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ENHANCED CORROSION RATES OF AISI 316 STAINLESS STEEL WELDMENTS IN THE MARINE ENVIRONMENT DUE TO BACTERIA.

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ABSTRACT

Stainless steel coupons of various types, including autogenous weldments, were subjected to bacterial attack in artificial seawater and monitored using electrochemical impedance and small amplitude cyclic voltammetry. Unpolished coupons with a heat-affected zone (HAZ) were attacked first and appeared to be the most susceptible. The corrosion mechanisms of the different coupon-types were shown to be very different in nature.

INTRODUCTION

Serious failures of several alloys due to microbiological attack have been observed in industries with exposure to untreated water. These have included both circulating supply and stagnating systems such as dead-ended emergency piping (Kobrin, 1976; Tatnall, 1981). No established, central hypothesis for the corrosion of metals by microbial consortia has yet been proposed and tested. Several models have, however, been suggested for individual genera (Pope et al.,1984). These suggestions have revolved mainly around the more traditional organisms such as sulphate-reducing bacteria (SRB), acid-producing fermenters, and iron-oxidizing thiobacilli etc.

Although corrosion due to individual strains is well established, the location and interaction of those strains within a biofilm is not. Hamilton (1985) has elucidated the model of SRB which are protected from oxygen by oxygen-respiring aerobes. Thus in a biofilm SRB are to be found associated with the oxygen depleted metal surface concealed by aerobes and aerotolerant fermenters. The corrosion produced by such a community therefore has as much to do with the aerobes as the SRB.

Corrosion due to microorganisms tends to occur at discreet sites and "generalized corrosion", as exemplified by alloys in low pH environments, is a rare event. Particularly prominant among the site-specific failures have been weldments. In this article we report the rapid deterioration of some autogenous welds (without filler metal) in contact with a mixture of marine microorganisms from sediment.

EXPERIMENTAL

Several stainless steel coupons were fabricated for trial against unselected marine bacteria. These coupons were of 316L Nuclear Grade material : C 0.016%, Mn 1.66%, P 0.024%, S 0.011%, Si 0.47%, Cr 16.3%, Ni 10.13%, Cu 0.18%, Mo 2.11%, Co 0.2%, N 0.054%. The alloy sheet was obtained from Eastern Stainless Steel Co., Pittsburgh, PA., USA. The types of coupons tested included autogenous welds in the as-welded condition (AW: unpolished weld), polished (600 grit) autogenous welds, and polished base metal. Samples were welded with the gas tungsten-arc process (GTAW). The ferrite content in the fused zone was 3.8 ferrite number (FN) measured by Magne-Gage.

The 2x2 cm^2 coupons were embedded in epoxide resin and placed in the bottom wall of two (15 cm i.d., 1 m L) polypropylene pipes. The coupon surfaces were made flush with the inside wall of the pipes. Titanium counter electrodes and calomel reference electrodes were provided for each coupon (figure 1). In all, 18 coupons were exposed, in the two pipes with three replicates for each condition (see above), to either sterile or inoculated media. The pipes were monitored during a fourteen day exposure period for pH, organic acid content (volatile fatty acids) and numbers of suspended cells. The coupons were periodically examined by open-cell potential, electrochemical impedance spectroscopy (EIS), and small amplitude cyclic voltammetry (SACV). Finally, some of the coupons were subjected to cathodic polarizations to obtain values for Icorr and cathodic Tafel parameter. The remainder were available for surface analysis.

Electrochemical impedance analysis was carried out using a Solartron 1250 frequency response analyser and 1286 potentiostat controlled by a Hewlett-Packard 310 microcomputor. Frequencies between 10 KHz and 3 mHz were selected with an interval of 5 or 10/decade. Signal amplitude was set at 5 mV rms. SACV measurements were carried out galvanostatically with a maximum sweep of $\pm$1E-8 Amps. at 0.2 mV/sec (equivalent for the system). Cathodic polarization sweeps started at the open-cell potential and proceeded at 0.2 mV/sec to -0.8 V.

The media consisted of the following (g/L distilled water): fibrous cellulose 2, cellobiose 1, chitin 0.125, yeast extract 0.1, starch 0.5, "Instant Ocean" (Aquarium systems, Ohio) 30, complex vitamins (Dowling et al., 1988a) and trace elements (Pfennig et al., 1981). After separate autoclaving in large glass vessels, the pH of the cooled media was adjusted to 7.5 with sterile Na_2CO_3.

Inoculation was of the organisms that grew from an inoculum of 10 mls of black sulphide-rich marine sediment in a test-tube of cellulose/chitin media.

Organic volatile fatty acids produced by the microbiota were monitored by packed column gas chromatography using a Schimadzu GC-9A with SP-1220 packing (Supelco, Bellafonte, PA).

The system was sterilized with 4 % formaldehyde after which the interiors were washed with sterile distilled water. Sterility was maintained in the control pipe by introducing 5 mM sodium azide.

RESULTS

The fluctuations in open cell potential are recorded in figure 2. Notably, by day 3, the potential of all the inoculated coupons fell to around -0.48 V/SCE, and stayed in this region for the duration of the experiment, while the sterile coupons remained at approximately -0.05 V/SCE. While the potential of the as-welded coupons exposed to bacteria decreased to -0.51 V/SCE within the first 24 hours, the potentials of the the polished coupons did not achieve those low potentials for a further 24 hours in the case of the polished welds and 48 hours for the base metal.

A summary of the evolution of the polarization resistance (Rp) of the coupons is presented in table 1. Figures 3a and 3b show the differences observed in impedance for the different coupons exposed to the microorganisms at days 1 and 8. Figure 4 compares the impedance of the polished base metal in sterile and inoculated conditions at day 12. After eight days exposure to the artificial seawater, high frequency capacitive loops were observed in all the coupons exposed (figure 5). Rp for the sterile coupons were only obtained by SACV due to the very large reactance of the corrosion cell and the difficulties in using extremely low frequencies (< 0.003 Hz). The Rp values for the as-welded coupons in the presence of the microbes showed a rapid decrease (increase in corrosion rate) mimicked to a lesser extent by the polished coupons (days 1 and 2). After 3 days however, the polished coupons appeared to have uniformly lower values for Rp than the as-welded coupons. In all cases the small values for Rp indicated that the corrosion rate was faster for the inoculated than the sterile coupons.

Organic acid analysis showed that acetic acid and butyric acid were produced by the bacteria during the experiment in the following quantities and low pH :

DAY	Acetic (mM)	Butyric (mM)	pH
2	ND	ND	4.73
8	2.5	1.6	4.03
12	2.7	3.7	3.83
14	3.5	4.7	3.86

Analysis of the sterile system showed no detectable volatile fatty acids and a pH maintained at 6.8.

Microscopical observation of the inoculated media (day 14) by phase contrast using a Petroff-Hausser counting chamber showed $6.6x10^9$ cells/ml. The surface of the coupons were inspected at 100X and 200X after removal from the pipes. Several globular type oxide deposits were observed along the fusion line in the as-welded coupons. Careful microscopical examination revealed that some of the oxides were attacked, resulting in hemispherical pits (figure 6). More of these oxide-depleted pits were observed on the coupons exposed to the bacteria than those in sterile conditions. No such failures were seen on any of the polished coupons.

DISCUSSION

Failure of welds in raw water systems due to microbiological deterioration is a considerable problem. Unfortunately little work has focused upon this area and most of that has been in the nature of a case study (Kobrin, 1976; Tatnall, 1981). Metallurgical analyses show that austenitic (face-centred cubic) stainless steels are "sensitized" to some degree depending on the variables (peak temperature, base metal composition, and rate of cooling etc.) used in the welding process (Lundin et al., 1986). Weld sensitization is particularly associated with the heat affected zone (HAZ) which was present in the welded samples of this study.

In order to observe corrosion by microbial consortia, complex, insoluble carbon sources were used (eg. cellulose and chitin). These substrates were allowed to accumulate at the bottom of the pipes during the experiment as they might when a pipe is allowed to fall stagnant. In such a condition, welds tend to corrode rapidly at the bottom. Thus "suspended" particles may well exacerbate corrosion problems after falling out of suspension.

The evolution of the open-cell potential (OCP) in all coupons (figure 2) showed that the presence of the bacteria decreased the potential in all cases to around -0.48 mV/SCE while that of the sterile coupons remained relatively constant over the 14 days. The OCP of the as-welded coupons changed within the first 24 hours which indicates that it was more susceptible to initiation of corrosion than the polished welds or base metal.

EIS confirmed that the AW coupons were attacked during the first two days by the bacteria by showing a smaller Rp value. After this initial period the average corrosion rates of the polished surface coupons (both welded and base metal) were higher probably due to the larger area unprotected by chromium oxides (mostly Cr_2O_3) tints which were observed in the HAZ. These tints covered a significant proportion of the surface area of the as-welded coupons and have been shown to affect the corrosion bahaviour of various austenitic steels (Kearns, 1985). EIS measurements agreed well with those obtained by SACV at low reactances, however at very high reactances there are discrepancies between the two techniques and more reliance was placed on SACV (MacDonald, 1987). Average corrosion rates showed that the coupons in the sterile pipe corroded slowly compared to those exposed to bacteria (table 1). Examination of the EIS diagrams showed several consistant differences between the coupons. All of the sterile coupons had extremely high reactances, providing only a small section of the theoretical semicircle obtained by complex plane plot (Dowling, 1988b). These could not be extrapolated to the real axis due to the high error involved and values for Rp were thus unobtainable by EIS (table 1). In contrast, the corrosion rates in the inoculated coupons were high enough so extrapolation was possible and a reasonable value for Rp obtained. Figure 4 shows the contrast between polished base metal tested in sterile and inoculated conditions. The numbers on the diagram show that without the bacteria the reactance is very high even at high frequencies such as 1.0 Hz. The inoculated coupons however provide sufficiently low reactance to obtain an accurate extrapolation for Rp, moreover it is possible to observe that the corrosion mechanism is considerably more complex than just a single capacitive loop. The lower portion of a second capacitive loop with higher reactance than that associated with the double layer capacitance and polarization resistance appears at frequencies less than 0.1 Hz. This may be due to adsorbed corrosion products, however no such capacitive loop appears to be associated with the as-welded coupons (figure 3B).

It seems likely that the electrochemical phenomena and impedance diagrams associated with the double-layer capacitance and charge transfer in the as-welded coupons were affected by other events such as oxide tinting of the surface and some galvanic corrosion due to microsegregation. These and other differences with the polished coupons undoubtedly contribute to a significantly different impedance diagram.

After 8 days a high frequency loop was observed (figure 5) with capacitance of approximately 10 uF/cm^2. This capacitive loop occurred in all the coupons examined and may have been due to a film formation and appeared to be independant of microbiological effect.

Examination of the as-welded coupons by incident-light microscopy showed the presence of oxide deposits in the fused zone which may have been excavated by bacteria (figure 6). These deposits were produced during the welding process (Heiple, 1986) as slag and acted as pit initiation sites for the bacteria. The deposits occurring on the coupons exposed to the bacteria occupied hemispherical depressions underneath which a pit had formed.

This work shows that the presence of bacteria significantly increased the corrosion rates of 316L stainless steel coupons. The major corrosion mechanisms may be related to the production of acetic and butyric acids which would lower the local pH. The results demonstrate important and reproducible differences in corrosion mechanisms, the true nature of which cannot be deduced from this data. Further experimentation must be carried out in less complex systems to identify and explain the different electrochemical phenomena observed.

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Table 1: Summary of the values for the polarization resistance (Rp) in ohms (for 4cm2 coupons) obtained by electrochemical impedance spectroscopy (EIS) or small amplitude cyclic voltammetry (SACV) over two weeks exposure.

DAYS	Sterile			Inoculated		
	316B	AW	PW	316B	AW	PW
1	U	U	U	180000	30000	180000
2	U	U	U	9000	30000	8000
5	U	U	U	1750	10000	1750
6	17076	11833	14000	1464	3592	1499
7	ND	ND	ND	2000	9000	2000
8	U	U	U	1400	ND	1800
12	U	U	U	1400	2000	2000
13	29590	19766	23240	1800	4597	1971
14*	1E-7A 40 mV	1E-7A 98 mV	2E-8A 100 mV	3E-6A 120 mV	1E-6A 80 mV	3E-6A 100 mV

U: Unobtainable due to insufficiently low frequency.
ND:Not determined. 316B: Polished base metal.
AW: As-welded. PW: Polished weld
*: Cathodic polarization to determine Icorr. and Tafel parameter.

FIGURE I

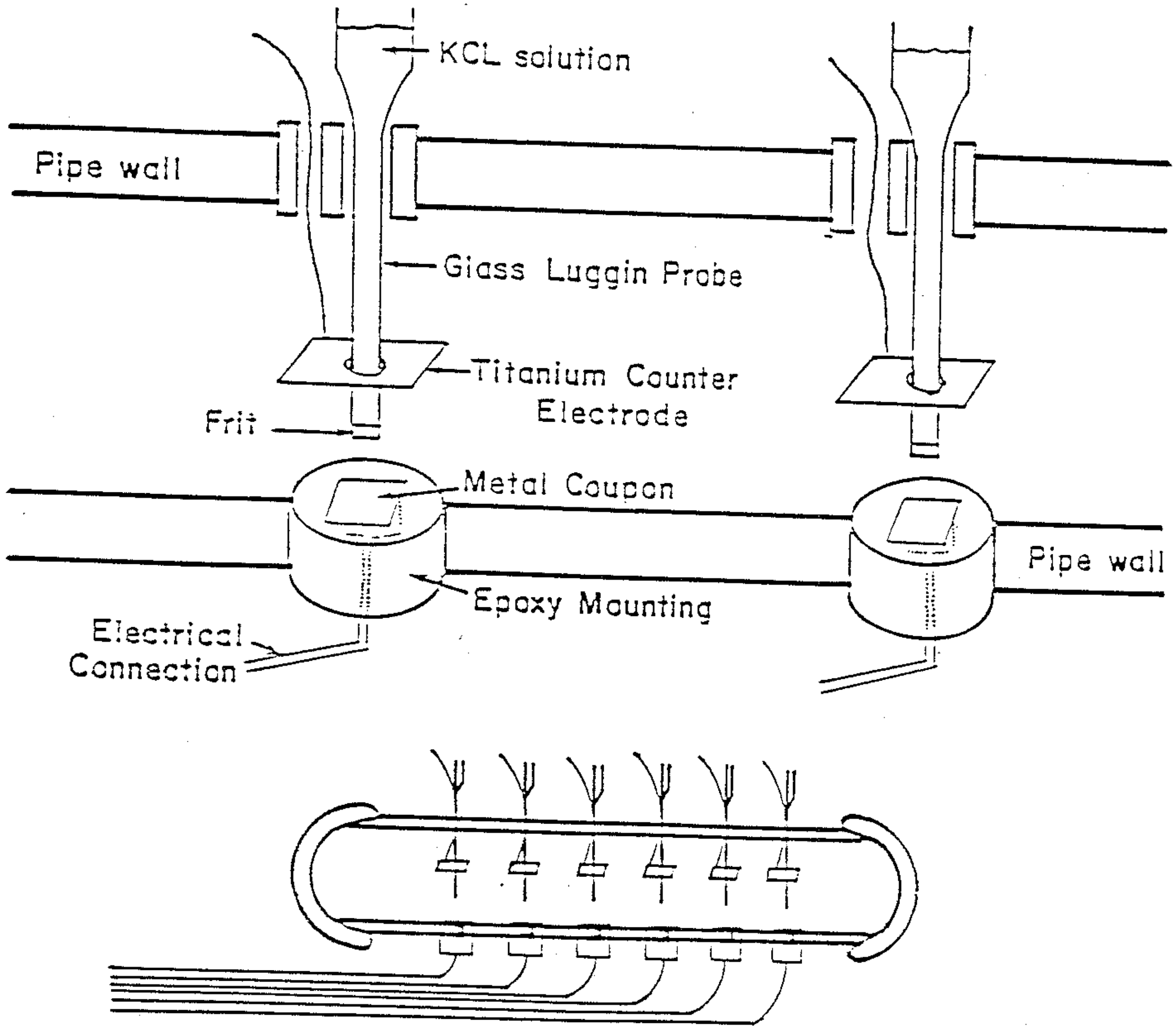
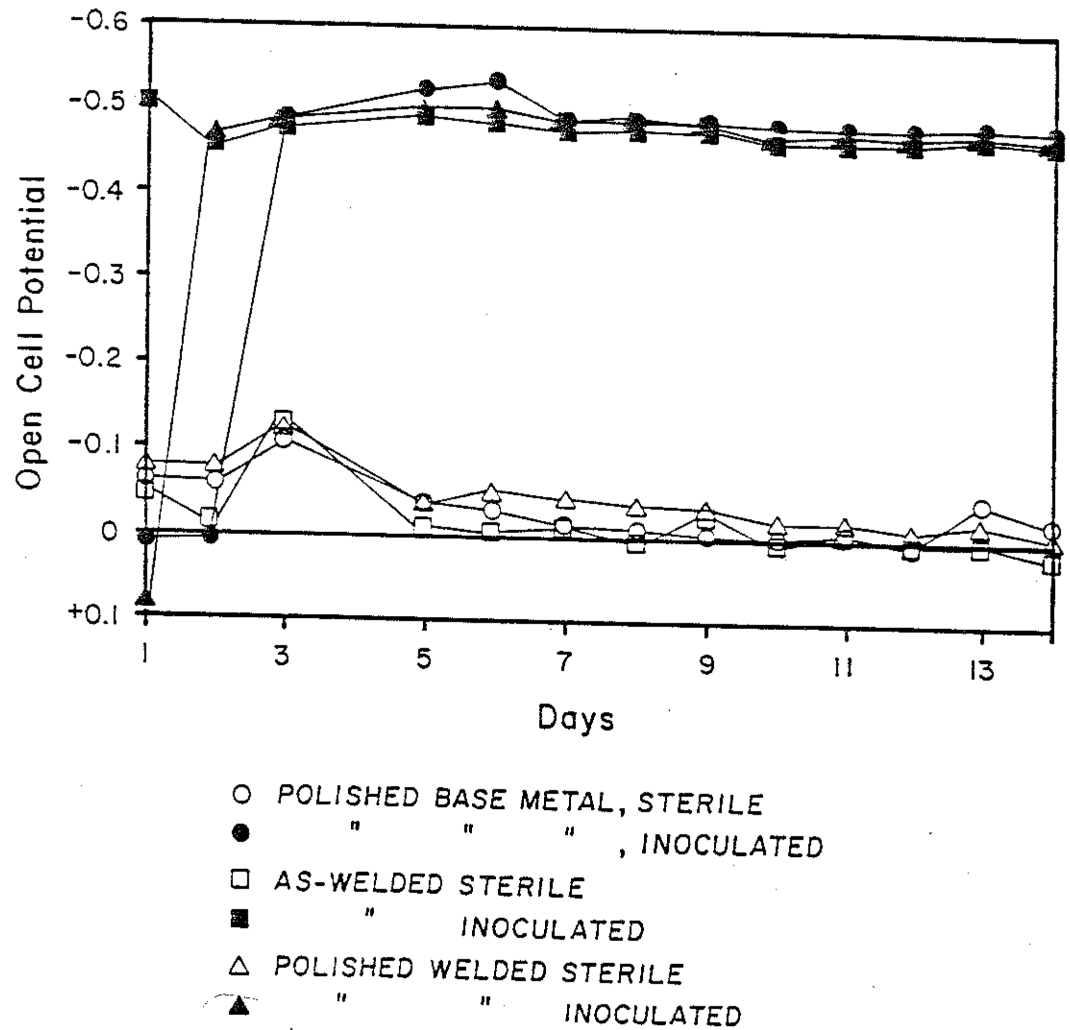
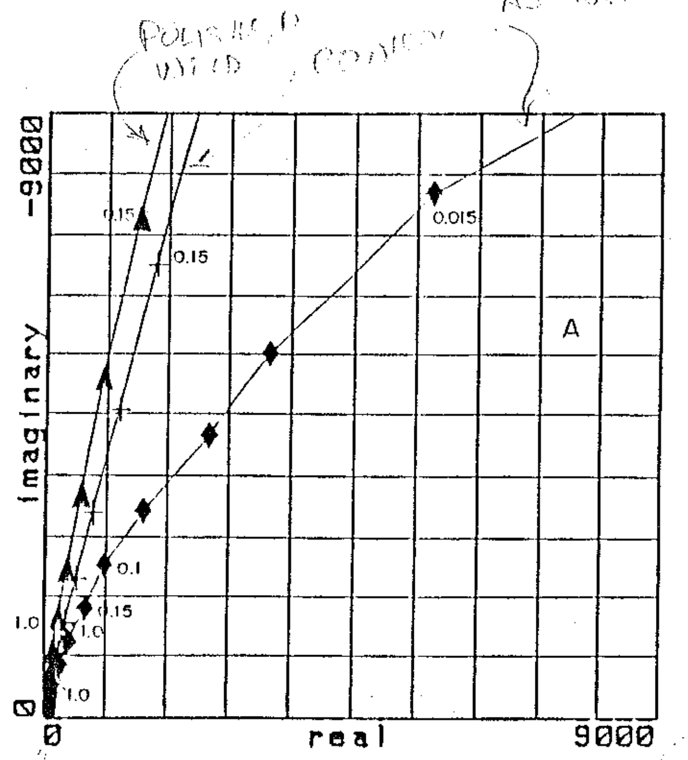

KCL solution
Pipe wall
Glass Luggin Probe
Titanium Counter Electrode
Frit
Metal Coupon
Pipe wall
Epoxy Mounting
Electrical Connection

FIGURE 2.

Open-Cell Potential of Coupons Over Two Weeks



1 Day



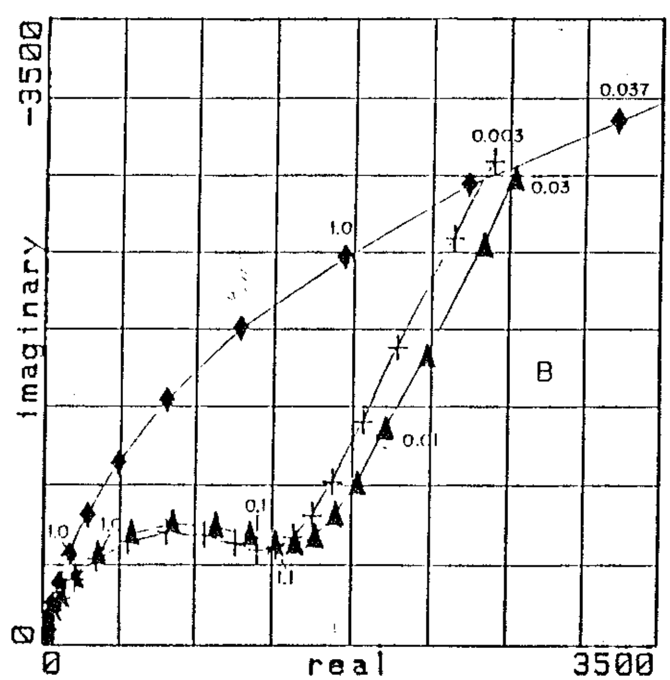


Figure 3: Coupons exposed to bacterial attack after 24 hrs (A) and 8 days (B). ◆ As-welded ▲ polished weld, and + base metal.

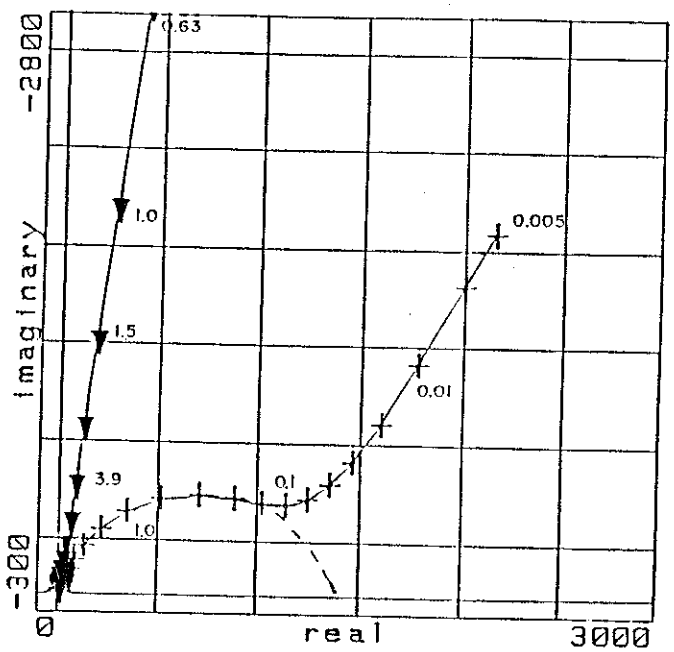


Figure 4: Base metal exposed to sterile ▼ , and inoculated + conditions after 12 days.

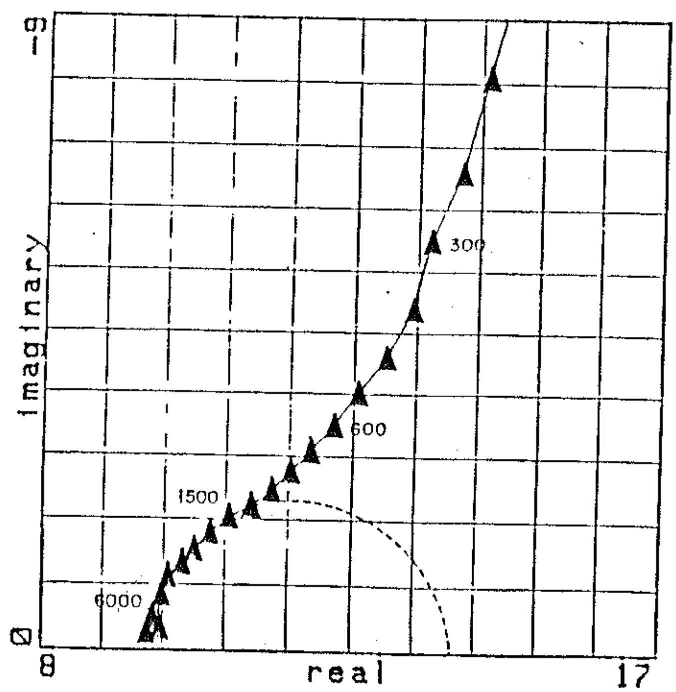


Figure 5: High frequency capacitive loop observed after 8 days in all conditions.

Figure 6: Attacked globular oxides observed at the edge of the fused zone in a small depression. The larger pit is approximately 0.36 mm in diameter.