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Corrosion 89

INFLUENCE OF WELDING VARIABLES ON MICROBIOLOGICALLY INFLUENCED CORROSION OF AUSTENITIC STAINLESS STEEL WELDMENTS

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ABSTRACT

Biofilms develop on metallic surfaces in contact with natural waters. Biofilms can contain microorganisms which accelerate corrosion. The chemical composition and microstructure of weldments, as produced by welding processes and heat treatment, can influence the degree of accelerated corrosion. It may be possible to avoid costly pitting failures if the weldment could be made less susceptible to microbiologically influenced corrosion (MIC) by proper selection of filler metal, welding process variables, or heat treatment.

Field testing and subsequent laboratory electrochemical analyses were conducted to examine the role of welding and heat treatment variables on MIC of austenitic stainless steel weldments. Pipe specimens were fabricated (GTAW) of both 304L and 316L for field testing. Filler metals were selected to produce three percentages of ferrite content (low, medium, and high). Weldments of each ferrite content were evaluated in both as- deposited and solution-annealed conditions. Field testing involved exposure of the weld specimens for approximately one year to a small trickle of water directly from a well known to produce MIC. Mounds indicating biomass formation appeared on the welds after two weeks' exposure.

Laboratory electrochemical analyses involved measurements of corrosion potentials as a function of time and critical pitting potentials for weld and base metal samples in microbial solutions.

INTRODUCTION

The presence of a microbial film, also called a biofilm, and the action of various microbes does not introduce a new type of corrosion, but rather may influence the types of corrosion that are well known. Microbiologically influenced corrosion (MIC) is the term used for the phenomenon where corrosion initiates or is accelerated by microorganisms. Biofouling is a general term describing all forms of biological growth on surfaces in contact with natural waters.

Industry currently recognizes MIC as a serious problem affecting the construction and operation of many facilities, including nuclear power plants. Although MIC can occur on a variety of alloys [1,2], pitting failures of austenitic stainless steels are often associated with weldments[3,4]. Industry uses these alloys for their corrosion resistance; when structures made of these alloys leak, serious, sometimes hazardous problems and costly repairs result.

Types 304L and 316L were chosen for this study because they are common austenitic stainless steels that have been the source of many MIC failures. The types are often selected by industry for their superior corrosion resistance. Limiting the carbon content to 0.03 percent makes the type an L-grade. Using L-grade material usually avoids sensitization, the susceptibility of stainless steels to intergranular corrosion. The filler metals chosen provide a range of ferrite contents for evaluation. (The deposited weldment is a duplex structure composed of two phases, austenite and ferrite.) Some samples were solution annealed and pickled to determine if heat treatment would improve the corrosion resistance.

MATERIALS AND FABRICATION

The compositions of the AISI 304L and 316L grade pipe used in this study are listed in Table 1. Commercial-grade ASTM A312, schedule 10, pipe sections were welded together using the gas tungsten arc (GTAW) welding process. This is a fusion welding process in which the base metal is melted and filler metal is added. The compositions of the filler metals are listed in Table 2. The welds were made using filler metal corresponding to low, medium, and high ferrite numbers (Table 3).

One weld of each ferrite content was joined together to make a subassembly. This section was solution annealed at 1950 +/- 25 degrees F for 1/2 hour per inch of thickness and water quenched. The section was pickled (removing the oxide from the surface by immersing in a nitric/hydrofluoric acid bath) before welding to the balance of the pipe. The pipes were then cut lengthwise in half to form troughs, as shown in Figure 1.

FIELD EXPOSURE

The troughs were taken to a field site and covered with tight fitting lids. The troughs were exposed to untreated well water, directly from a well, suspected of contributing to MIC problems.

The field experiments were performed outdoors without treating or altering the well water. The water analysis is given in Table 4.

Mounds indicating biomass formation appeared on some welds after two weeks exposure, as shown in Figure 2. Brushing away the mounds revealed pinholes, as shown in Figure 3. The mounds reformed overnight.

FIELD RESULTS

After approximately one year of exposure to the untreated well water, the troughs were removed, visually examined, and radiographed. Three observations were made. None of the solution annealed and pickled welds were attacked. Approximately equal numbers of low, medium, and high ferrite content welds developed MIC indications and pits, Figures 4 to 7. The majority of the attack was to the weld heat-affected zone (HAZ) and the weld metal.

LABORATORY EVALUATION

After removal, the 304L samples were evaluated in the laboratory. The tests examine the corrosion potential versus time and pitting potentials of the samples. Of primary importance was determining the difference between the solution annealed and the as-welded samples that made the solution annealed samples less susceptible to MIC. The corrosion potential, also called the open cell potential (OCP), is a function of the kinetics of the cathodic and anodic reactions and related processes of precipitation and diffusion.[5]

Measuring and obtaining reproducible pitting potentials is difficult. [6]Experimental methods which appear valid for some alloy/environment combinations often yield misleading results for other alloy/environment combinations. [7] The alloys involved in this study exhibit an active-passive behavior. Passivity is the result of a protective film (metal oxide) on the metal surface.[8] What this means is that for these metals the dissolution rate is very low over a large potential range.

Producing MIC in the laboratory has been elusive for most researchers. Limitations and problems abound. One significant parameter not evaluated in these experiments was temperature. The field samples were exposed outside to ambient temperatures that often exceeded 100 degrees F. Microorganisms' growth rates increase with increasing temperature.

TYPES OF BACTERIA USED

There is a debate over whether to use pure strains of bacteria or mixed culture in laboratory experiments. Pure strains are not representatative of natural water, but enable the study of how specific classes of microorganisms are involved in the corrosion process. Mixed strains, while not representing field experience, allow microorganisms to interact.

Preliminary testing with pure strains were inconclusive. A mixed strain was used comprised of a <u>Bacillus</u> (an aerobic spore- former), a <u>Pseudomonas</u> (a slime-former), and an <u>Acinetobacter</u> (an acid-producer). The strains were isolated, identified using classical microbiological techniques and the lipid-based, computer-assisted identification system developed by Microbial ID, Inc, Newark, DE.

MEDIUM USED

The composition of the medium (the solution designed for microbial growth) is shown in Table 5. After preparation, the pH was adjusted to 7.0 with NaOH. The solutions were autoclaved for 20 minutes at 120 degrees C. The resistivity for the medium was determined to be 260 ohm-cm.

The medium, a modified Hutner's, was selected on the basis of supporting several different organisms, including the ones chosen for evaluation. Succinic acid is the carbon source for the microbes. Cellulose was added to assist in the formation of the biofilm.

EXPERIMENTAL PROCEDURE

Open cell potential versus time

The objective of these tests was to determine how the open cell potential changed with time for the same samples in sterile medium and in medium with bacteria. The OCP represents the onset of pitting or the consumption of oxygen. The onset of pitting is generally represented by a sudden drop in potential; the consumption of oxygen is generally a gradual decrease in potential.

Previous work by Scotto showed that for stainless steel in seawater, metal surface colonization by bacterial and algal populations alters the cathodic oxygen reduction process, presumably as a result of enzymic catalysis. The action of the microorganisms helps to initiate localized attack and accelerate corrosion resulting in more aggressive attack in the "natural" (microbe-rich) as compared to the sterile environment.[9]

Our tests were conducted in modified electrochemical cells as shown in Figure 8. The test samples were sectioned and mounted as shown in Figure 9. The samples were cut so that for the weld metal samples the weld metal only was exposed. For base metal samples the end grain was exposed. Brass screws were soldered to the back of the test samples. Following mounting in cold-curing epoxy and metallographically preparing the surface to 9 micron diamond finish, samples were passivated in 50% HNO_3 for 1/2 hour and washed in water. The metal/epoxy interface was coated with epoxy so that 0.3 cm^2 was exposed to the solutions. Prior to testing, the exposed surface of the sample was lightly repolished with 9 micron diamond paste to remove the passive film from the surface but allow the passive film to remain under the epoxy.[10] This technique has been shown to reduce the tendency for crevice corrosion at the interface between the metal surface under study and the insulating material. After polishing, the samples were degreased and cleaned in punctilious alcohol.

The test cells were gas sterilized in 30% ethylene oxide at 50 degrees C for eight hours. The medium was pumped into the cells aseptically through sterile neoprene tubing. The consortia of three species (batch cultures) was inoculated aseptically and the OCP monitored for 72 hours. All tests were duplicated.

Cyclic anodic polarization tests

Immediately after the OCP testing, cyclic anodic polarization tests, also called pitting scans, were run. In this test, the potential was increased at a scan rate of 0.167 millivolts per second up to a maximum 1.2 volts (vs SCE) and the current monitored. Pitting scans are helpful in determining the tendency of a material to pit or crevice corrode in a specific environment. It is often used for alloys designed to be pit resistant.

The objective of these tests was to determine if the alloy/environment combination will give rise to pitting. If materials are susceptible to pitting corrosion in a given environment, running the cyclic anodic polarization curve will tell when and if pitting has initiated. After each test, the samples were examined for pitting and crevice corrosion under a 10X microscope.

EXPERIMENTAL RESULTS

Open cell potential versus time

Figure 10 shows how the open cell potential, Ecorr, varies with time for a typical sample in the consortium of three bacteria and sterile solution. As was expected, the Ecorr values are more active in the bacterial solution than in the sterile medium. There is a large decrease in potential at approximately 24 hours. This trend was followed for all three weld metals in both conditions, as-welded and solution annealed.

A comparison of Ecorr (at 72 hours) of the three solution annealed welds to the three as-welded for the bacterial solution showed two solution annealed ER 308 weld metals are more active in the bacterial solution by about 100 mV.

The Ecorr values (at 72 hours in the consortia of three bacteria) comparing the solution annealed and the wrought- annealed 304L base metal showed no significant difference in contrast to the weld metals. The solution annealed base metal has an average Ecorr of -0.055 V versus -0.045 V for the wrought-annealed sample. (The commercial grade pipe was solution annealed at 2000 degrees F and water quenched.)

Cyclic anodic polarization tests

The pitting scans were performed in the sterile medium and in the consortia of three bacteria after monitoring OCP for 72 hours.

Figure 11 shows a typical pitting scan plot for alloys that exhibit active-passive behavior such as 300 series stainless steels. Included on the plot are the various terms used to define the behavior of the alloy. Of particular importance are E_{np}, E_p, and I_{corr}.[11]

According to Szklarska-Smialowska, E_{np}, the critical potential for pit nucleation, is characterized by an increase in current with little increase in potential. This is the potential above which pits nucleate and propagate. The more positive E_{np}, the more resistant the material is to pitting.

E_p, the protection potential, is the potential below which no pitting occurs and above which (and below E_{np}) pits already nucleated can grow.

I_{corr}, the corrosion rate, can be estimated from the pitting scan.

It is important to recognize that pits can initiate from the 72 hours test exposure or from the pitting scan test itself.

DISCUSSION OF RESULTS

Ringas and Robinson noticed in their work using a different medium, sulfate-reducing bacteria, and austenitic stainless steel that the shape of the curves in sterile medium and in bacterial culture differed.[12] Generally, in the sterile medium the alloys displayed a large passive region. On the reverse scan, there was no hysteresis (because no pits had initiated) and no protection potential obtained. The shape of the pitting curve of the same sample in the bacterial solution often showed pitting initiation (Enp) and a large hysterisis loop.

In our study, open cell potential versus time tests showed that little or no pitting, or breakdown of the passive film, occurred in sterile medium. This is consistent with Scotto's work in sterile seawater as well as Ringas' in sterile medium. In the bacterial solution, our experiments showed that the potential decreased for approximately 24 hours and then increased, but not to the original potential. The potential decrease may be the result of oxygen depletion by the microbes or pitting initiation; the increase due to repassivation of the metal surface with time.

Of significance is the amount of difference in Ecorr at the end of the 72 hour exposure between the as-welded and solution annealed welds. One possible explanation for the difference is that solution annealing results in a more homogeneous structure, higher chromium in the weldment , and greater corrosion resistance. In a study investigating pitting corrosion of weld metals, Garner has shown that loss of corrosion resistance is directly related with alloy depletion in the austenitic dendrite structure of the weld metal.[13]

The pitting scans typically showed that in sterile medium little or no pitting occurred on the welded samples. In bacterial solutions, the environment was more aggressive and pitting resulted for the as-welded samples and was infrequent and less severe for the solution annealed welds. This is consistant with the field results.

The solution annealed base metal in sterile medium showed no Enp and no pits initiate. The same sample in the bacterial solution showed no clear-cut Enp, although pits formed. The Ep was approximately the same as the Ecorr. Icorr in the bacterial solution was slightly higher (about 50 nanoamperes/cm^2) than in the sterile.

The wrought-annealed base metal showed an Enp and pitted in both sterile and bacterial solutions. The sample in the sterile solution had an Ecorr approximately 100 mV higher than Ep. In addition, Icorr was approximately an order of magnitude greater in the bacterial than in the sterile solution.

CONCLUSIONS

Three observations can be made from the field exposure:

- o None of the solution annealed and pickled welds were attacked
- o Approximately equal numbers of low, medium and high ferrite content welds developed pits
- o The majority of the attack was to the heat-affected zone and the weld metal.

The solution annealing may have improved the corrosion resistance for the 308 welds by transforming the ferrite into austenite, increasing the chromium content producing better corrosion and pitting resistance. The solution annealing may have improved the corrosion resistance of the 312 welds by transforming the metastable ferrite into a more stable state. In addition, the 312 has much (about 9 percent) more chromium, increasing its corrosion resistance.

The laboratory results showed:

- The OCP in the sterile solution stayed relatively constant with time for both solution annealed and as-deposited welds, and the 304L base metal in both conditions.
- The OCP in the bacterial solution decreased by a range of approximately 125 to 250 mV over the first 24 hours and then drifted up with time for the balance of the 72 hour test. This trend held for each condition. There were subtle differences between the rate of decreases. The samples exhibiting a gradual decrease in OCP versus time may be reacting to oxygen consumption. In other cases there was a sharp decrease in potential. In general, these samples were pitted following the cyclic anodic polarization curve.The sharp decrease in potential may have been due to pit initiation.
- The solution annealed welds in the sterile solution had a large passive region and, by and large, produced no hysteresis in the pitting scan, and no pitting occurred for the two 308 welds.
- In the bacterial solution pitting, and hysteresis, occurred in one out of three tests for the solution annealed 308 weld with low ferrite content, and both tests of the 308 weld with medium ferrite content.
- In the bacterial solution, the solution annealed 312 weld showed no pitting or hysteresis in all three tests. The same sample in the sterile solution pitted and showed hysteresis in all three tests.
- The three as-deposited welds had a small passive region, a pit nucleation potential, and pitting and hysteresis occurred in the sterile medium.
- In the bacterial solution, the three as-deposited welds had approximately the same passive region, usually a pit nucleation potential, and pitting and hysteresis occurred. Icorr tended to be slightly higher in the bacterial solution than in the sterile for each of the three as-deposited welds.
- The solution-annealed base metal remained passive, had no Enp, and no pitting occurred in sterile medium. The same sample in the bacterial solution had no Enp but pitting and hysteresis occurred.
- The as-wrought base metal had a small passive region, an Enp, and pitting occurred in both sterile medium and bacterial solutions.

The chemical composition and microstructure of weldments, as produced by welding processes and heat treatment, can influence the degree of accelerated corrosion. This study attempts to consider how certain variables affect passivity, specifically as it relates to MIC. It is hoped that at a later date a model can be developed that incorporates the individual effects.

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TABLE 1
Chemical Analyses of Base Metal

	C	Mn	P	S	Si	Cr	Ni	Mo
304L	0.019	1.40	0.027	0.017	0.46	18.20	9.25	0.26
316L	0.024	1.780	0.032	0.017	0.59	17.17	11.17	2.17

	Cu	Co	N
304L	0.36	0.16	NA
316L	NA	0.21	0.04

TABLE 2
Chemical Analyses of Filler Metal

	C	Mn	Si	Cr	Ni
low (ER 308L)	0.018	1.98	0.28	20.08	10.17
medium (ER 308L)	0.016	1.79	0.54	20.46	10.06
high (ER 312)	0.12	1.75	0.39	29.94	8.77

TABLE 3a
Measured Ferrite Numbers (using Magne Gage)

Filler Metal	304L Base Metal Solution Annealed	304L Base Metal As-Welded	316L Base Metal Solution Annealed	316L Base Metal As-Welded
308 (low)	0	6.5	0.3	3.6
308 (medium)	1.4	8.1	2.0	8.3
312 (high)	28*	28*	28*	28*

*limit of gage

TABLE 3b
Calculated Ferrite Number (using DeLong Diagram)

BASE/FILLER METAL	FN	Cr_{eq}	Ni_{eq}
304L/ER 308 (low)	6.8	20.14	13.15
304L/ER 308 (med)	9.8	20.68	12.96
304L/ER 312 (high)	29.4	27.16	14.22
316L/ER 308 (low)	6.6	20.46	13.64
316L/ER 308 (med)	9.6	21.00	13.46
316L/ER 312 (high)	29.2	27.48	14.72

TABLE 4
Water Analysis

Contaminant Name	Well No. 1 result (mg/l)	Well No. 2 result (mg/l)
Arsenic	0.022	0.031
Barium	<0.5	<0.5
Cadmium	<0.005	<0.005
Chromium	0.013	0.023
Fluoride	6.9	9.5
Lead	<0.02	<0.02
Mercury	<0.001	<0.001
Nitrates	2.0	3.0
Selenium	<0.005	<0.005
Silver	<0.02	<0.02
Alkalinity	144.	178.
Calcium	13.	7.9
Chloride	226	126.
Copper	<0.05	<0.05
Hardness	58.	34.
Iron	<0.1	<0.1
Magnesium	6.3	3.6
Manganese	<0.05	<0.05
pH	8.1	8.1
Sodium	250.	206.
Sulfate	96.	87.
TDS	740.	580.
Zinc	<0.05	<0.05

Pumping system automatically changed from one well to the other.

TABLE 5
Composition of Medium

Chemical	Quantity (g)
mineral salts*	200 ml
succinic acid	3.0
Tryptic soy	1.0
Hutner's mineral base	20 ml
cellulose	2.0
NaCl	0.6
distilled water	1800 ml

* NH_4Cl	0.05 g/l
Hutner's mineral base	10 ml/l
$MgSO_4$ $7H_2O$	0.5 g/l
KH_2PO_4	0.27 g/l
$CaCl_2$ $2H_2O$	0.05 g/l
distilled water	1 l

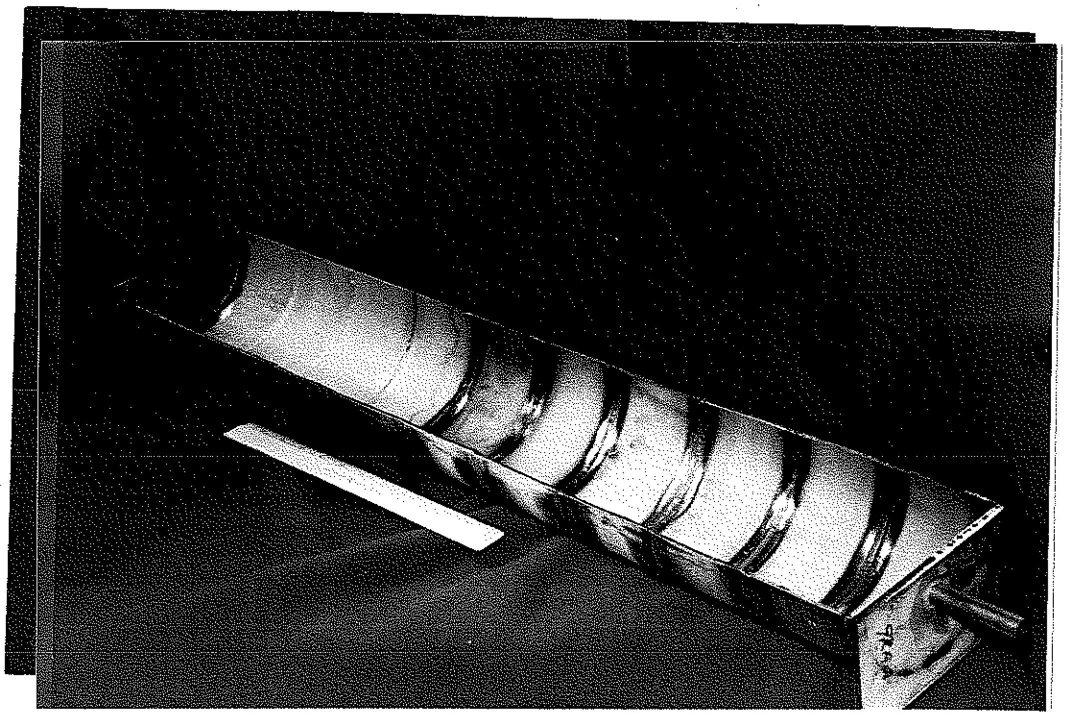

Figure 1. Trough

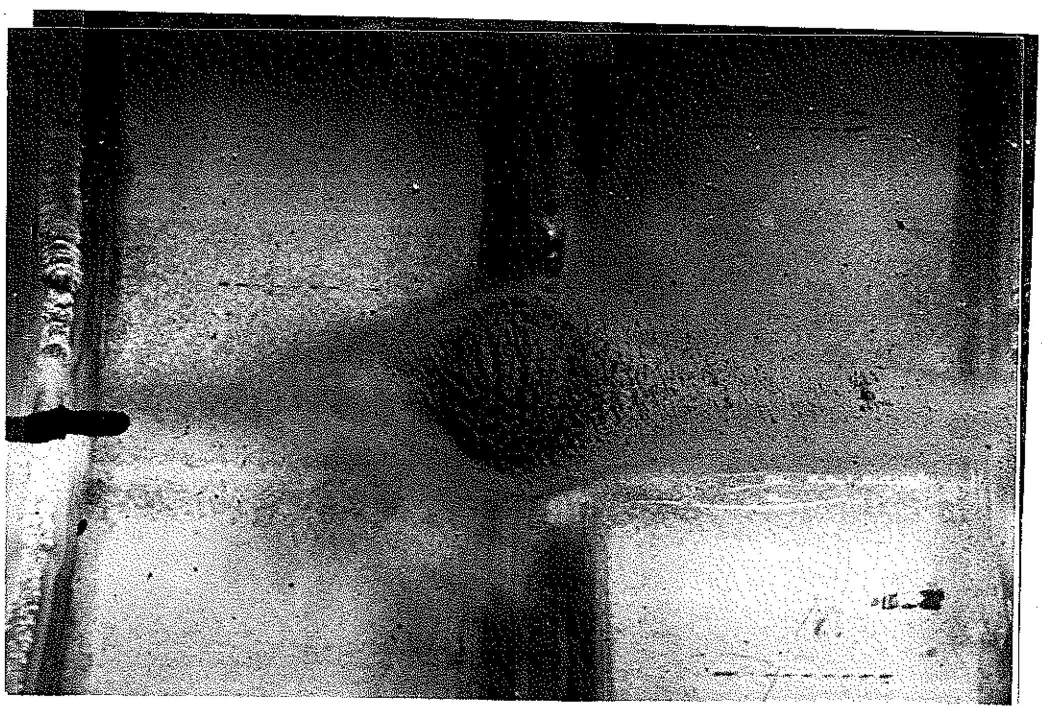

Figure 2. Mound on weld after exposure for 2 weeks.

Figure 3. Pinhole near Weld after brushing away mound

Figure 4. Pit and dislocation showing near weld after one year's exposure

Figure 5. Pit and disloaction near weld after one year's exposure.

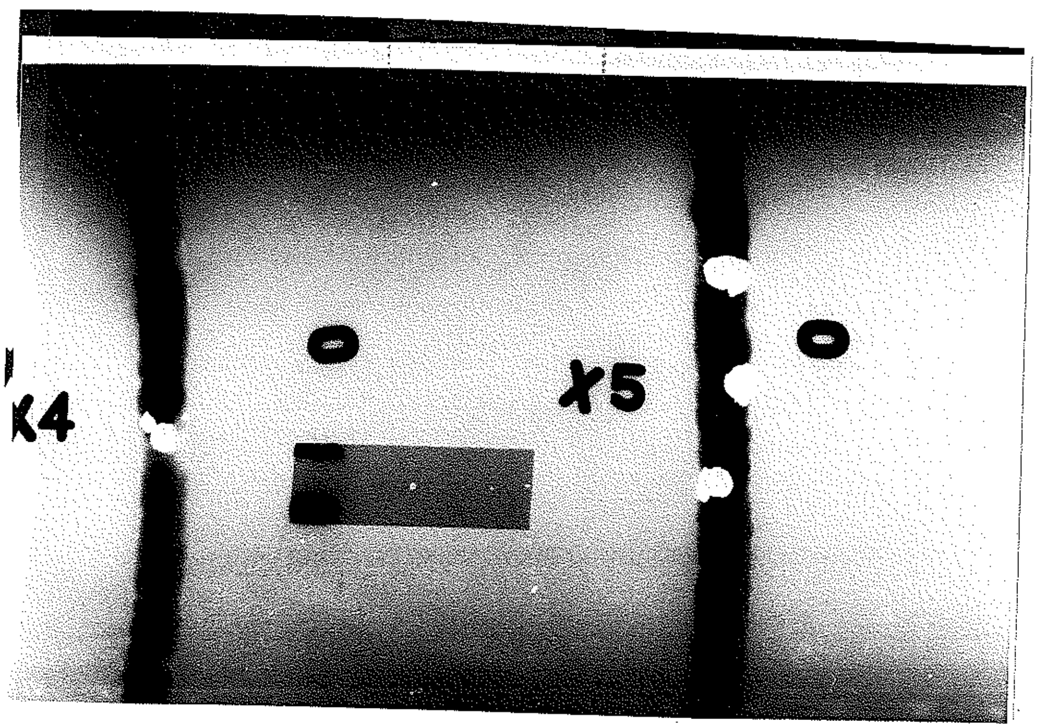

Figure 6. Photograph of radiograph showing pits to two welds.

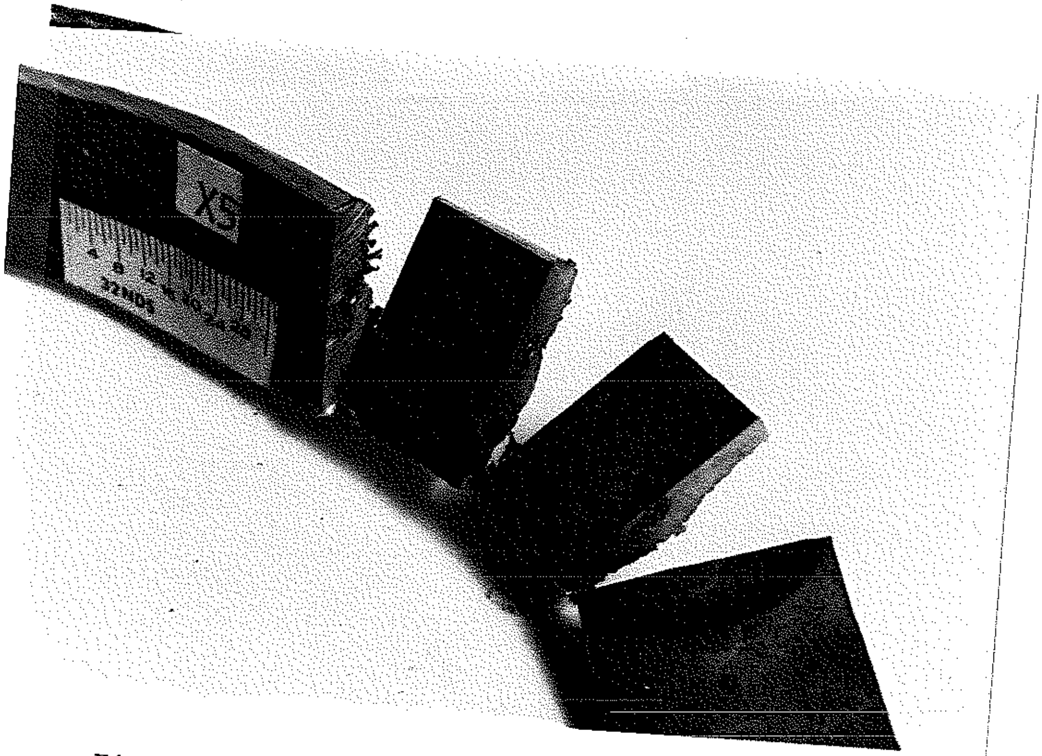

Figure 7. Cross-section of weld through pits shown in figure 6.

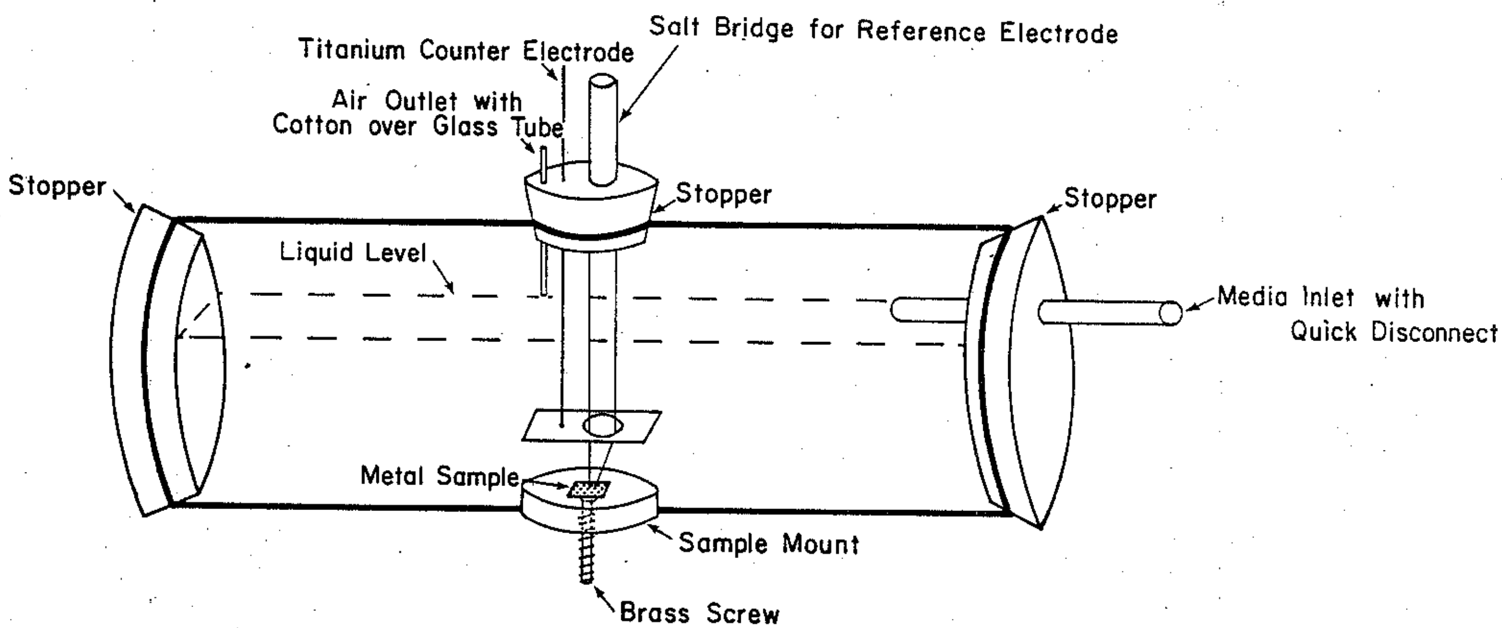

Figure 8. Modified electrochemical cells.

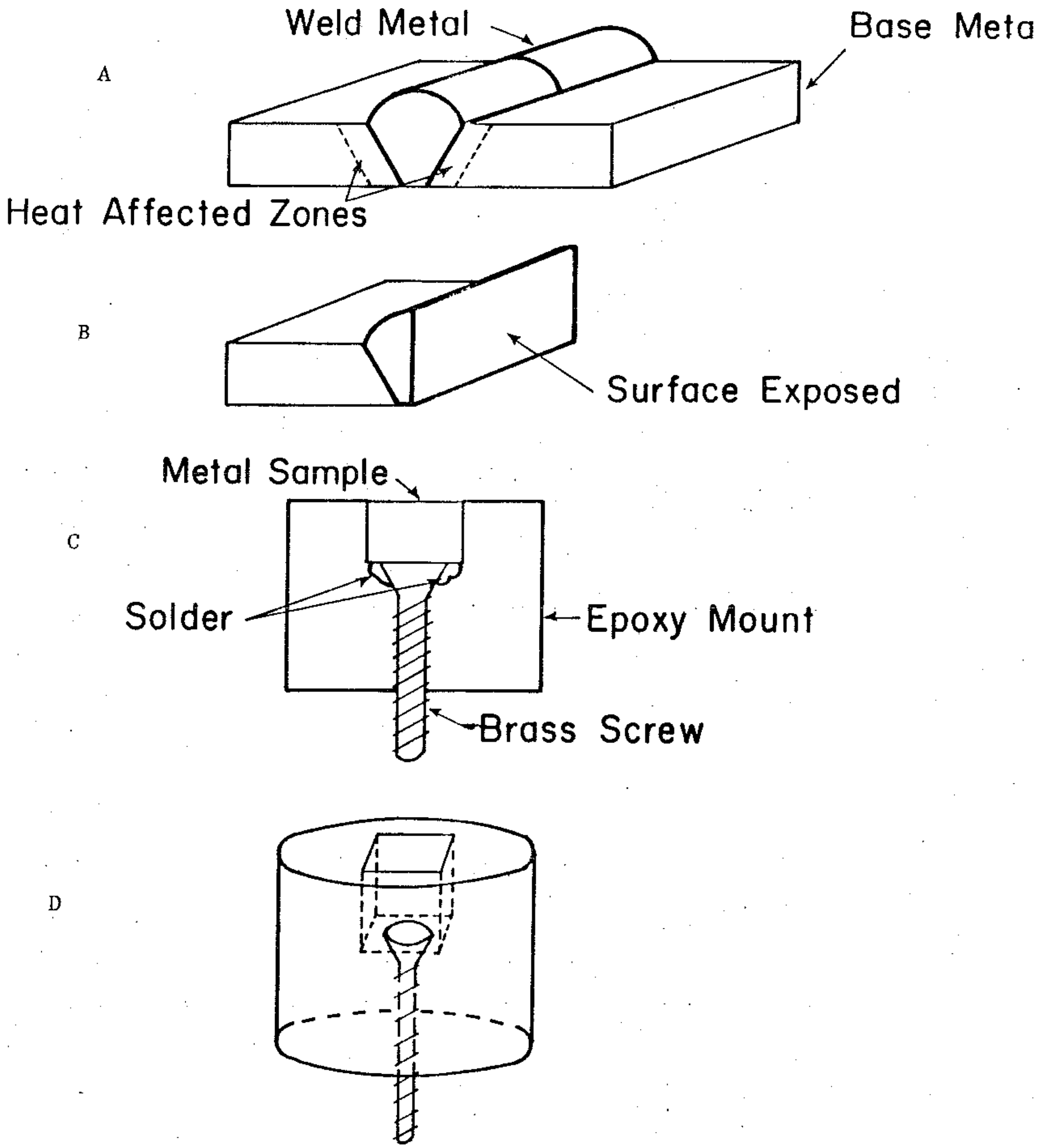

Figure 9. A) Cross-section of weld, B) Cut weld
C) Sample arrangement, D) Finished mount.

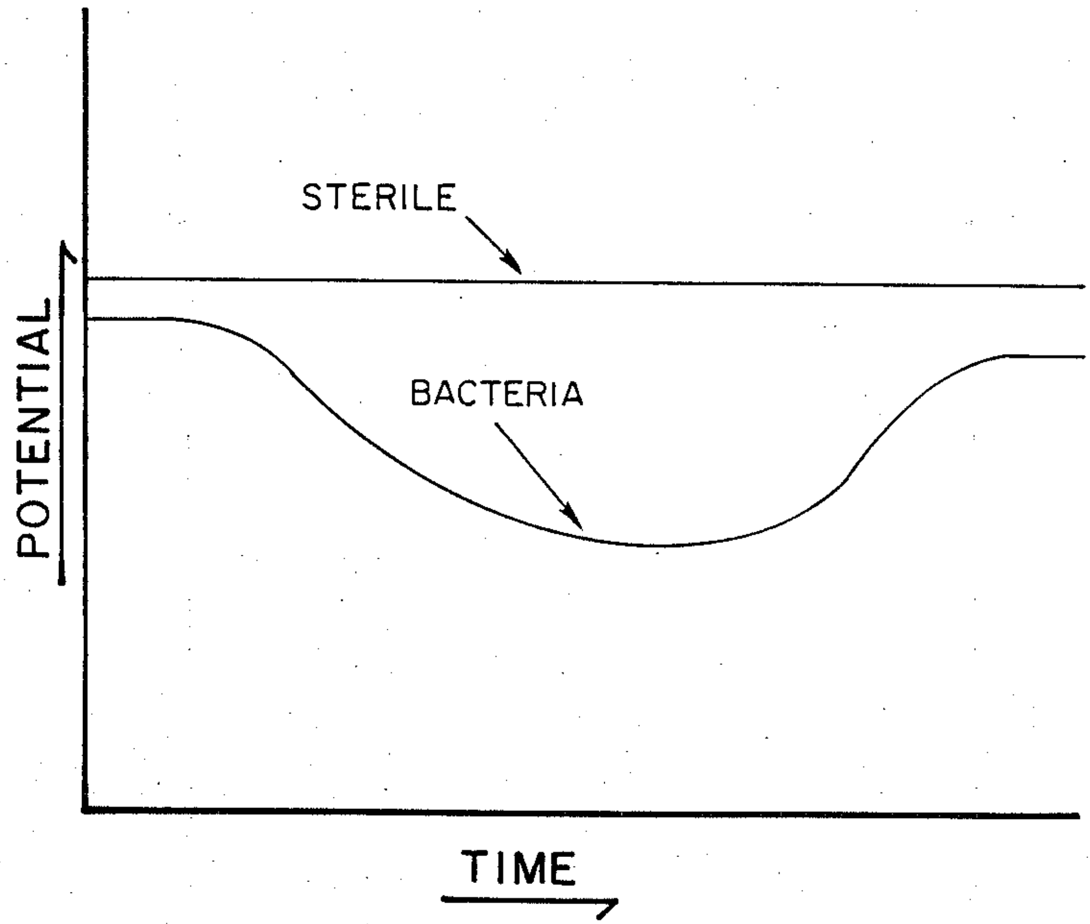

Figure 10. Opencell potential versus time.

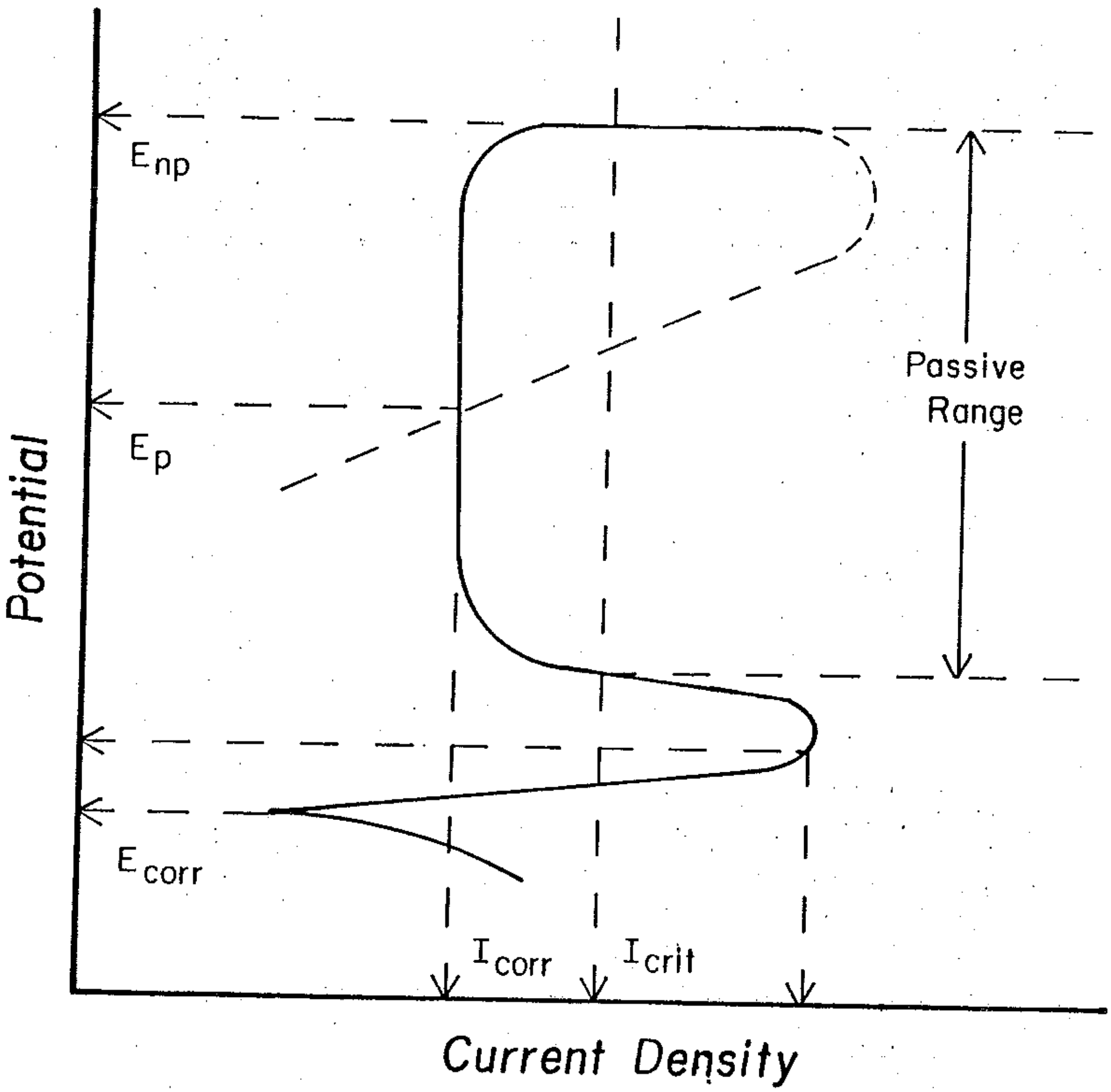

Figure 11. Schematic representation of pitting curve.