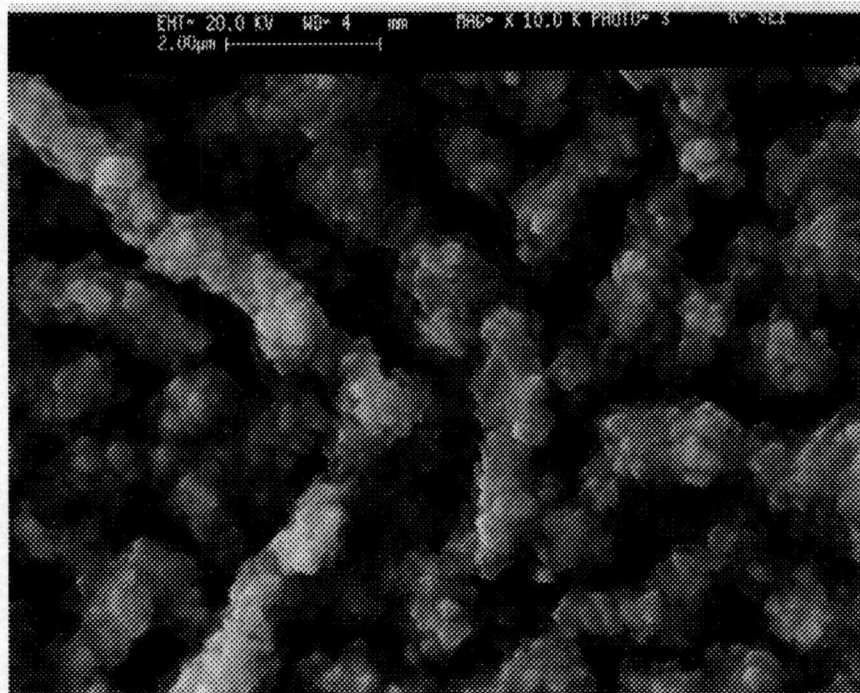


Figure 3-104. SEM micrograph of dark gray oxide of the 2400°F Gleeble specimen showing oxide morphology.

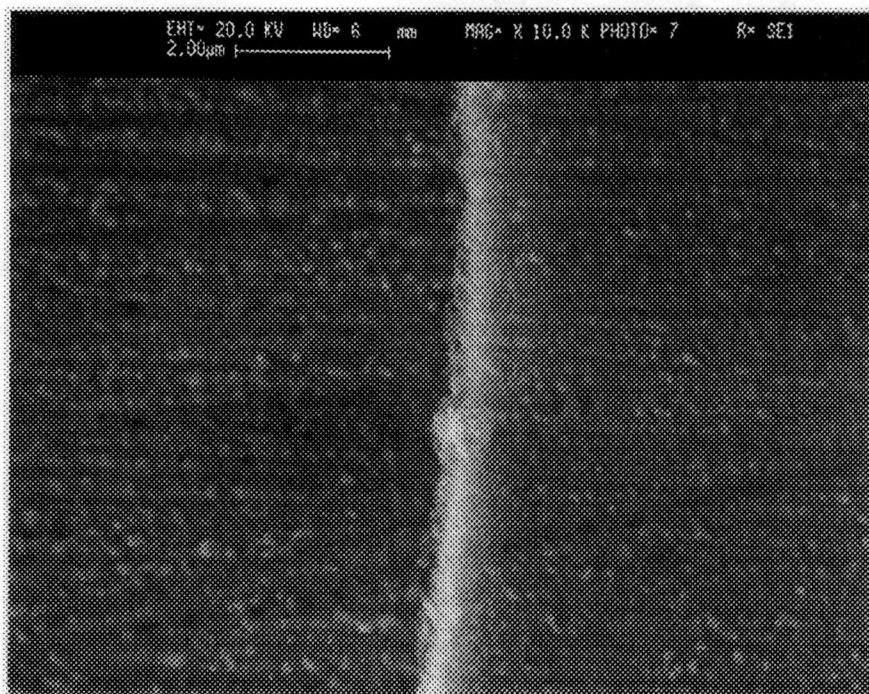


Figure 3-105. SEM micrograph of brown oxide of the 1600°F Gleeble specimen showing oxide morphology.



Figure 3-106. SEM micrograph of light yellow oxide of the 800°F Gleeble specimen showing oxide morphology.

The oxide character was evaluated by transverse sectioning of an oxidized surface of an as-welded 304L/308L weldment which was gold-coated and electroplated with nickel so as to preserve oxide integrity. The coated weldment was mounted in epoxy and polished to a metallographic finish. Because the polished sample was flat, SEM examinations were performed by the back scatter electron imaging method, with the results as shown in Figures 3-107 to 3-109. Figure 3-107 reveals a stainless steel substrate, weld oxide (dark band), gold coating (bright band), and plated nickel regions. The dark gray oxide region (arrow A) is shown in Figure 3-108 at higher magnification. The oxide generally appears to consist of a mottled material with the dark irregularities appearing to be cavities in the oxide. This fenestrated oxide indicates it has a porous structure. It also is seen that the polishing marks, present in the stainless steel and the nickel, are not present across the oxide. This suggests that the oxide structure was not completely retained and probably was modified to some extent during sample preparation. Nevertheless, the porous structure and topographic nature of the thick oxide as revealed by the transverse sectioning are consistent with that revealed from the oxide topographic studies, as shown in Figure 3-100. The oxide located in the straw-colored region, as shown in Figure 3-109, was difficult to examine because of its thinness and the lack of adequate resolution.

When a metal is exposed to an oxidizing environment, oxidation occurs on the metal surface. The oxidation process includes oxide nucleation and growth. As oxidation continues the oxide grows on the nuclei. The oxide grows laterally along the metal

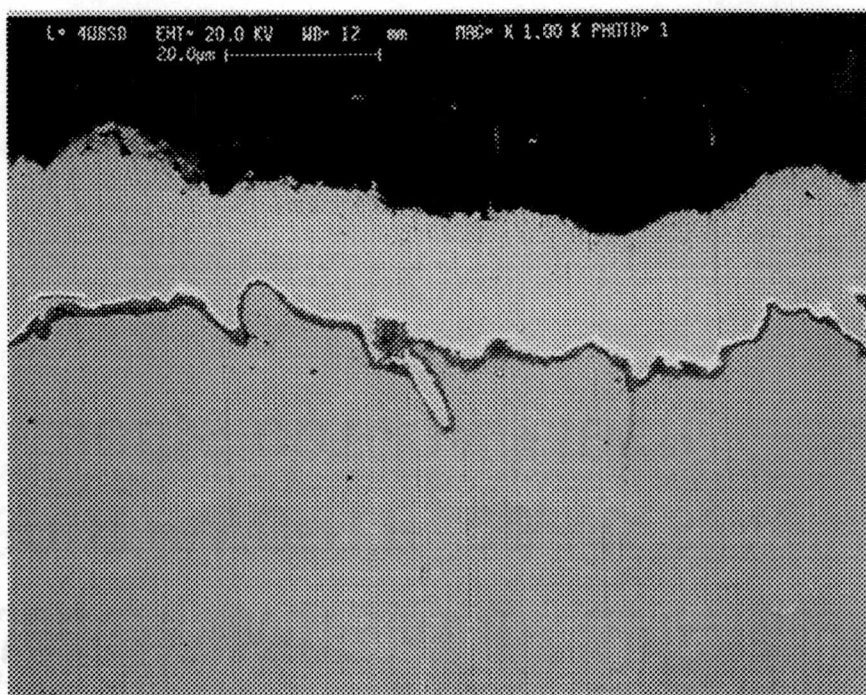


Figure 3-107. Transverse section of an as-welded 304L/308L weldment showing oxide in the dark gray oxide region (mag. 1000X).

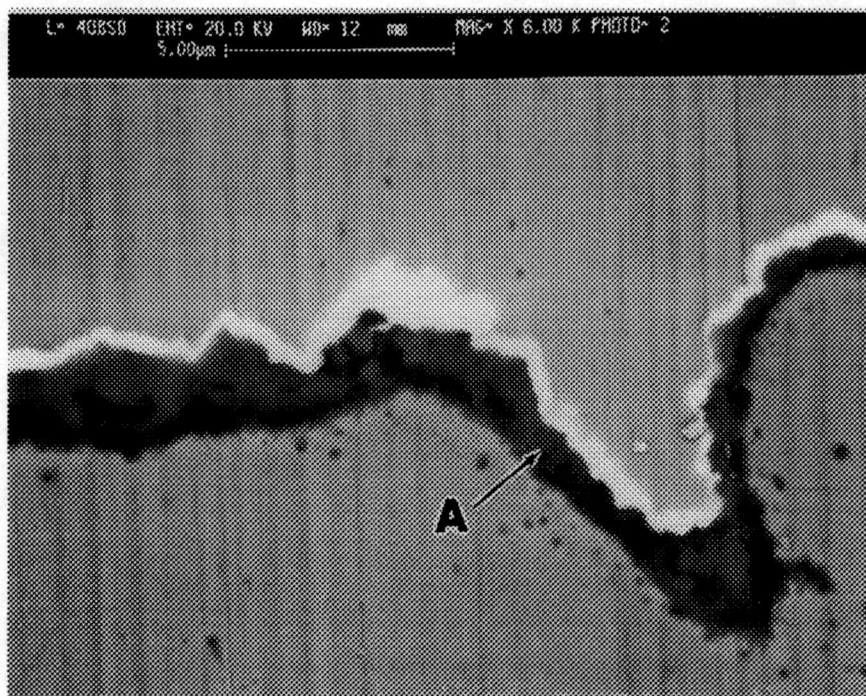


Figure 3-108. Transverse section of an as-welded 304L/308L weldment showing oxide in the dark gray oxide region at 6000X.

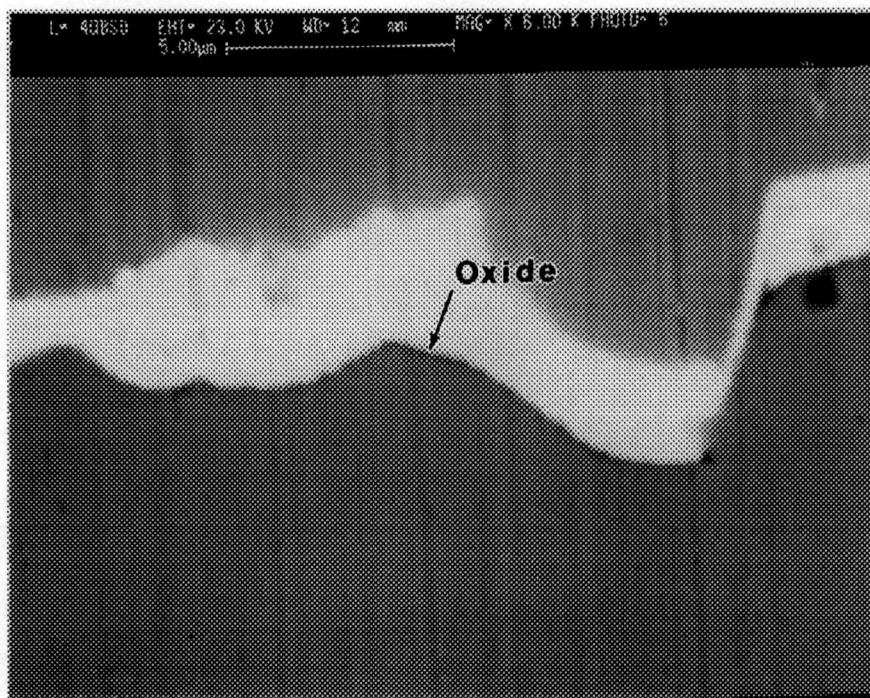


Figure 3-109. Transverse section of an as-welded 304L/308L weldment showing oxide in the straw-colored oxide region (mag. 6000X).

surface until complete oxide coverage occurs. The oxide then continues to grow along perpendicular to the surface controlled by diffusion processes.

It is hypothesized that since the oxidation process initially forms many nodule-like nuclei over the surface (Figures 3-101 and 3-105) and thereafter the oxide prefers to grow on the nuclei (Figures 3-100 and 3-104), the thick oxide (dark gray or 2400°F oxide) has a characteristic morphology of granule-like oxides forming a porous material over the surface. This structure plays an important role in the crevice corrosion behavior for the high temperature weld heat tint regions. The thin oxide, (straw-colored or 800°F oxide) which forms at a lower temperature, at slower diffusion rates for the oxidizable elements. In this oxide, it is conceivable that the oxidation had less nuclei formed over the metal surface, as well as the slower growth controlled by diffusion. This process appears to cause the thin oxide to develop as a more continuous film over the surface. However, cracks form in the thin oxide due to thermal or mechanical strain, and holes are left in the oxide due to incomplete oxide coverage. These physical defects play a crucial role in the pitting corrosion behavior for the thin oxide.

3.5. The Corrosion Mechanisms

The overall corrosion results including laboratory and field tests revealed that 304L stainless steel weldments with welding oxide are subject to crevice corrosion when the imposed crevice is applied on the dark-gray high-temperature oxide. Without the imposed crevice, the weldment demonstrates corrosion resistance in fresh water systems

although the passive breakdown potential is greatly decreased. It also was found that pitting corrosion occurs at regions of low rather than high temperature oxide when the weldment is exposed to a ferric chloride solution. The Gleeble and heat-tinted weldment specimens illustrated that the low-temperature straw-colored oxide is subject to pitting corrosion. The chemical compositions of the oxides and the underlying metal substrate, as analyzed by XPS and AES, indicated that the metal underneath the oxide remains unchanged in chemistry. Therefore, deterioration of corrosion resistance is not caused by chromium depletion of the metal substrate. Furthermore, as indicated previously in the passivation mechanism, a layer of chromium-deficient metal causes presumably uniform metallic ion dissolution, which is not likely to bring about localized corrosion.

SEM examinations on the morphologies of a variety of different temperature oxides revealed that the morphology of high temperature oxide, i.e., the dark gray oxide, may account for the crevice corrosion associated with this oxide. The high temperature oxide tends to form a sponge-like structure on the metal. This structure does not specifically degrade the metal in terms of localized corrosion behavior because it covers the metal uniformly. However, if an imposed crevice is applied to the metal, as shown schematically in Figure 3-110, the imposed crevice material and the metal form a sandwich-like geometry with the oxide in between. The oxide with the sponge-like structure serves as a passage to solution. As a result, a crevice geometry which could have an unlimited crevice length is formed along the surface. It is conceivable that this crevice deteriorates corrosion behavior of the metal because at some location along the crevice length the IR drop would be large enough to place the metal out of the passivation

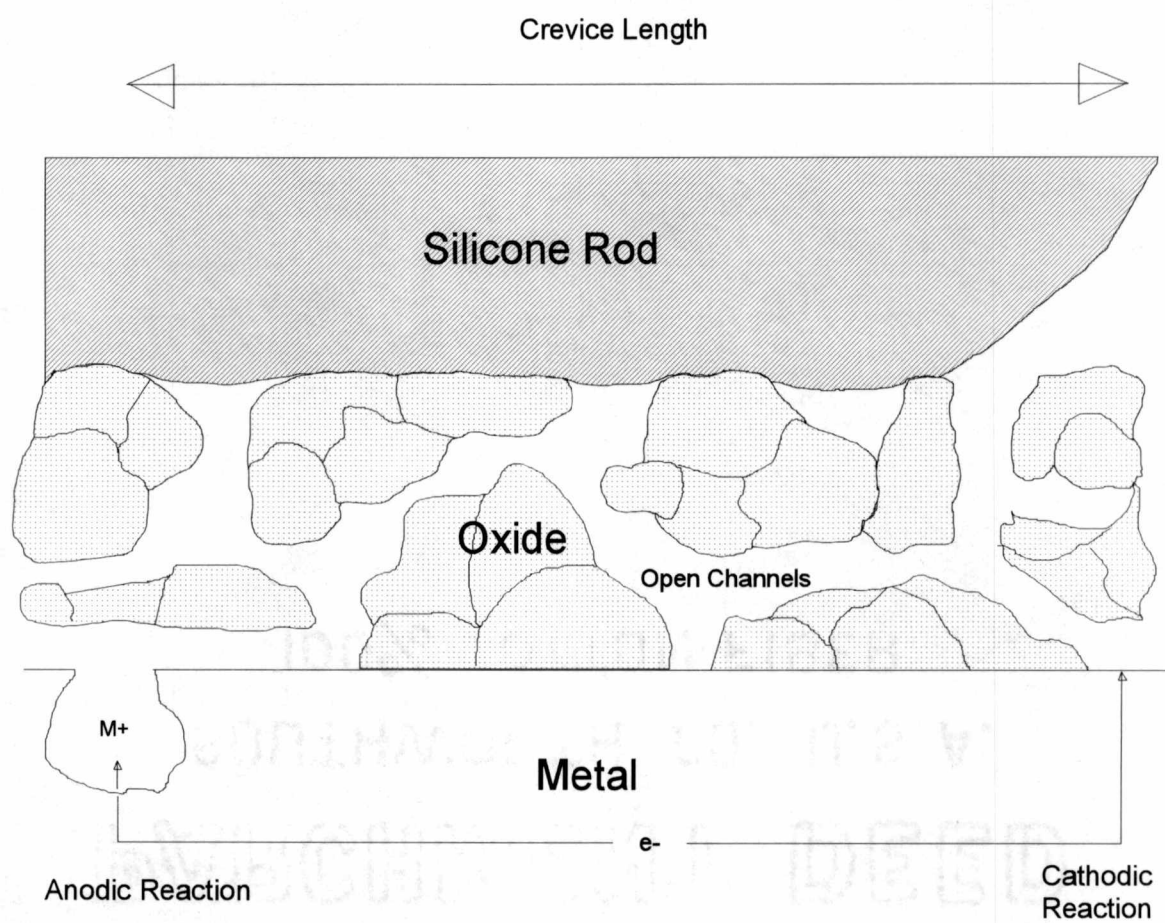


Figure 3-110. Model of the crevice corrosion mechanism.

range and into the active corrosion range.⁷⁹ Consequently, active corrosion would take place at this location and all the other factors, such as metal-ion hydrolysis and chloride concentration, would contribute to the corrosion process. The previous corrosion results have shown that corrosion occurs underneath the imposed silicone rod or the epoxy mask, thereby demonstrating good agreement with the above crevice corrosion mechanism.

The silicone rod forms a sharp corner with the metal surface at the silicone/metal contact interface. Without the presence of the oxide, this geometry creates a crevice with a limited length. Whether crevice corrosion occurs or not depends on the corrosion resistance of the material and aggressiveness of the solution. Certainly, the short crevice length produces a small IR drop. The corrosion results demonstrated that when the oxide is removed from the weldment surface, e.g., by pickling, the weldment with the imposed crevice by the silicone rod does show crevice corrosion resistance in the fresh water systems. However, this might not be the case when the weldment is exposed to ferric chloride solution.

The SEM examinations on low temperature oxide, i.e., the straw-colored oxide, revealed a smooth surface on which oxide existence was confirmed by the XPS analysis. Under the proposed crevice corrosion mechanism, crevice corrosion on the straw-colored oxide would not occur because of the homogeneous nature of the oxide morphology. The corrosion results on the Gleeble samples were consistent with this proposed mechanism in that crevice corrosion occurred on the dark gray oxide rather than the straw-colored oxide in the bacterial solution.

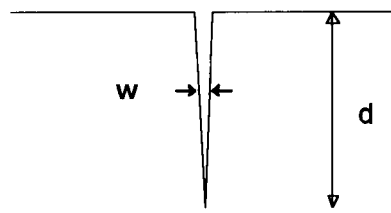
Explanation for the pitting corrosion on the low temperature oxide is not as obvious as that for the crevice corrosion on the high temperature oxide. Based on the XPS and AES results, the low temperature oxide (800°F Gleeble specimen or light yellow oxide of the heat-tinted weldment specimen) has a similar depth profile to that of the high temperature oxide (1600°F Gleeble specimen or blue oxide of the heat-tinted specimen). The low temperature oxide perhaps shows a very slight chromium depletion in the metal near the oxide/metal interface (Figures 3-90 and 3-94). This depletion is possibly caused by the low diffusion rate of chromium during oxidation at low temperature. At high temperature, the diffusion rate is sufficiently high that the entire matrix material may serve as an unlimited chromium source. However, this slight chromium depletion is not sufficient to account for the striking pitting corrosion behavior of the low temperature oxide.

Although the low temperature oxide is visible by the naked eye, owing to its light yellow color, SEM micrographs (Figures 3-103 and 3-106) revealed that the surface appears extremely smooth. At 10,000 magnification, the oxide morphology does not disclose any inherent flaws associated with its corrosion results. However, very fine visible nodules cover the surface, indicating initiation of the oxide nucleation. It is noted that the blue or straw-colored oxide (Figure 3-102) exhibits some physical defects such as oxide cracks and incomplete oxide coverage, which also might be present on the light yellow oxide.

The aspect ratio of a surface defect is defined as the depth divided by the width of the defect. It is known that, for a given exposure time, an increasing aspect ratio

significantly enhances the electrolyte aggressiveness in the defect, i.e., decreasing pH and increasing chloride concentration. Consequently, as the aspect ratio (AR) increases, the pitting potential (E_{pit}) decreases and the passivation potential (E_{pp}) increases, as illustrated in Figure 3-111. According to the previous SEM examination on the oxides, it was found that the aspect ratio for the defects in the straw-colored oxide was greater than that for the dark gray oxide.

A schematic diagram showing a possible corrosion mechanism for the low temperature oxide is presented in Figure 3-112. It is presumed that oxidation forms a continuous oxide film over the surface at the low temperature. There are physical defects in the oxide such as cracks and holes which possibly arise from thermal or mechanical strain during welding, thermal expansion mismatch between the oxide and the metal on cooling, and incomplete oxide coverage due to different material densities of the oxide and the metal. There also exists chemical deterioration in that a slight chromium deficiency is present in the metal underneath the oxide. This chromium depletion could induce corrosion at locations such as the crack or the oxide hole where the bare metal is exposed to the solution. Because the crack or hole in the oxide forms an occluded geometry, maintenance of passivation is difficult. Moreover, the large oxide area surrounding the crack or hole supports the cathodic reaction. This leads to a large cathodic to anodic area ratio which results in a large anodic current. In addition, the large aspect ratio of the surface defects makes the solution more aggressive in the defects, which reduces the pitting potential of the metal in these locations. As a result, pitting occurs at these locations and both the physical and chemical defects contribute to the corrosion.



Aspect Ratio: $AR = d/w$

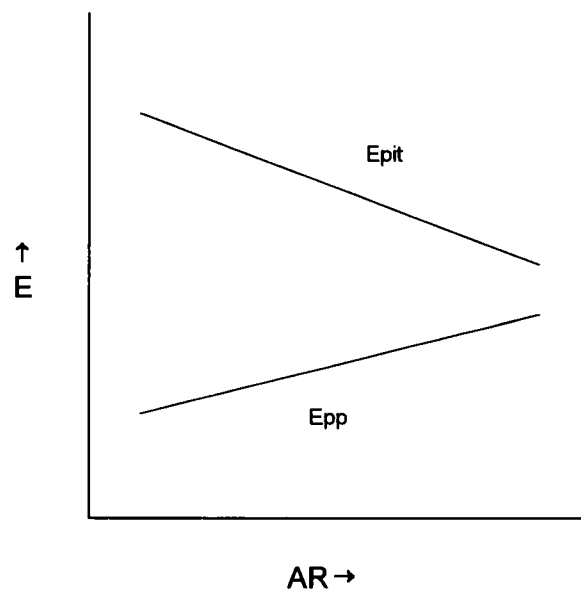
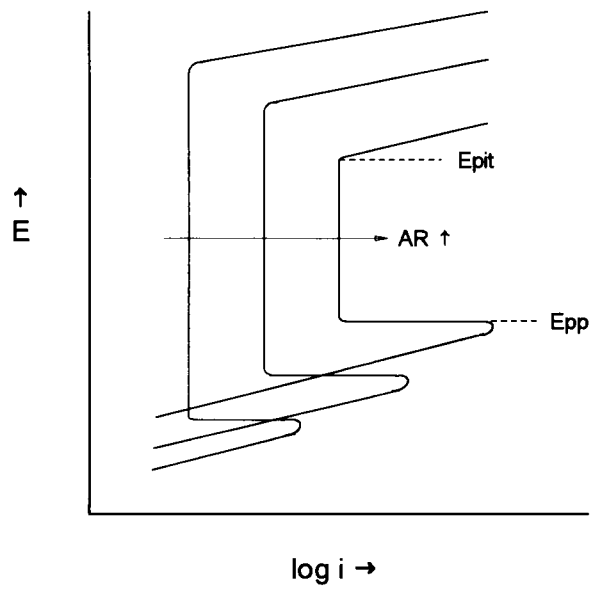
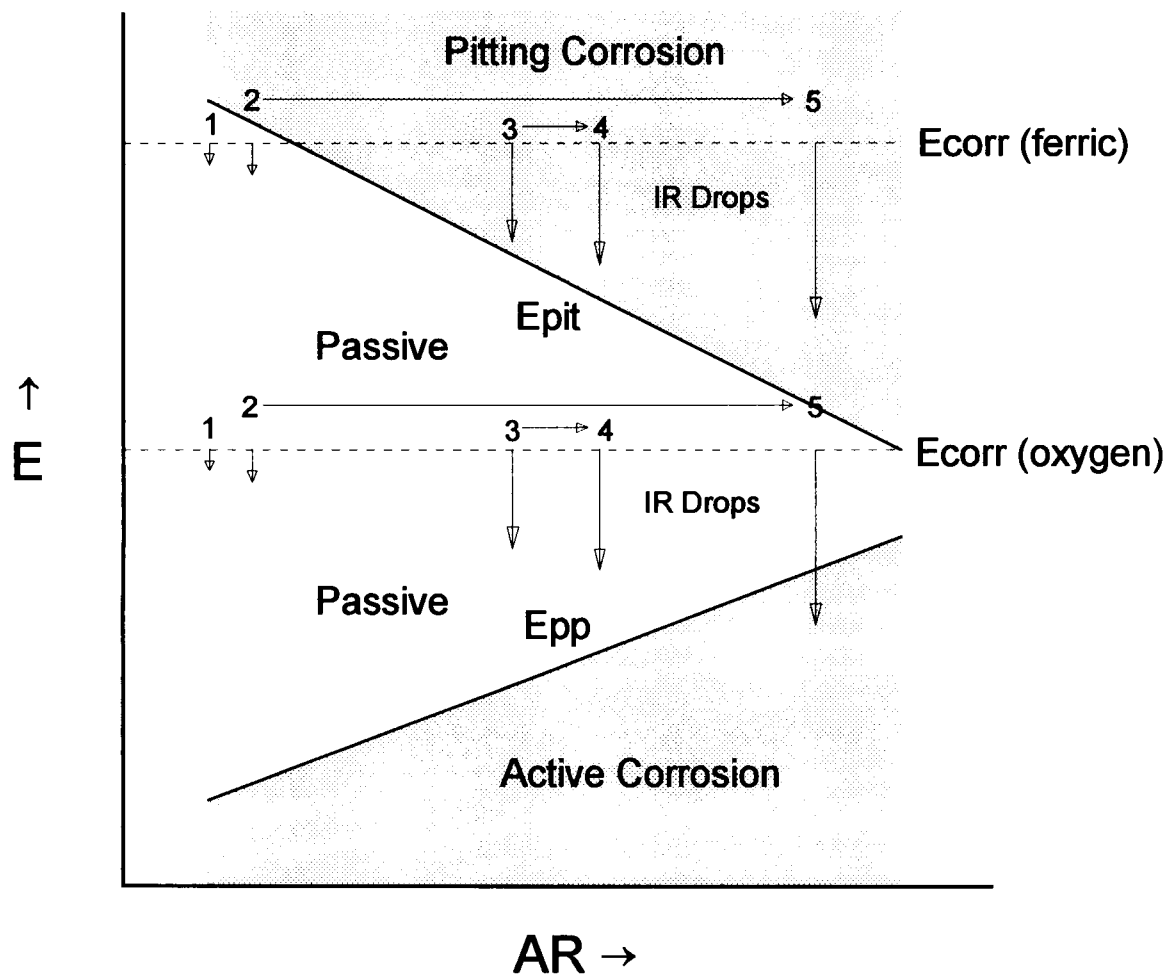


Figure 3-111. Schematic diagrams showing the aspect ratio effects on E_{pit} and E_{pp} .

In summary, the pitting and the crevice corrosion mechanisms associated with the high and low temperature oxides in ferric chloride and oxygenated solutions can be described by a potential versus aspect ratio diagram, as shown in Figure 3-113. The pitting potential decreases and the passivation potential increases as the aspect ratio becomes greater. The corrosion potential in a ferric chloride solution is more noble than in an oxygenated solution. The high temperature oxide is thicker than the low temperature oxide. However, although the physical defects have a greater depth, they have a much greater width than those in the low temperature oxide. Accordingly, the aspect ratio of the defects in the high temperature oxide is less than those in the low temperature oxide. The IR drop caused by a defect is greater as the aspect ratio increases. As shown in Figure 3-113, in the absence of an imposed crevice, the low temperature oxide should be more susceptible to pitting corrosion than the high temperature oxide. It is seen that for the ferric environment, the pitting potential is exceeded at point 3 corresponding to the aspect ratio for the low temperature oxide, but is not exceeded at point 2 corresponding to the aspect ratio for the high temperature oxide. In the oxygenated environment, and in the absence of an imposed crevice, metals with both the high and low temperature oxides exist in the passive region. In the presence of an imposed crevice, the aspect ratio for the high temperature oxide is increased from point 2 to point 5 because of the nature of the sponge-like oxide structure. This increase, along with the IR drop, places the metal into the active corrosion region in the oxygenated solution. The aspect ratio for the low temperature oxide would increase from point 3 to point 4, but the change does not affect its corrosion behavior in the oxygenated



Note: IR drops caused by defects:

1. in base metal
2. in heavy oxide
3. in thin oxide
4. in thin oxide with crevice former
5. in heavy oxide with crevice former

Figure 3-113. Potential versus aspect ratio diagram.

environment since the metal remains in the passive region. In the ferric environment, the pitting potential is exceeded at points 4 and 5, indicating that pitting corrosion would occur for both the high and low temperature oxides. In conclusion, the corrosion behavior of the stainless steel weldment is determined by its corrosion potential, the oxide characteristics, the aspect ratio of a defect, the IR drop, and the presence of an imposed crevice geometry.

CHAPTER 4

CONCLUSIONS

4.1. MIC Laboratory Tests

1. The bacterial consortium "influenced" the corrosion process by accelerating it somewhat, but other factors also were important.
2. In long-term exposures to bacterial and sterile control solutions containing 100 ppm chloride, localized corrosion in the form of nodules occurred only at crevice locations in the weld-oxide heat-tint areas, never at crevice locations in the base-metal areas. The extent of nodule formation was somewhat greater in the bacterial solution.
3. In the above long-term exposures, when the welding heat tint was removed by pickling or electropolishing, no corrosion nodule formation occurred in either the bacterial or control solution.
4. Electrochemical anodic-polarization evaluations with non-creviced specimens showed passivation, and, therefore, negligible corrosion rates, for the pickled surface in both control and bacterial solutions, and for the heat-tint surface in the control solution;

4.2. MIC Field Tests

1. Without crevice geometries, all of the weldments performed satisfactorily. This satisfactory performance was specifically shown for 304L and 316L based weldments.
2. With crevice geometries, the heat-tint regions of all the weldments, but not the base metal, underwent accelerated localized corrosion leading to nodule formation.
3. With crevice geometries, over the range of weldments evaluated, the detrimental heat-tint effect was more dominant than the anticipated beneficial effects associated with the use of more corrosion-resistant base-metal/filler-metal combinations.
4. With crevice geometries, if the heat tint was removed chemically (pickling), electrochemically (electropolishing) or mechanically (grinding), localized corrosion and nodule formation did not occur.

4.3. Welding Oxide

1. The welding oxide was successfully reproduced by Gleeble simulation at different peak temperatures, and by GTAW for the root pass with shielding gas and SMAW for the subsequent pass without shielding gas.

2. XPS and AES analyses revealed that no apparent chromium depletion occurred in the metal underneath the oxide. The oxide was mainly composed of iron oxide, chromium oxide, and manganese oxide. Atomic concentration depth profiles of the oxide showed a similar type profiles in the high temperature oxide (dark gray) and low temperature oxide (straw-colored or light yellow).
3. SEM examinations of the surface morphology of the oxide indicated that the dark gray oxide had a porous, granule-like oxide structure, and the straw-colored oxide had a continuous film oxide structure with the presence of some physical defects.
4. Crevice corrosion occurred only at the high temperature oxide in the fresh water. The classic crevice corrosion mechanism accounted for the crevice corrosion on the high temperature oxide with its associated porous structure.
5. Pitting corrosion occurred only at the low temperature oxide (light yellow) in ferric chloride solution. This pitting corrosion was rationalized in terms of the combination of physical and chemical defects in the oxide.

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