

Evaluation of Techniques for Measuring the Corrosion Activity of Carbon Steel Welds

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ABSTRACT

Three test methods, namely immersion tests, galvanostatic anodic dissolution tests and the scanning vibrating probe technique, have been evaluated as candidate methods for ascertaining the susceptibility of welds in carbon steels to preferential corrosion. The use of hardness measurements by profiling and mapping was also evaluated. Three welds were tested for which the production had been controlled to produce different types of corrosion behaviour. In addition, a weld that had failed 'in-service' was used to validate the findings of this assessment.

In the immersion tests, lasting 9 months, the three controlled sample welds exposed to ASTM D1141 seawater behaved as expected, in terms of which region of the weld was most susceptible to corrosion.

The results of the rapid galvanostatic anodic dissolution tests compared well with the immersion tests, with the same regions of the controlled welds showing susceptibility to corrosion. The galvanostatic anodic dissolution test on the failed weld produced corrosion in the regions that had been susceptible to corrosion in service. However, at very high current densities the differential corrosion loss between different regions of the weld was not maintained and careful control of this parameter is therefore necessary in testing.

The scanning vibrating probe technique successfully identified the areas susceptible to preferential corrosion in the controlled sample welds and the in-service failure. The electrolyte used was ASTM D1141 seawater diluted 10:1 with distilled water. However, these trends were not apparent when tests were conducted in distilled water, due to the lower solution conductivity.

Hardness mapping produced a 2-D visual representation of the specimen hardness. This was very effective in locating small regions of high hardness, in contrast to conventional hardness profiling, and would be effective in locating hot spots for hydrogen embrittlement. However, no correlation between hardness and corrosion susceptibility was observed in the three cases examined.

The galvanic anodic dissolution test is recommended as a rapid and reliable test to determine the relative corrosion susceptibility of carbon steel welds. The scanning vibrating probe technique can also be effective but at considerably greater expense.

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CONTENTS

<u>1</u>	<u>INTRODUCTION</u>	1
<u>2</u>	<u>EXPERIMENTAL</u>	2
2.1	<u>MATERIALS</u>	2
2.1.1	<u>Controlled weld X (1 % Ni consumable, 3-4 mm root gap)</u>	3
2.1.2	<u>Controlled weld Y (Ni – free consumable)</u>	3
2.1.3	<u>Controlled weld Z (1 % Ni consumable, no root gap)</u>	3
2.1.4	<u>Weld that had failed in service</u>	3
2.2	<u>IMMERSION TESTS</u>	3
2.3	<u>SCANNING VIBRATING PROBE (SVP) TECHNIQUE</u>	4
2.3.1	<u>Principle of the scanning vibrating probe method</u>	4
2.3.2	<u>Test conditions used</u>	4
2.4	<u>GALVANOSTATIC TESTS</u>	4
2.4.1	<u>Principle of the test</u>	4
2.4.2	<u>Test carried out on controlled sample welds X, Y and Z</u>	5
2.4.3	<u>Service failure weld</u>	5
2.5	<u>MICROHARDNESS TESTING</u>	5
2.5.1	<u>Microhardness profiling</u>	5
2.5.2	<u>Microhardness scanning</u>	6
<u>3</u>	<u>RESULTS</u>	6
3.1	<u>IMMERSION TESTS</u>	6
3.2	<u>EVALUATION USING SVP</u>	7
3.2.1	<u>Evaluation of welds X, Y and Z in distilled water</u>	7
3.2.2	<u>Evaluation of welds X, Y and Z in diluted seawater</u>	7
3.2.3	<u>Evaluation of service failure weld</u>	8
3.3	<u>GALVANOSTATIC TESTING</u>	8
3.3.1	<u>Galvanostatic testing of controlled welds X, Y and Z</u>	8
3.3.2	<u>Galvanostatic testing of the weld that had failed in service</u>	9
3.4	<u>MICROHARDNESS TESTING</u>	9
3.4.1	<u>Microhardness Profiling</u>	9
3.4.2	<u>Microhardness Scanning</u>	9
<u>4</u>	<u>DISCUSSION</u>	10
4.1	<u>CORROSION OF CONTROLLED WELDS X,Y AND Z</u>	10
4.2	<u>SCANNING VIBRATING PROBE TECHNIQUE</u>	11
4.3	<u>GALVANOSTATIC TESTING</u>	12
4.5	<u>MICROHARDNESS MEASUREMENTS</u>	12
<u>5</u>	<u>CONCLUSIONS</u>	13
	<u>ACKNOWLEDGEMENTS</u>	14
	<u>REFERENCES</u>	14
	<u>APPENDIX 1</u>	16

INTRODUCTION

Preferential weld corrosion has been a major problem historically and remains a significant concern for industry. The term preferential weld corrosion describes selective attack of the weld itself rather than the parent plate but is sometimes used in a somewhat loose way to describe corrosion of other features of a weldment, for example, the heat-affected zone (HAZ). The origin of preferential attack is usually a combination of a more active weld material (the weld would tend to be more susceptible to corrosion than the parent material if in isolation) together with galvanic coupling to the parent material. The influence of coupling is accentuated by the poor area ratio, i.e. a small anodic weld/large cathodic base material. The key features of preferential weld corrosion have been reviewed by Turnbull¹ elsewhere.

Lundin² drew the following conclusions from a detailed investigation. In the welding of C-Mn steels, the silicon-killed steels are the most anodic and the unkilld steels with low silicon content are the most cathodic. Of the weld metals, the normal basic-coated electrodes exhibit the more anodic potential and the acid types the most cathodic, whilst the potentials for the weld metal from rutile electrodes are placed in an intermediate position. The weld metals are usually more anodic than the parent steel plate with a corresponding silicon content.

However, Bradley and Rowlands³ concluded that the silicon content of the weld had no direct effect on corrosion of steel weldments in seawater but that low hydrogen electrodes would give rise to enhanced corrosion of the weld. Hicks⁴ suggests the use of low alloy weld steels so that the weld is always cathodic to the base plate. Nevertheless, corrosion of the HAZ can still pose problems for some applications and will be dependent on the rate of cooling and Mn level in the steel, which affect the grain size and the extent of martensite formation. The net effect is that the HAZ could be anodic to the parent plate.

Recent work at TWI⁵ has shown the importance of nickel content in the weld metal compared to the parent plate with the higher nickel content in the weld being perceived to result in the weld acting as a net cathode with respect to adjacent parent plate.

Macroscopic anodes and cathodes will develop only if there is a sufficiently conducting medium. When the conductivity is low or the medium is in the form of a thin liquid layer, the potential drop in the solution will shorten the distance over which anodes and cathodes can effectively interact. In those circumstances, significant localised corrosion can occur in regions that are perceived to be net cathodic, as has been observed⁶.

There is a range of methods for testing the corrosion properties of welds and their sensitivity to preferential weld corrosion and these were reviewed by Griffiths and Turnbull⁷ in 1999. These tests are generally designed to be conducted in a laboratory on a sample weld to provide confidence in the welding procedure. However, in practice a welder may deviate from the specified welding procedure and produce a poor quality weld. There is a need for non-destructive techniques for identifying a weld that is susceptible to preferential weld corrosion after fabrication.

The scanning reference electrode technique has been used to assess the preferential corrosion of weldments for use in offshore applications when freely corroding and with applied potentials⁸. The technique was found to be sensitive and reliable compared to immersion and

potentiostatic anodic dissolution tests. The results of the tests were used to develop two indices for assessing susceptibility to preferential corrosion: the first index (RI) was calculated from the hardness of the HAZ, parent plate, and the highest hardness of martensite that the parent plate could form. The second index (ChE) used the copper, nickel and silicon content of weld metal and parent plate to assess their relative nobilities.

The scanning vibrating probe is relatively new and could provide information about corrosion activity on a small scale. However, its utilisation to investigate the corrosion of welds has been limited. Pistorius⁹ used a number of techniques, including the scanning vibrating electrode, to investigate the role of sulphur in the localised corrosion of welds in high manganese carbon-steels. The authors suggest that hardened microstructures within the HAZ, such as bainite and martensite, do not form galvanic couples with the surrounding microstructure but the formation of networks of sulphides in the fusion line area is the most likely explanation for grooving parallel to the weld line in corrosive environments.

The aims of the current project were twofold: to evaluate the effectiveness of a rapid test which could be used after fabrication to identify a weld which is susceptible to corrosion and secondly to assess the capability of the scanning vibrating probe to provide information on the corrosion of welds. Tests were conducted on three welds produced by TWI and designed to exhibit specific corrosion behaviour, and on a weld that had failed in service. The rapid test evaluated was the galvanostatic test whilst long term immersion tests were conducted to provide reference data. Measurements of microhardness were made to establish the extent of linkage with the corrosion behaviour.

2 EXPERIMENTAL

2.1 MATERIALS

Three welded carbon steel plates of nominal thickness 15 mm were supplied by TWI Ltd. All three welds were produced using the tungsten inert gas process for the root run and second pass, and the manual metal arc process for the remaining fill and cap passes. The different materials are summarised in Table 1.

Table 1
Weld materials used

Weld Identity	Consumable	Parent Material Si / wt %	Parent Material Ni / wt %	Root Gap Mm (nominal)	Weld Width mm	Predicted susceptible area
X	1 % Ni	0.35	0.07	3-4	29	HAZ near final pass
Y	Ni-free	0.23	0.22	3-4	22	Weld metal
Z	1 % Ni	0.35	0.07	0	15	Parent plate close to weld

A weld that had failed in service was used to validate the test methods in terms of their ability to provide information that could have been used to predict the performance of this weld.

Controlled weld X (1 % Ni consumable, 3-4 mm root gap)

This was manufactured to have a high nickel content in the weld and a low nickel content in the parent plate. Recent work at TWI⁵ has shown that a higher level of nickel in the weld metal compared to the parent plate results in the weld being cathodic to the parent plate. Therefore, the parent plate would be expected to be anodic to the weld metal. A 1 % Ni consumable was used with a root gap of 3-4 mm to allow full root penetration. The parent metal was high in Si and low in Ni.

An additional weld bead was deposited at low heat input (0.5 kJ mm^{-1}) adjacent to the weld to produce a particularly hard, untempered, microstructure in the HAZ on one side of the joint.

Controlled weld Y (Ni – free consumable)

This was manufactured to have a low nickel content in the weld and a high nickel content in the parent plate. The weld metal would therefore be expected to be anodic to the parent plate. The combination of a parent material with low silicon and high nickel content and a standard Ni-free consumable (A15 TIG wire and Filarc S65 MMA electrodes) was utilised.

Controlled weld Z (1 % Ni consumable, no root gap)

This was manufactured to have high nickel content in the weld and low nickel content in the parent plate. The parent plate would therefore be expected to be anodic to the weld metal. This weld was produced using the same materials as weld X (1 % Ni consumable, 3-4 mm root gap), but the root gap was closed. The weld root will, in effect, be autogeneous (i.e. contain little or no filler metal). Corrosion testing of this weld should indicate whether or not preferential weld metal corrosion can occur in situations where the root gap has closed due to inadequate control of the welding process.

Weld that had failed in service

A weld that had failed in-service was used to validate the test methods and this was supplied without information on composition or process conditions to provide a blind testing sample.

IMMERSION TESTS

The immersion tests were conducted in ASTM D1141 seawater under freely corroding conditions using three specimens of each weld type (X, Y, and Z) with dimensions 150 mm x 50 mm x sample thickness. The specimen was suspended in the solution with the longest side vertical by the connecting wires used to measure the potential. The specimens were glass-bead blasted to remove any pre-existing corrosion product and washed with acetone and alcohol prior to testing. The solution was changed every four days to maintain the pH between 7.9 and 8.2. The overall exposure time was nine months. The electrode potential of one specimen of each weld type was monitored on a daily basis using a saturated calomel electrode for the entire duration of the exposure. The solution temperature was between 19°C and 22°C for all the tests.

After removal from solution, the specimens were rinsed in distilled water. Profiling of the sections was then carried out to determine which areas of the originally flat cross-section had corroded preferentially. A Talysurf stylus instrument with a stylus radius of 1 mm, a load of 2 mN and a scanning speed of 5 mm s⁻¹ was used without filtering.

2.3 SCANNING VIBRATING PROBE (SVP) TECHNIQUE

Principle of the scanning vibrating probe method

The SVP uses a platinum-tipped electrode to measure and map the small voltage drop induced by net current flow in the solution just above the specimen surface. This current flow will reflect the degree of anodic and cathodic activity of the surface. The voltage drop measurement is achieved by vibrating the electrode perpendicular to the surface at a frequency of 81 Hz and measuring the potential at the extremes of amplitude of the vibration. The difference in potential is then amplified and the probe position moved to the next measurement point along a line. The collected line data can then be displayed as voltage drop vs position plot or the voltage drop values may be colour-coded to give a pictorial representation in a raster pattern.

Test conditions used

A Uniscan SVP 100 instrument was used. The specimen dimensions were 250 mm x 15 mm x plate thickness (~15 mm) with the weld line perpendicular to the long axis. The specimen length, 250 mm, was much greater than the width of the welds (see Table 1), to reproduce the large parent plate to weld area ratio that would be typical in service. Scanning was undertaken in the plane of the weld section at a scan rate of 2 mm s⁻¹ with the probe tip positioned 100 µm from the specimen surface. The specimens were prepared to an 800-grit SiC finish (and cleaned) just before immersion in the SVP tank.

In order to evaluate the effect of the conductivity of the electrolyte on the measurements, tests were carried out in distilled water of conductivity 1.7 µS cm⁻¹ and using ASTM D1141 synthetic seawater diluted 10:1 with distilled water to give a solution conductivity of 6.5 mS cm⁻¹. Scanning was continuous and was typically completed in a timescale of 20-40 minutes with a resolution of 64 or 128 lines per scan.

The electrical circuit used in all the SVP tests is given in appendix I. The electrolyte temperature was maintained between 19°C and 22°C for all the tests.

2.4 GALVANOSTATIC TESTS

Principle of the test

When a constant anodic current is applied to accelerate corrosion the more active regions of the metal should corrode preferentially. After exposure, the specimen is examined and the extent of penetration of the metal surface assessed visually or by profiling. The solution temperature was maintained between 19°C and 22°C for all the tests.

Test carried out on controlled sample welds X, Y and Z

Following the earlier study by Garner¹¹, tests were carried out with an applied anodic current density of 0.88 mA cm^{-2} using specimens of dimensions $150 \text{ mm} \times 150 \text{ mm} \times$ plate thickness with the weld positioned in the centre of the longest side. Pre-existing corrosion product on the surfaces was removed by glass-bead blasting. The specimens were washed with acetone and alcohol before they were immersed in a 10 L plastic container filled with ASTM D1141 seawater of initial pH 8.2 and the current applied. A platinum electrode was used as the auxiliary electrode. The test duration was 21 days and the solution was replaced at four-day intervals. Air was bubbled through the solution to sustain aeration and to continuously agitate the solution.

After removal from solution, the specimens were rinsed in distilled water, photographed and profiled as for the immersion tests.

Service failure weld

Specimens approximately 20 mm long by 5 mm wide by sample thickness (~10 mm) were cut from the material supplied, with the weld in the centre of the section. The sides and cap of the weld were coated with polyurethane sealant to constrain the accelerated corrosion to the root area that was exposed to the corrosive medium in service. The exposed surface was tested in the as received condition without surface treatment or cleaning.

The electrolyte was ASTM D1141 synthetic seawater and three test conditions were evaluated; (i) a test of three weeks duration with a current density of 0.88 mA cm^{-2} as used previously¹¹; (ii) a test using a current density of 4.4 mA cm^{-2} for 5 days and (iii) an ultra-fast test at a current density of 88 mA cm^{-2} for 4 hours.

The specimens were visually examined during the test and after completion. This proved satisfactory and profiling was not carried out.

2.5 MICROHARDNESS TESTING

Microhardness profiling and microhardness scanning of each weld was carried out after metallographic preparation to a $1 \mu\text{m}$ diamond finish.

Microhardness profiling

Microhardness profiling was carried out on all three controlled welds in the plane of the weld section at a load of 4.98 N. Indentations were made at 0.5 mm intervals along the centre line, parallel to the edge of the plate, and incorporating the parent plate, HAZ and weld metal. This longitudinal hardness profile was repeated at four other locations, above and below the centre line and spaced 2.5 mm apart. An NPL calibrated graticule was used to measure the width of the indents.

2.5.2 Microhardness scanning

Two-dimensional microhardness maps of the weld, HAZ and adjacent parent plate were produced using the NPL scanning microhardness facility¹⁰. This machine operates by automatically indenting the specimen over an area defined by a grid of measurement points. At each location, indentation depth and load are measured as the load is applied.

Microhardness is determined using the principles outlined in the draft ISO standard for Instrumented Hardness Tests, ISO DIS 14577. The position of the surface is identified by fitting a polynomial to the initial 5 % of the loading curve. The displacement at maximum load incorporates elastic and plastic deformation. A linear fit to the top 20 % of the unloading curve (representing elastic unloading) is extrapolated to zero load to determine the depth of material in contact with the indenter at maximum load (h_c). This is a measure of the plastic deformation at maximum load. The microhardness, H , (force per unit area associated with plastic deformation) is then calculated using:

$$H = F/(24.5 \cdot h_c^2)$$

F is the maximum load and $24.5 \cdot h_c^2$ is the area of the indenter in contact with the material at maximum load.

Measurements were made using a Vickers indenter with a load of 0.2 N at typical spatial intervals of 0.1 mm over a 100 x 200 point grid. The measurement time for the indentation was approximately 5 seconds per point.

3 RESULTS

3.1 IMMERSION TESTS

The potentials of welds X and Z both started at about -0.74 V (SCE) and rose to an almost constant value of -0.69 V (SCE) after 15 weeks exposure. In contrast, specimen Y started at -0.74 V (SCE), rose sharply to -0.63 V (SCE) in the first week, then steadily decreased to -0.69 V (SCE) after Week 6 and thereafter remained constant.

Visual examination of the welds was found to be a satisfactory method of judging the degree of preferential corrosion. For weld X (1 % Ni consumable, 3-4 mm root gap), the parent material corroded more than the weld material and a shallow groove developed along the edge of the final weld pass in contact with the parent plate. The location of this groove is shown in Figure 1, the groove running perpendicular to the plane. For weld Y (Ni – free consumable), the weld corroded in preference to the parent plate (see Figure 2). In the case of weld Z (1 % Ni consumable, no root gap), the parent plate corroded in preference to the weld metal especially in the area close to the weld (see Figure 3). Undercutting of the weld cap occurred parallel to the welding direction. Preferential corrosion could be seen in the area of the root although the effect was very slight. This suggests that autogenous welding of this material does not confer deleterious corrosion susceptibility as the cap and root corroded in a similar way. In all cases, the test reproduced the behaviour predicted based on the compositions of the weld metal and base plate.

A light brown scale formed on welds X, Y and Z in the areas that were corroding slowly. In cases where small patches could be seen it was apparent that at some stage of the experiment scale had covered a greater area than this and had become detached during testing. For weld X the scale covered the weld cap with the exception of a fine line along the edge of the final weld pass. For weld Y the scale completely covered the specimen apart from the weld metal and a region in the parent plate 3-5 mm either side of this. For weld Z the scale covered about 60 % of the specimen in large patches and covered the weld cap in every case.

3.2 EVALUATION USING SVP

Evaluation of welds X, Y and Z in distilled water

A specimen of each weld type was scanned in the plane of the weld section in distilled water (see Figure 4 for weld Y (Ni-free consumable). Relative electrochemical activity could clearly be identified as scattered patterns of anodes (blue or black) and cathodes (white or red). This scan was started after an exposure time of approximately 10 minutes and took a further 40 minutes to complete. The corrosion patterns can be identified visually and are represented in Figure 5; the anodic areas can be seen as brown patches on the surface. As one would expect there is a correlation between the appearance of the corrosion product and the local variations in anodes and cathodes. Microscopic examination of the specimen showed that the corrosion sites were broadly associated with the boundaries between weld passes. Figure 4 also shows that the potential drop in the solution extends beyond the boundaries of the specimen, as the sides were not coated.

Since the time to complete a scan is about 40 minutes, Figure 4 does not represent a simple snapshot in time. If the corrosion behaviour were to change rapidly, the apparent distribution of corrosion activity could be affected. The evolution of the corrosion activity was investigated by repeatedly scanning a section of weld Y (Ni-free consumable) in distilled water over a period of four days (Figures 6, 7 and 8). The scans produced clearly show the transition from discrete anodic and cathodic sites to net anodic behaviour in the weld metal (particularly the weld cap) and net cathodic behaviour in the parent plate, with some discernible cathodic behaviour in the HAZ regions. The fact that macroscopic anodes and cathodes were formed indicates that the solution conductivity was high enough to enable current flow between these regions. The solution was not replenished during these tests and the conductivity of the solution rose from $1.9 \mu\text{S cm}^{-1}$ at the start of the test to $12.4 \mu\text{S cm}^{-1}$ after 4 days

Evaluation of welds X, Y and Z in diluted seawater

The activity of the three welds in ASTM D1141 simulated seawater diluted 10:1 with distilled water is shown in Figures 9-11. The data produced by the SVP are useful for determining patterns and locating predominantly anodic or cathodic when colour representations of this data are displayed. The reference scale on these figures is designed for qualitative comparison with offset factors being used. Hence, absolute comparison of voltages between different figures are not meaningful but the trends are still valid. In contrast to distilled water, macroscopic anodes and cathodes were established relatively quickly in diluted seawater, most clearly for specimens Y and Z (Figures 10 and 11). The apparent activity of weld X (1 % Ni consumable, 3-4 mm root gap) was more difficult to interpret because the activity at

the surface of the specimen was changing rapidly within the 40 minutes scan period (Figure 9). In this case, scanning started at the weld root and finished at the weld cap. The rather long scan duration has implications for interpretation of data when the reaction progresses relatively quickly. To demonstrate the significance of the evolution of the corrosion reaction a series of line-scans were undertaken of the weld cap over one location (the cap of weld X) at different time intervals (50 times over a period of 78 minutes). Figure 12 is a composite formed from this series of line scans with time evolving from top to bottom of this figure. Individual data from the first and last line scans are shown in Figure 13. At the moment of immersion highly anodic areas, shown in black, are active in the parent plate on either side of the weld. These become progressively less anodic with time. After four days exposure the gross pattern of corrosion can be seen from the line scan (Figure 14) although the detail has been lost due to the thick covering of corrosion product on the surface of the specimen. At this stage, the weld metal is clearly cathodic to the parent plate.

These results emphasise the need to account for exposure time in applying SVP data to service prediction.

3.2.3 Evaluation of service failure weld

Figure 15 shows in section the weld that had failed in service, in this case with the weld root at the top of the figure. The projected initial root is shown schematically to indicate the extent of metal loss. Grooving had occurred in the HAZ on both sides of the weld and the root had been removed. The SVP scan of the service weld in ASTM D1141 simulated seawater diluted 10:1 with distilled water (Figure 16) highlighted regions of anodic activity (blue areas), particularly in the HAZ near the root, which is also at the top of the figure, consistent with the behaviour seen in service. In this case the exposure time before commencement of the scan was 40 minutes and the time to complete the scan a further 40 minutes.

3.3 GALVANOSTATIC TESTING

3.3 Galvanostatic testing of controlled welds X, Y and Z

The appearance of the specimens after applying a current density of 0.88 mA cm^{-2} for 21 days is shown in Figures 17-19. Weld X (1% Ni consumable, 3-4 mm root gap) showed a preferentially high corrosion rate in the boundary between the weld and the parent plate and to a lesser degree in the parent plate in an area near the weld (Figure 17). A fine groove could be seen along the edge of the weld bead of the final pass running perpendicular to the plane of the paper in Figure 17. Examination of weld Y (Ni-free consumable) indicated significant corrosion of the weld with a pronounced step across the boundary with the parent plate (Figure 18). The weld passes can be seen as ridges in the section of the weld metal. Weld Z (1% Ni consumable, no root gap) showed preferential removal of material in the boundary between the weld and the parent plate (Figure 19), as for weld X (1% Ni consumable, 3-4 mm root gap). More detailed examination indicated that within this region of attack, shallow grooves ran parallel to and on either side of the weld root. This was not as clearly observed in the immersion tests on this weld. A similar effect was seen at the weld cap. Hence, there would appear to be no significant influence of autogenous welding on corrosion susceptibility as concluded previously.

Measurement of the profiles of the specimens after testing was difficult due to the roughness of the surfaces and undercutting seen after testing. These tend to obstruct the smooth movement of small styli which catch on the sharp ledges. A large diameter ball shaped stylus was used to alleviate this problem. Interpretation of the profiles was possible in some cases and this is demonstrated by Figures 20-22. The profile of controlled weld X indicated (Figure 20) non-uniform behaviour either side of the weld centre. This was not so clearly visible on the specimen. Figure 21 shows a profile consistent with the preferential corrosion of the weld metal observed for the case of controlled weld Y whilst Figure 22 shows the profile of controlled weld Z and the deep grooves seen visually. The profile tended to exaggerate the extent of the effect in this case.

For all three controlled welds, it was easier to identify the pattern of corrosion by visual examination in the galvanostatic tests than in the immersion tests. This was partly due to the absence of scale formation in the galvanostatic tests. In addition, the extent of localised corrosion appeared to be greater in the galvanostatic tests than in the immersion tests.

Galvanostatic testing of the weld that had failed in service

Testing at 0.88 mA cm^{-2} for a period of 21 days removed the protruding root of the weld initially and then caused groove formation either side of the root. Testing at 4.4 mA cm^{-2} produced similar results with removal of the root occurring after 4 days and formation of deep grooves on either side of the weld occurring after 11 days testing. In both cases, the tests reproduced the service behaviour depicted in Figure 15. At the very high current density of 88 mA cm^{-2} grooving of the specimen could be seen after two hours (Figure 23). When the test was continued for 4 hours, the exposed surface became levelled by the overall high corrosion rate and the differential effect was masked.

3.4 MICROHARDNESS TESTING

Microhardness Profiling

Examples of the microhardness profile of welds X, Y, and Z, stepped along the centre line of the section through the weld, are shown in Figures 24-26. Welds X and Z had broadly similar profiles, with a harder weld metal relative to the parent plate. This would be expected as these welds were produced using the same parent plate and filler materials. In contrast, weld Y (Ni-free consumable) indicated similar microhardness to the parent plate in the weld metal itself but with a large increase in microhardness in the HAZ. The profiles carried out in other locations did not provide much more insight than the centre-line profile and are not reproduced.

Microhardness Scanning

The microhardness scans of the three controlled welded specimens are shown in Figures 27-29. The absolute values cannot be compared directly with the values in Figures 24-26 as the method of determining hardness is somewhat different but the trends are similar. The advantages of this method of measuring hardness are the automation involved and the improved resolution associated with the low loads and small indentations ($3\text{--}4 \text{ }\mu\text{m}$). This enables identification of localised areas with a high hardness. For example, the hardened

HAZ between the final weld pass and the parent plate of weld X can be seen clearly in the more detailed local scan of Figure 30 which covers the area of the specimen to the top left of that shown in Figure 27. Figure 31 shows the martensitic microstructure of the hardened area of Figure 30. The distribution of hardness associated with the heat affected zone of Weld Y (Ni-free consumable) is also brought out well by the microhardness scan as shown in Figure 28.

4 DISCUSSION

A summary of the observations from the different corrosion tests allowing relative comparison is shown in Table 2.

Table 2
Summary of corrosion test results

Weld Type	Immersion Test	Galvanostatic Test	SVP (<i>All in diluted ASTM seawater</i>)
Controlled weld X (1 % Ni consumable, 3-4 mm root gap)	Parent plate corroded Groove formed along edge of final weld pass Scale formation over most of specimen	Preferential corrosion of boundary between weld and parent plate. Fine groove formed along the edge of the final weld pass	Gross pattern of corrosion (cathodic weld) after 4 days immersion revealed Localised preferential corrosion of the weld parent plate boundary revealed initially.
Controlled weld Y (Ni-free consumable)	Preferential corrosion of weld Scale formation over most of specimen except weld.	Preferential corrosion of weld	Gross pattern of corrosion found (anodic weld)
Controlled weld Z (1 % Ni consumable, no root gap)	Preferential corrosion of parent plate near weld-to-parent plate boundary Scale formation in slowly corroding areas	Preferential corrosion of parent plate near the weld and formation of shallow grooves along boundaries	Gross pattern of corrosion found (cathodic weld)
In Service failure	Deep grooves formed at the weld root <i>in service</i>	Removal of susceptible areas as seen in service at all current densities. Levelling occurred at very high current density.	Susceptible areas that failed in service in the weld root revealed

4.1 CORROSION OF CONTROLLED WELDS X,Y AND Z.

In the absence of in-service behaviour for the controlled welds, the immersion tests were used as the primary indicator of the long-term behaviour of the controlled welds and as a basis for validating the more accelerated or short-term exposure tests. The welds exhibited a range of behaviour. Although it has not been possible within the scope of this work to carry out detailed analysis of the welds supplied to determine the exact causes of this behaviour some general conclusions can be drawn regarding each weld.

Weld X (1 % Ni consumable, 3-4 mm root gap) corroded preferentially in the parent plate close to the weld metal. The preferential attack along the hardened HAZ between the final pass and the parent plate was not as significant as expected. Preferential corrosion of weld Y (Ni-free consumable) occurs in the weld metal due to the low nickel content of the weld compared to the parent plate and the high area ratio of cathode to anode that is effective in solutions of reasonably high conductivity. In the case of weld Z (1 % Ni consumable, no root gap) the parent plate corroded preferentially compared to the weld metal but the extent of corrosion was restricted by the low area ratio of anode to cathode. Other factors such as the microchemistry of the fusion line and HAZ play a more significant role for this weld as is shown by the grooves formed close to, and either side of, the cap and root parallel to the welding direction.

It was not possible to produce a completely closed root gap in weld Z although a degree of autogenous welding did occur. However, grooves form in a similar way in the cap and root areas and autogenous welding is not, therefore, the cause of this effect. The gross behaviour of the three welds supports the findings of TWI⁵ that increasing the nickel content in the weld metal decreases the susceptibility to preferential weld corrosion.

4.2 SCANNING VIBRATING PROBE TECHNIQUE

The results of scanning vibrating probe measurements depend critically on the electrolyte used. Distilled water revealed the behaviour expected in low conductivity solution (Figure 4), namely localised activity based on the formation of discrete anodic and cathodic sites interconnected over a short range. Diluted seawater revealed the behaviour expected in high conductivity solution with net anodic and cathodic behaviour produced by longer-range interactions (Figure 10). The pattern of corrosion in diluted seawater was consistent with that in the long-term immersion and galvanostatic tests. The choice of electrolyte should therefore be made based on the in-service environment of any welds that are examined and the purpose of the test.

The time to complete an area scan (40 minutes) is not insignificant and this will affect the interpretation of results from short-term exposure tests, as the corrosion activity would be evolving during the course of the scan. SVP area scans may only be considered a snapshot of the corrosion activity after a suitably long period of immersion (~20 hour) at which time the rate of change of activity will have slowed sufficiently. In any event, if designed to predict service behaviour, scans should be repeated with different periods of exposure, up to several days, as the relative corrosion activity may change over this period as experienced for Weld X in these tests.

To follow the early evolution of the corrosion activity line-scans at discreet locations may avoid the confusion of time-dependent effects.

Satisfactory calibration methods have not been developed to allow comparison of data collected using different amplifier settings and scan parameters. Current practice is to scan a gold plated pin with an impressed constant current immersed in the electrolyte to be used. The measurements of voltage made allow the local conductivity, over the range of vibration of the probe, to be made. This can then be used to convert the voltages measured when the specimen is scanned in the same electrolyte to be converted to currents and used to estimate corrosion rates. However, the proximity of the probe tip to the surface of the specimen means

that the measurements are made in a thin layer of electrolyte with properties in stagnant solutions possibly different to the bulk. This effect becomes more pronounced as the time of exposure increases.

One of the main drawbacks of the SVP instrument used is that it can only be used on topographically level surfaces. An instrument is being developed that takes account of surface irregularity¹² and this could be useful to scan the root or cap of a weld without grinding the surface.

4.3 GALVANOSTATIC TESTING

This method was used successfully to identify susceptible areas in the controlled welds and the in-service weld. Tests at current densities of 0.88 mA cm^{-2} and 8.8 mA cm^{-2} produced similar patterns of behaviour to that seen in exposure tests on welds X, Y and Z and to that shown by the in service failure. Care is needed with tests at high current densities, in this case 88 mA cm^{-2} , to avoid levelling of the specimen but this can be achieved by regular observation.

Garner¹¹ had reported that the galvanostatic test produced an equivalent amount of corrosion to a 6-month immersion test in seawater. In the tests described in this report the galvanostatic test as applied to controlled welds X, Y and Z resulted in more extensive corrosion in the susceptible region of the weld compared to a 9-month immersion tests. It would be surprising if such a neat quantitative relationship were to hold for a system which undergoes marked localised attack, e.g. in the form of grooving. The galvanostatic test is most effective in identifying corrosion-susceptible areas in a qualitative manner.

Galvanostatic testing is simple to carry out and visual examination can be used to identify susceptible areas. Profiling the specimen surface added little value given the time and effort required to make the measurements. The results of the galvanostatic test are not too sensitive to the electrolyte provided it is reasonably conducting. The test on the weld that had failed in service reproduced the corrosion in service although the test was conducted in diluted seawater which was not the corrosive media used in service. However, it should be remembered that longer-term phenomena such as scale formation do not occur in the galvanostatic test but may affect performance in service. A draft procedure¹³ for the galvanostatic test has been written.

4.5 MICROHARDNESS MEASUREMENTS

The two microhardness measurement techniques used here differ in the methods of measurement of the indentation and the data are presented in different formats. Scanning is more useful for the evaluation of the microhardness patterns seen in welds as a complete representation of the microhardness of the weld can be made and easily visualised (see Figures 27-29). The harder area of the final pass in weld X (1 % Ni consumable, 3-4 mm root gap) is clearly shown in Figure 30. The fine line separating the weld metal from the parent plate in this region is also shown and it is very likely that this would be missed using a profiling technique (Figure 24) as the spacing of the indentations would not usually be fine enough to reveal it clearly.

The hardness of controlled weld Z (1% Ni consumable, no root gap) shows the characteristic peaks associated with the hardened HAZ on both sides of the weld (Figure 26) and these areas were found to corrode preferentially (Figure 19) reinforcing the suggestion that higher hardness indicates corrosion susceptibility. The hardness profile for controlled weld Y (Ni-free consumable) shows that the weld metal and parent plate are of similar hardness separated by very pronounced hardness peaks in the HAZ (Figure 25). In this case the hard areas do not correlate with those that corroded preferentially. In this case the area of lowest hardness, the weld metal, corroded preferentially which is the reverse of the findings for welds X and Z.

Pistorius⁹ investigated the galvanic coupling of weld materials with the same composition but different microstructures and hardness values. He concluded that there was little difference in their corrosion behaviour and no consistent tendency toward anodic or cathodic behaviour. This conclusion has been reinforced by the work described here using hardness profiling and scanning. The results showed that in some welds there is a relationship between hardness and corrosion susceptibility, but this is not always the case and microhardness measurements should not be used on their own as a tool for predicting corrosion susceptibility. Nevertheless, the scanning microhardness technique would be a powerful tool for identifying local hardness hot spots susceptible to hydrogen embrittlement.

5 CONCLUSIONS

The results of the long term immersion, galvanostatic and scanning probe tests confirmed that a higher nickel content in the weld metal produces a weld which when immersed in conducting solution is cathodic to the base plate.

The scanning vibrating probe technique is reliable as an indicator of preferential corrosion although the data needs careful interpretation and consideration of the effects of time and the properties of the electrolyte is essential. The time to complete an area scan is not insignificant and this will affect the interpretation of results from short-term exposure tests, as the corrosion activity would be evolving during the course of the scan. SVP area scans may only be considered a snapshot of the corrosion activity after a suitably long period of immersion (e.g. 20 hour) at which time the rate of change of activity will have slowed sufficiently. In any event, if designed to predict service behaviour, scans should be repeated with different periods of exposure, up to several days, as the relative corrosion activity may change over this period. To follow the early evolution of the corrosion activity, line-scans at discreet locations may avoid the confusion of time-dependent effects.

The electrolyte conductivity should be adjusted to support the type of corrosion pattern, discrete anodes and cathodes or gross anodes and cathodes, that the in-service condition will produce. The need to balance this against the resolution required to identify susceptible areas should also be addressed and ASTM D1141 seawater diluted 10:1 with distilled water was found to achieve this in the case of gross anode and cathode action. Distilled water would be more appropriate for the situation where discrete anodes and cathodes form.

The galvanostatic test was found to be a rapid and reliable indicator of preferential corrosion in carbon steel welds, producing similar results to the long term immersion tests in terms of the region of the weldment which was susceptible to corrosion. Very high current densities

(about 88 mA cm⁻²) can yield results in a few hours but frequent observation of the specimen is necessary as levelling of the surface occurs when the specimen is tested for 4 hours.

Although some welds did suffer enhanced corrosion in areas with a high hardness, there was no consistent relationship between hardness and corrosion susceptibility. Therefore, hardness measurement cannot be used in isolation as a reliable indicator of corrosion. However, in cases where hydrogen embrittlement is a possibility the hardness mapping technique would be a valuable tool in locating local hard spots that would be susceptible.

ACKNOWLEDGEMENTS

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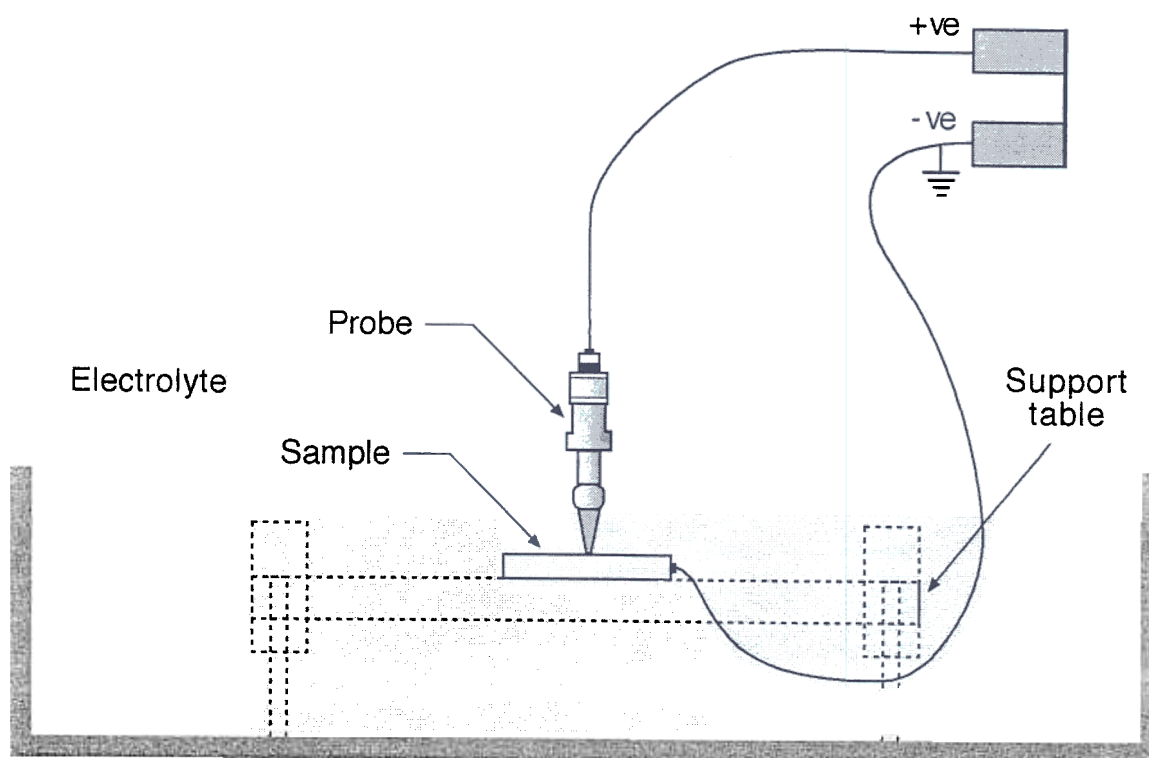
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APPENDIX 1

CIRCUIT USED IN SVP TESTS



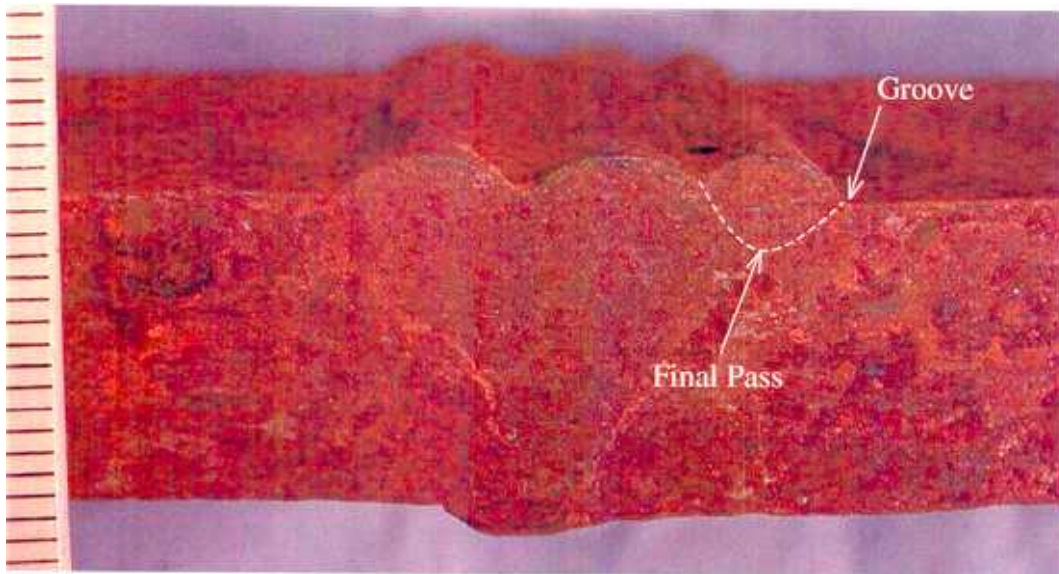


Figure 1. Appearance of weld X after immersion testing showing grooving near final pass.

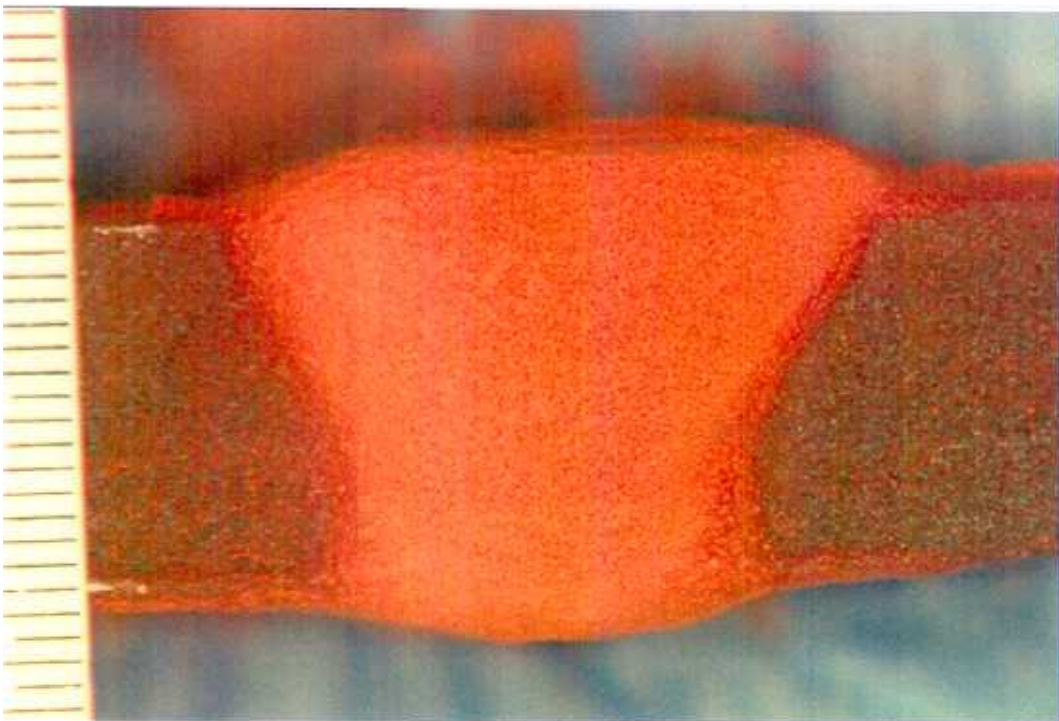


Figure 2. Appearance of weld Y after immersion testing showing anodic weld.

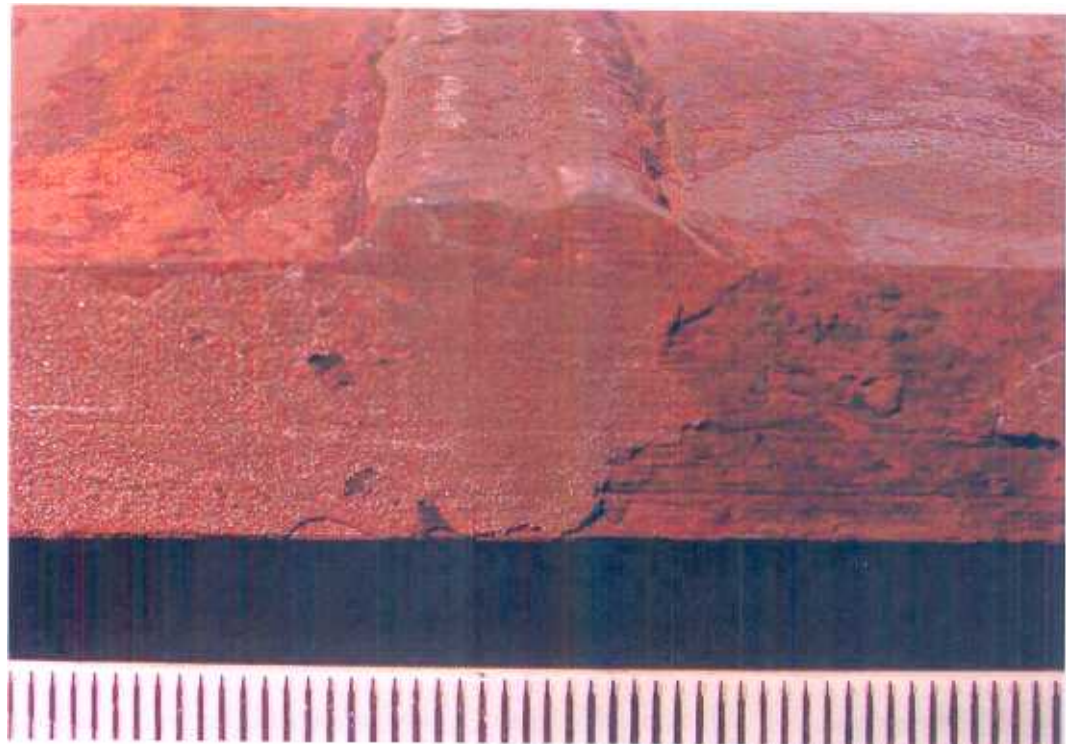


Figure 1. Visual appearance of the sample after immersion testing.

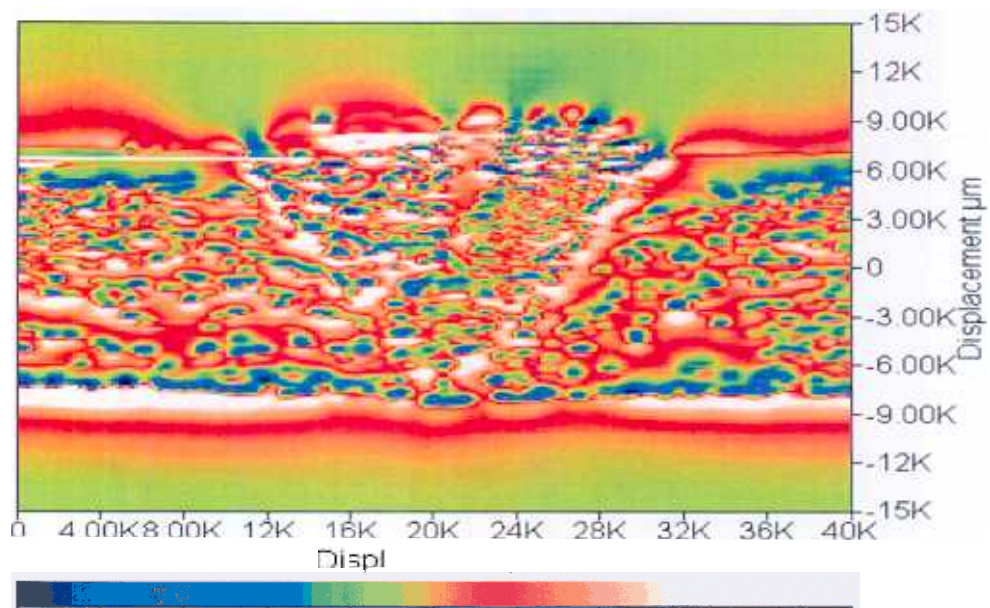


Figure 2. AFM scan of the sample after immersion testing showing discrete nodules and cathodes.



Figure 5. Visual appearance of weld Y after exposure to distilled water for 60 minutes showing corrosion at discrete anodes.

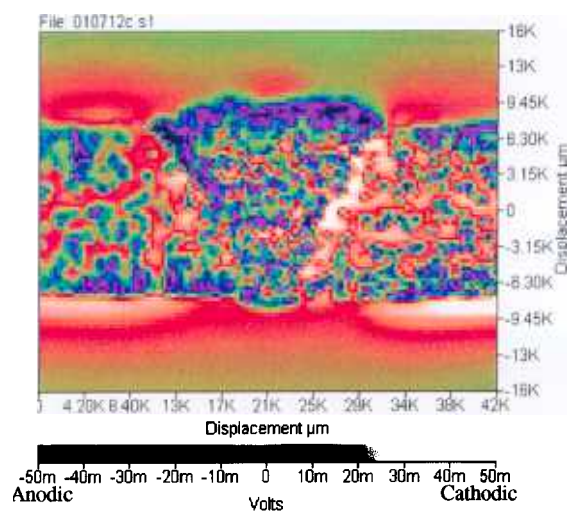


Figure 6. SVP scan of weld Y in distilled water after 2 hours exposure.

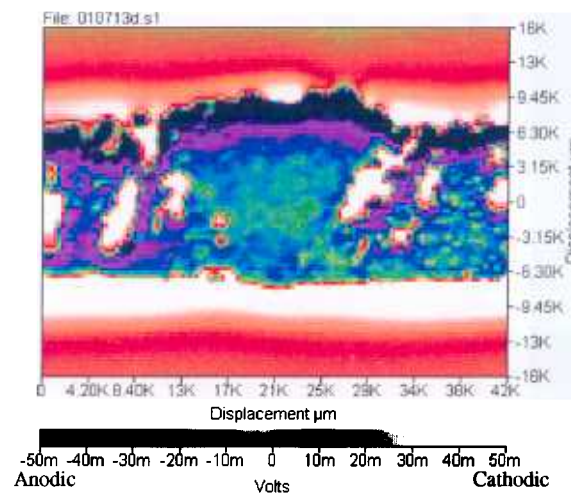


Figure 7. SVP scan of weld Y in distilled water after 24 hours exposure.

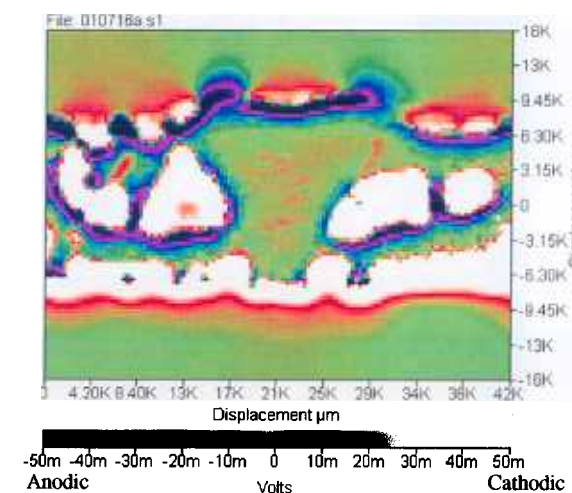


Figure 8. SVP scan of weld Y in distilled water after 4 days exposure

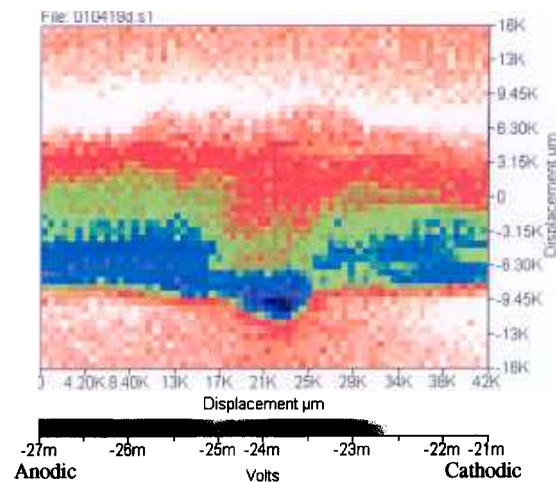


Figure 9. SVP scan of weld X in diluted ASTM simulated seawater after 60 mins exposure.

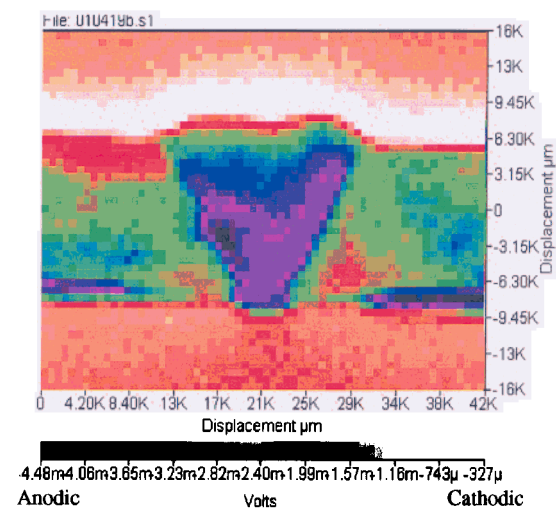


Figure 10. SVP scan of weld Y in diluted ASTM simulated seawater after 60 mins exposure.

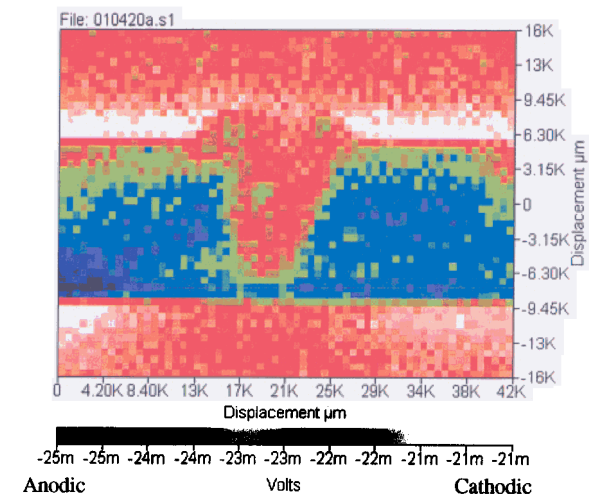


Figure 11. SVP scan of weld Z in diluted ASTM simulated seawater after 60 mins exposure.

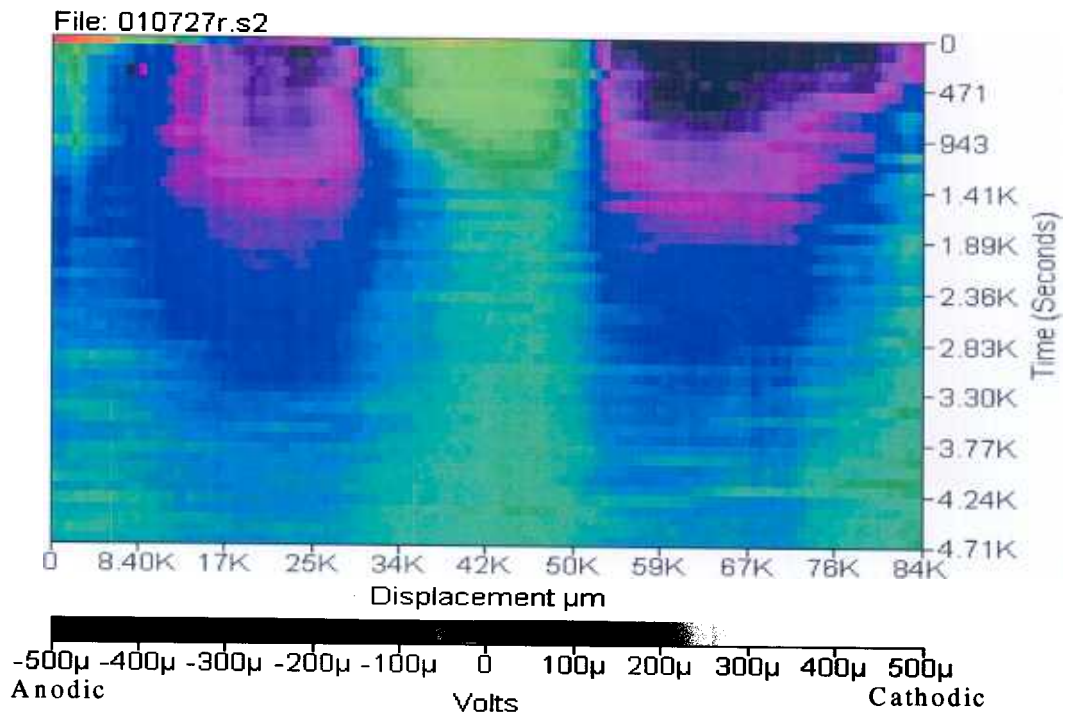


Figure 12. Series of 50 SVP line scans of weld X along the weld cap in diluted ASTM simulated seawater showing evolution of the corrosion process.

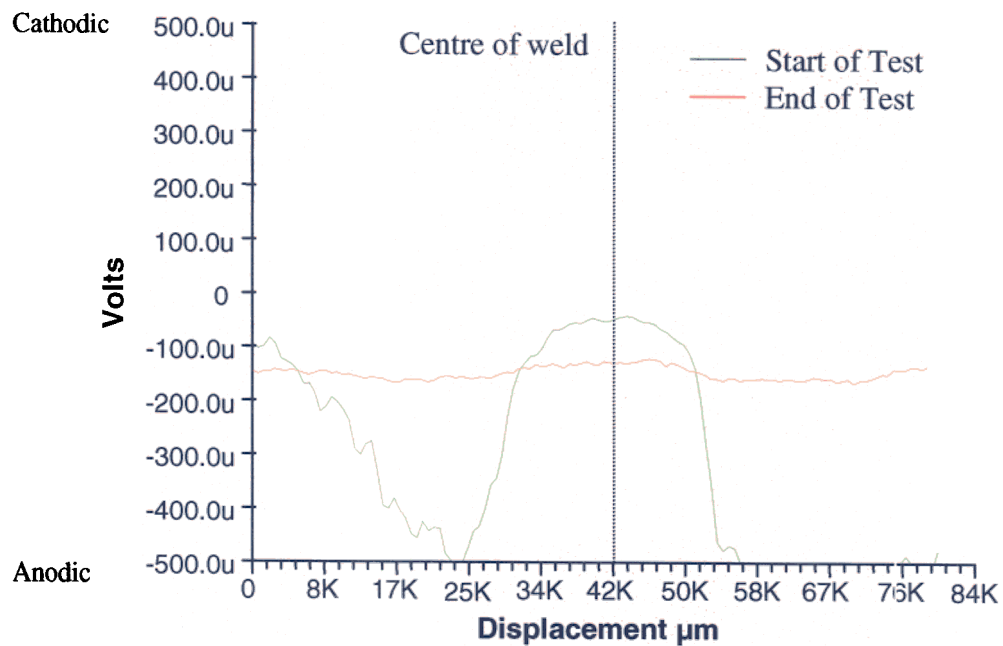


Figure 13. First and last scans from series shown in figure 12.

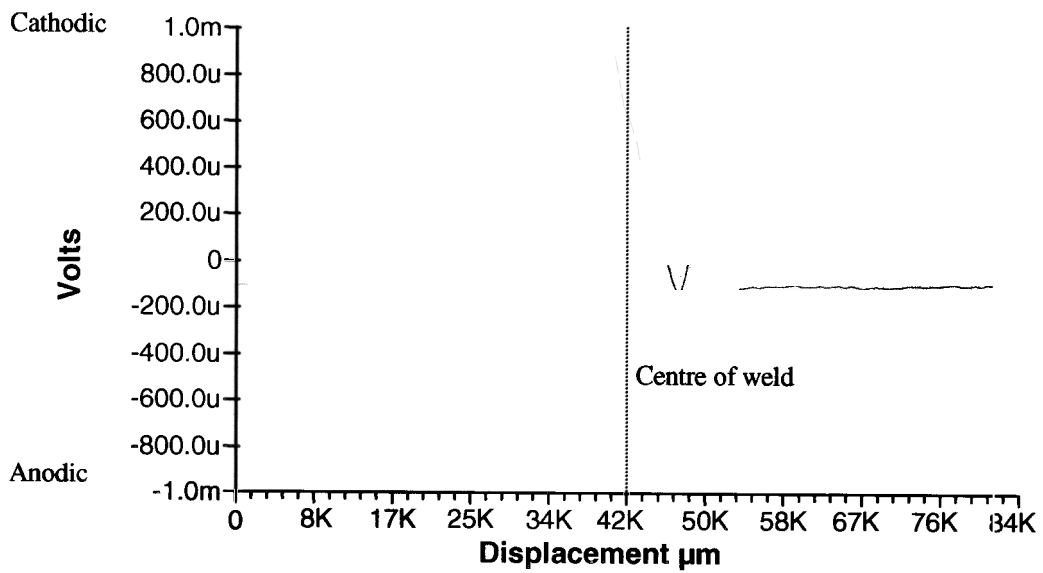


Figure 14. SVP line scans data of weld X along the weld cap in diluted ASTM simulated seawater after 4 days exposure showing gross pattern of corrosion.

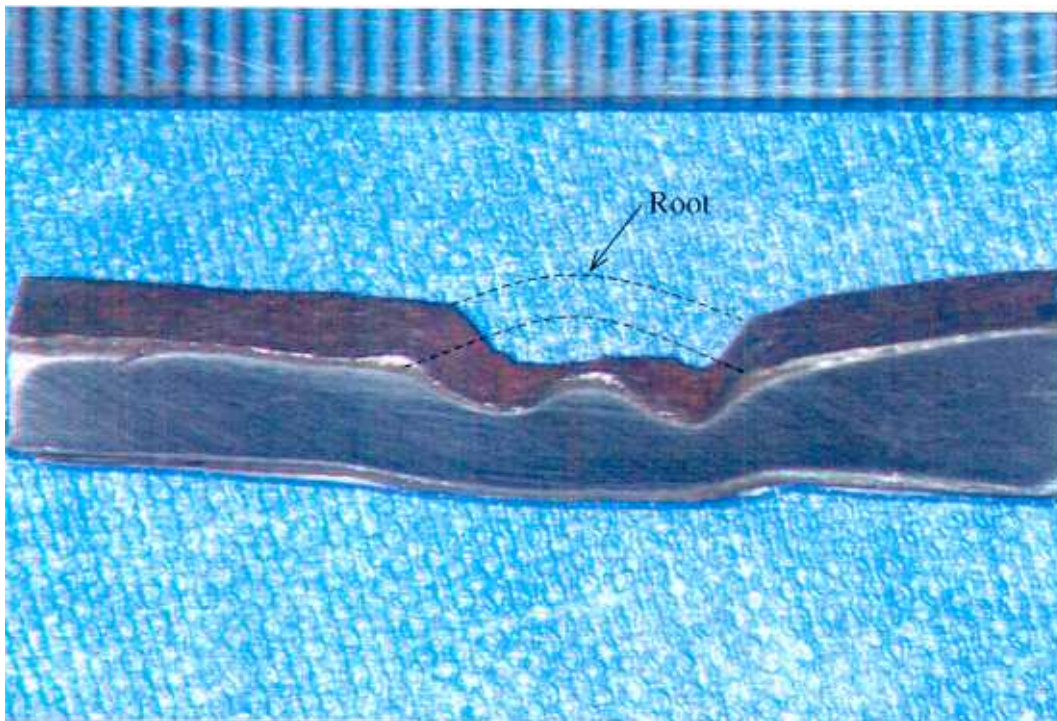


Figure 15. Appearance of weldment that had failed in-service showing formation of grooves near the weld root.

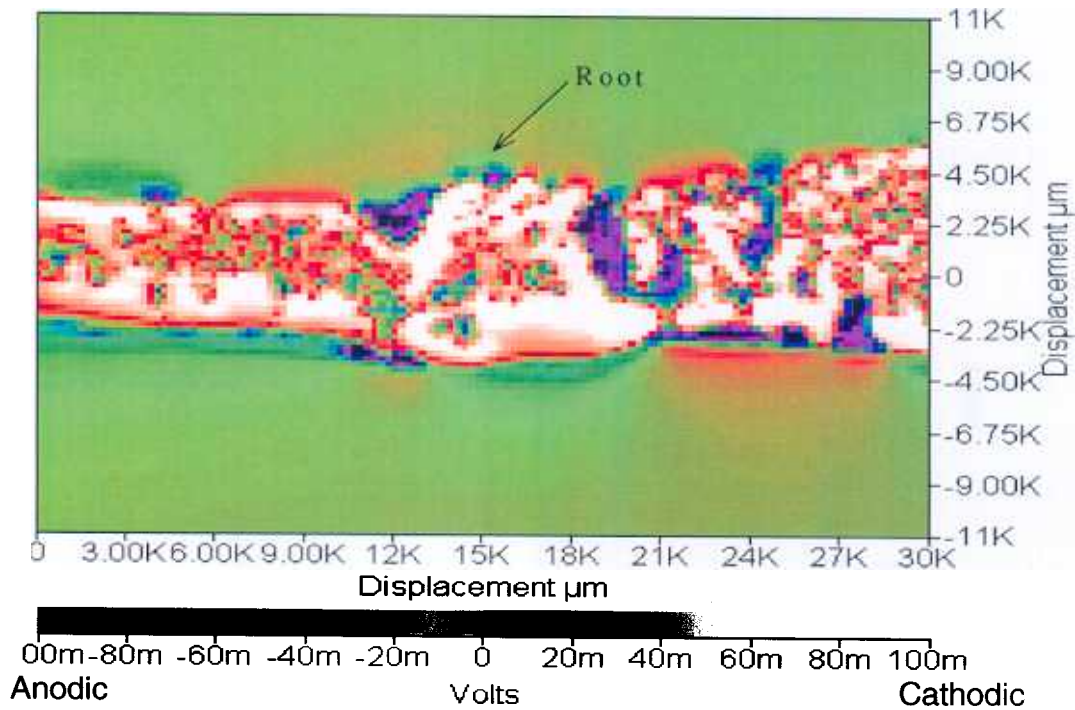


Figure 16. SVP scan in diluted ASTM seawater of weldment (in-service failure) showing susceptible areas (purple).

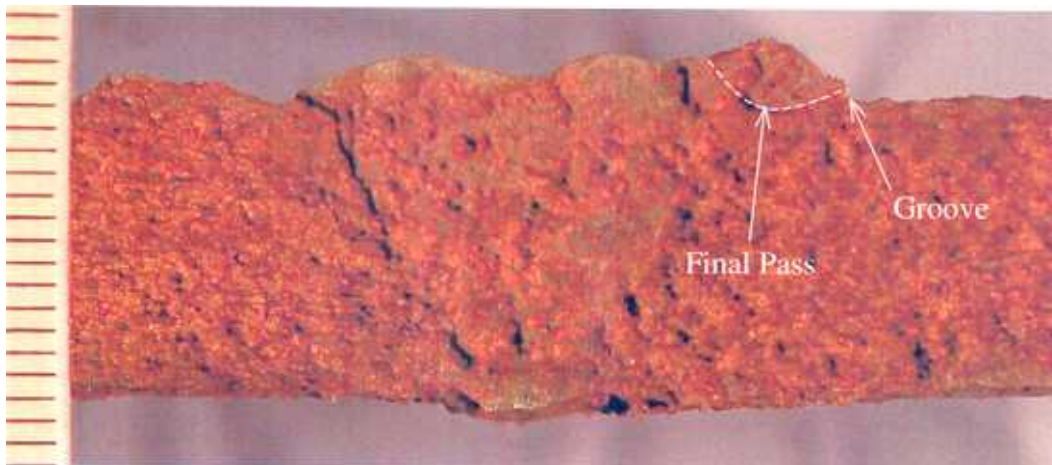


Figure 17. Appearance of weld X after 21 days galvanostatic testing showing preferential corrosion in the boundary between the weld and the parent plate as well as shallow groove near final pass.

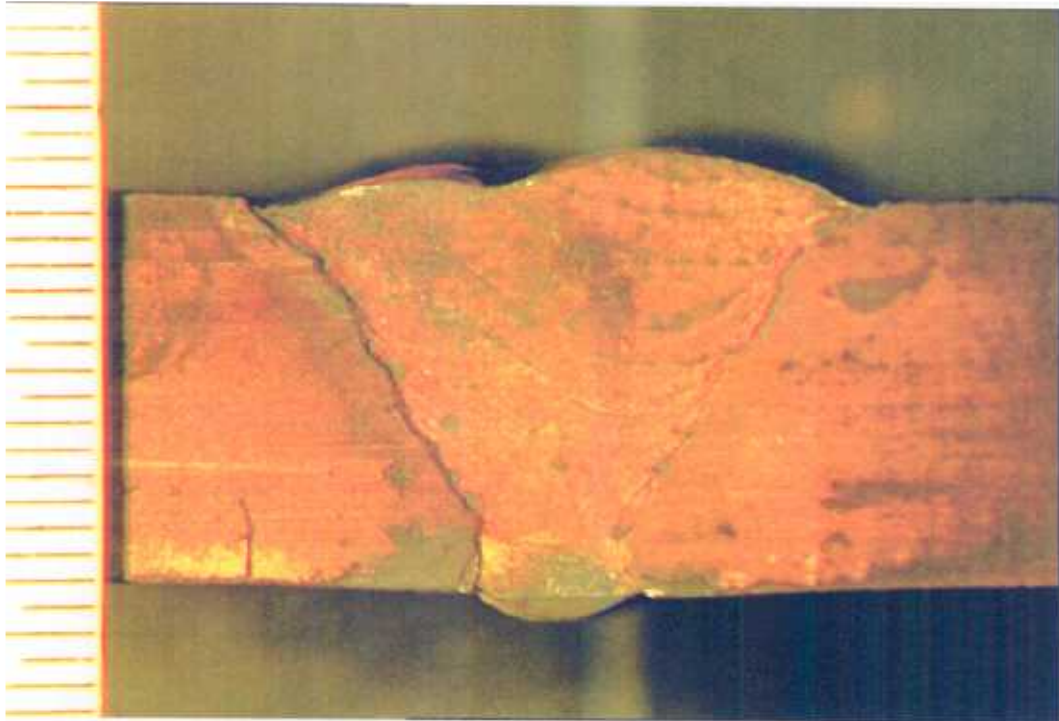


Figure 18. Appearance of weld Y after 21 days galvanostatic testing showing preferential corrosion of weld.



Figure 19. Appearance of weld Z after 21 days galvanostatic testing showing shallow groove at boundaries between the weld and the parent plate.

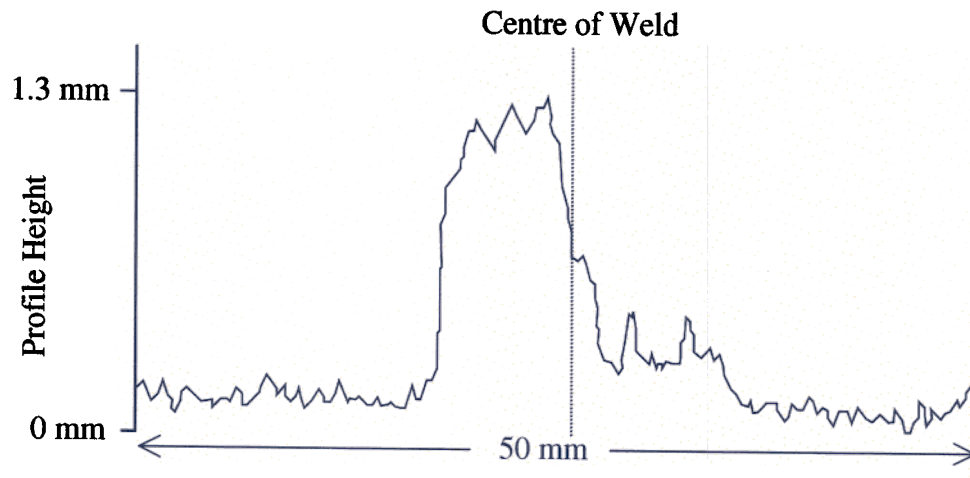


Figure 20. Profile of the section of weld X after galvanostatic testing showing preferential corrosion of parent plate.

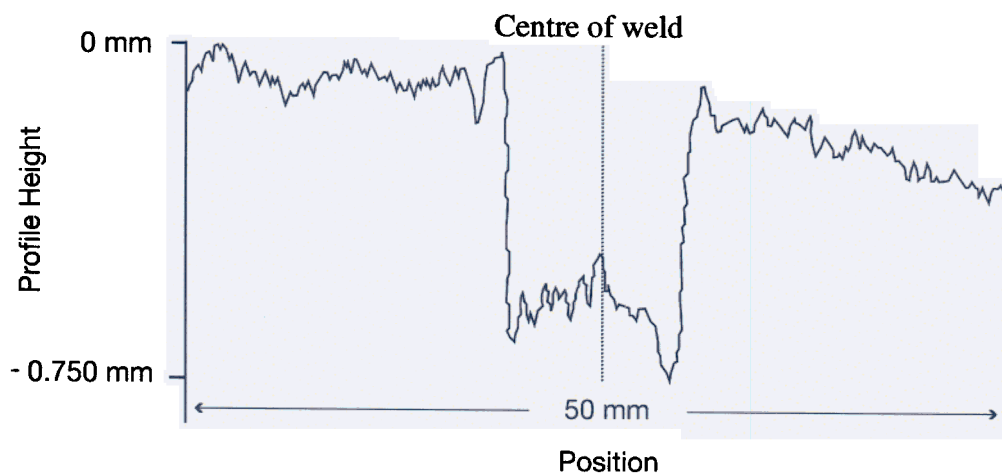


Figure 21. Profile of the section of weld Y after galvanostatic testing showing preferential corrosion of the weld.

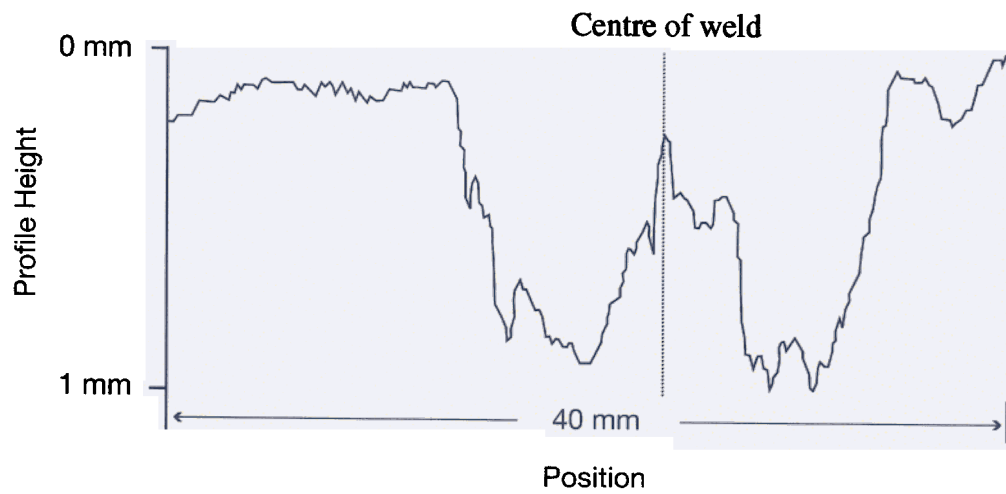


Figure 22. Profile of the section of weld Z after galvanostatic testing showing grooving between weld and parent plate.

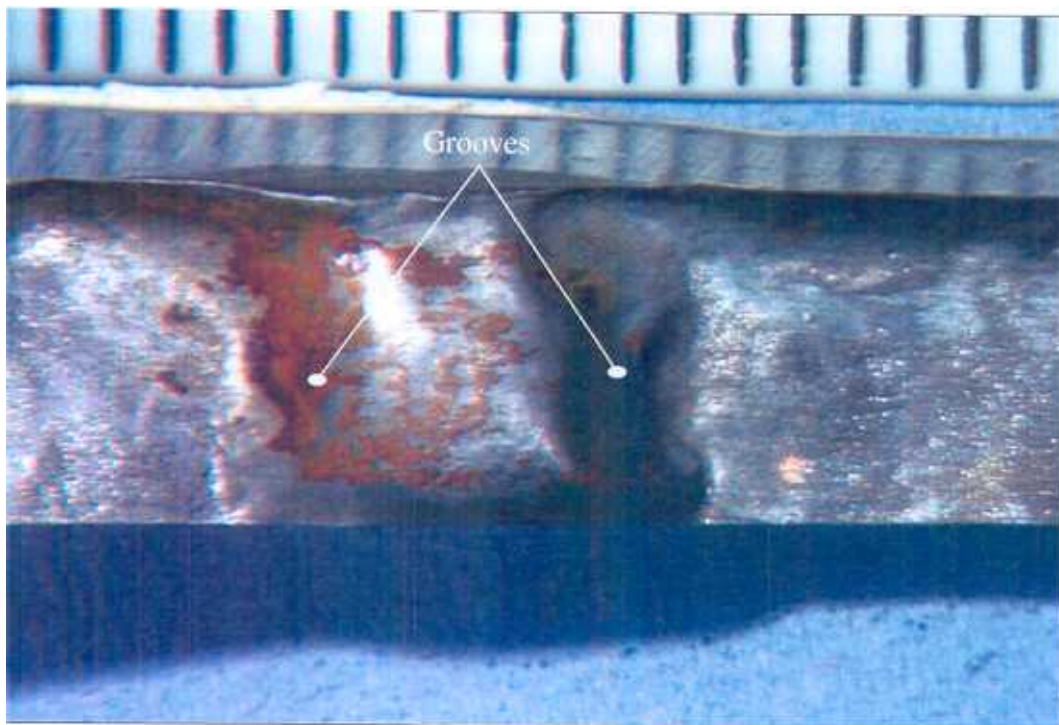


Figure 23. Appearance of weldment that failed in-service after galvanostatic testing showing grooves formed on either side of the weldment.

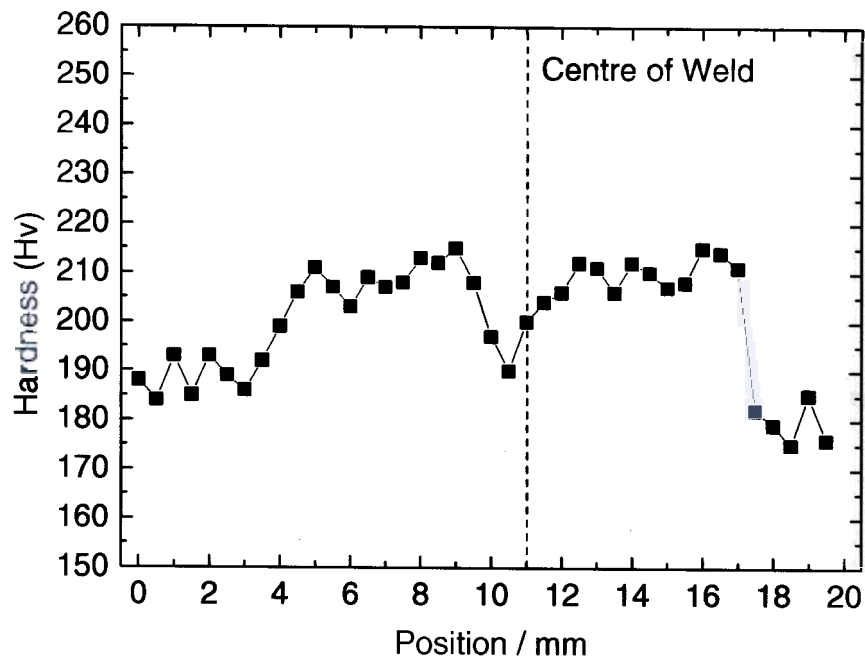


Figure 24. Microhardness profiles of weld X along the specimen centreline showing weld to be harder than parent plate.

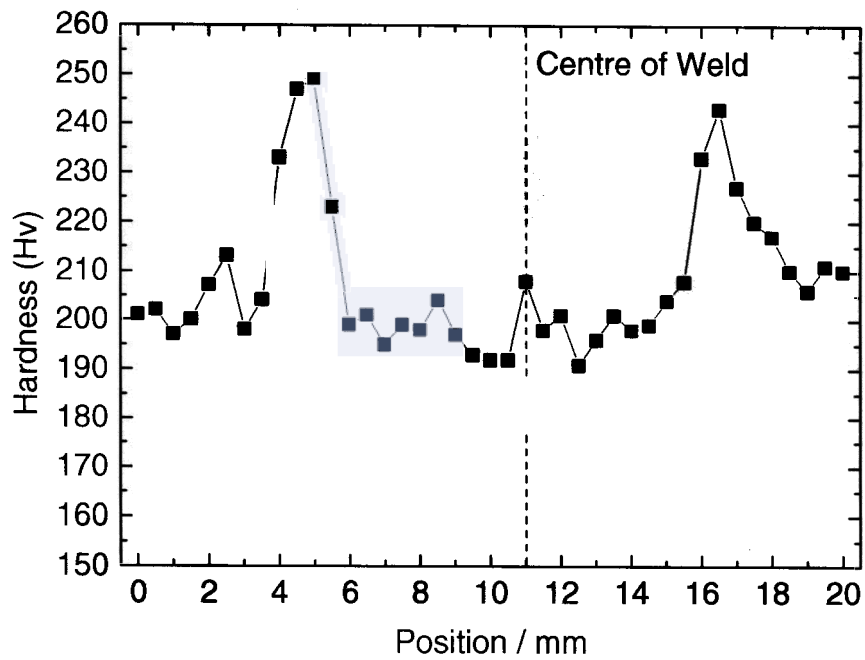


Figure 25. Microhardness profiles of weld Y along the specimen centreline showing hard peaks in the HAZ.

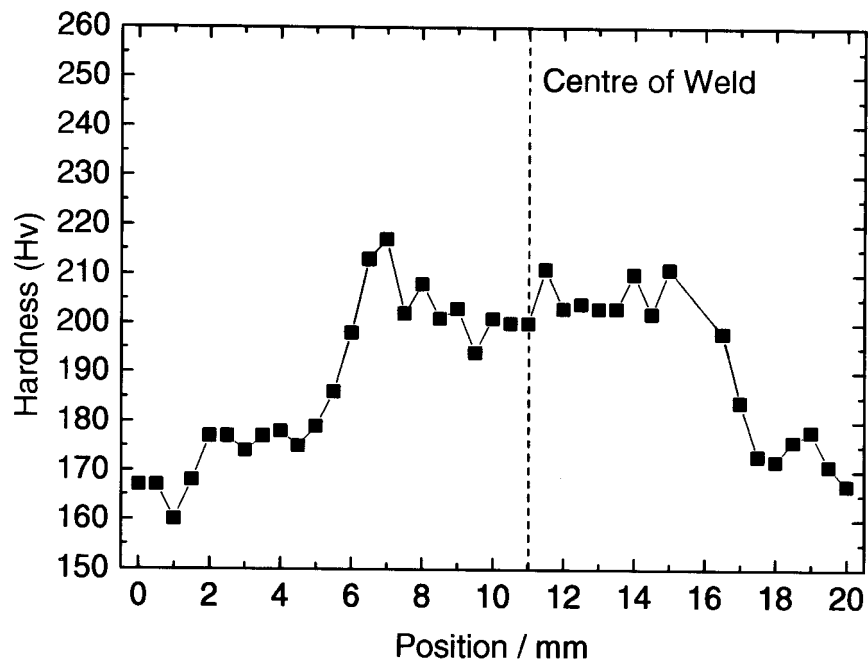


Figure 26. Microhardness profiles of weld Z along the specimen centreline showing weld to be harder than parent plate.

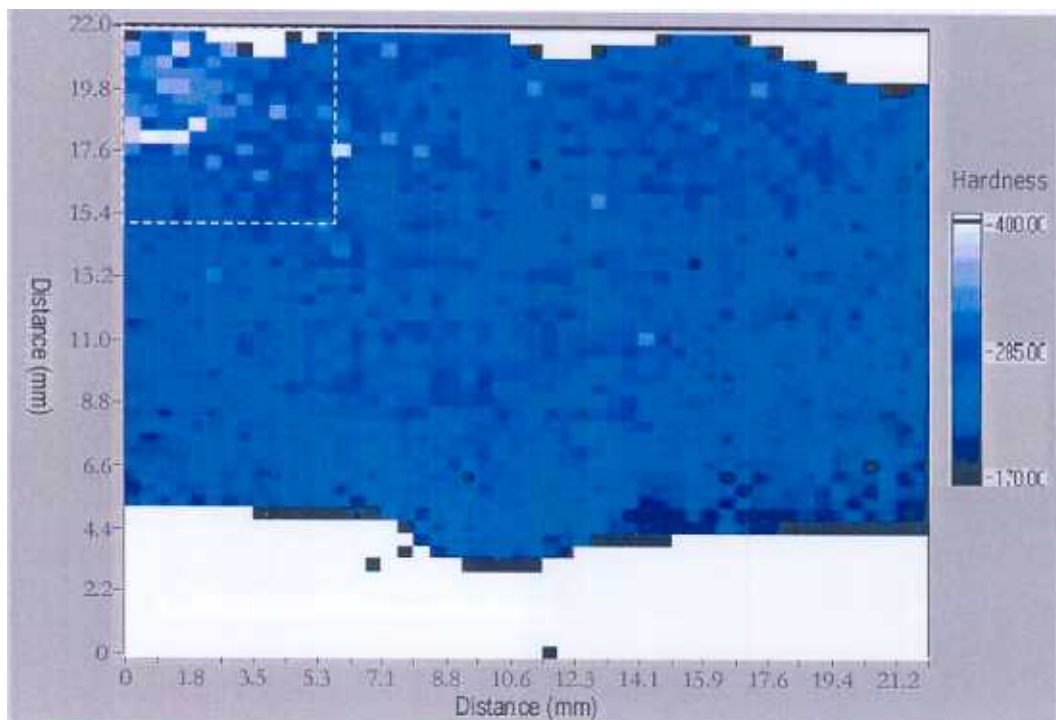


Figure 27. Microhardness scan of Weld X showing hard area near final pass. Insert area shown in figure 30.

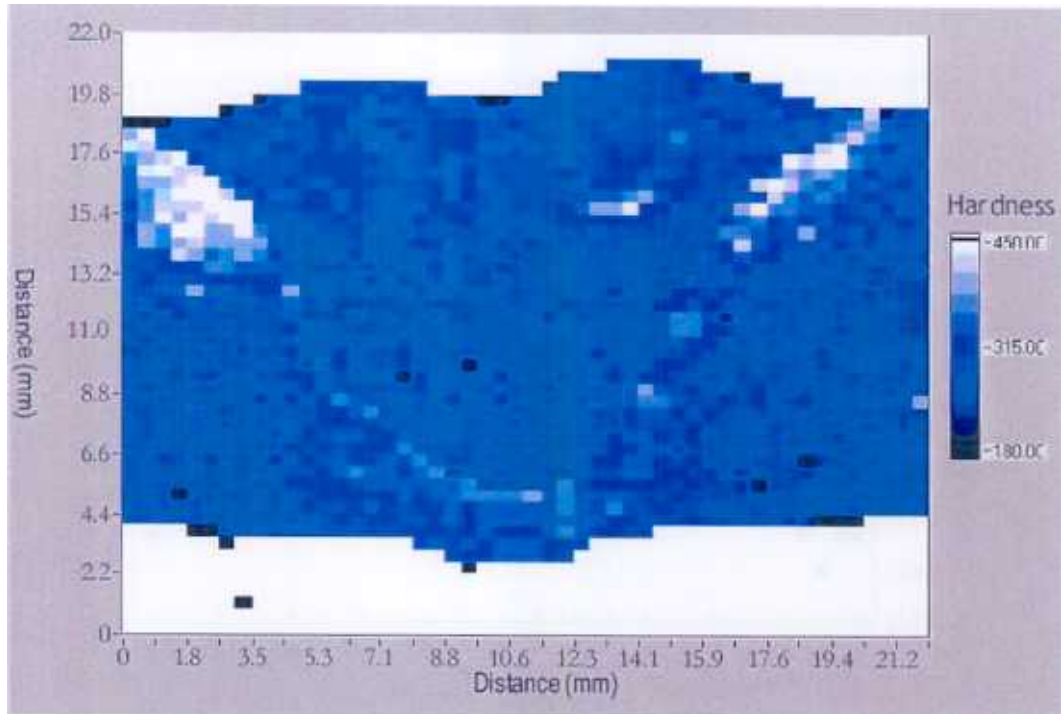


Figure 28. Microhardness scan of Weld Y showing hard peaks in the HAZ.

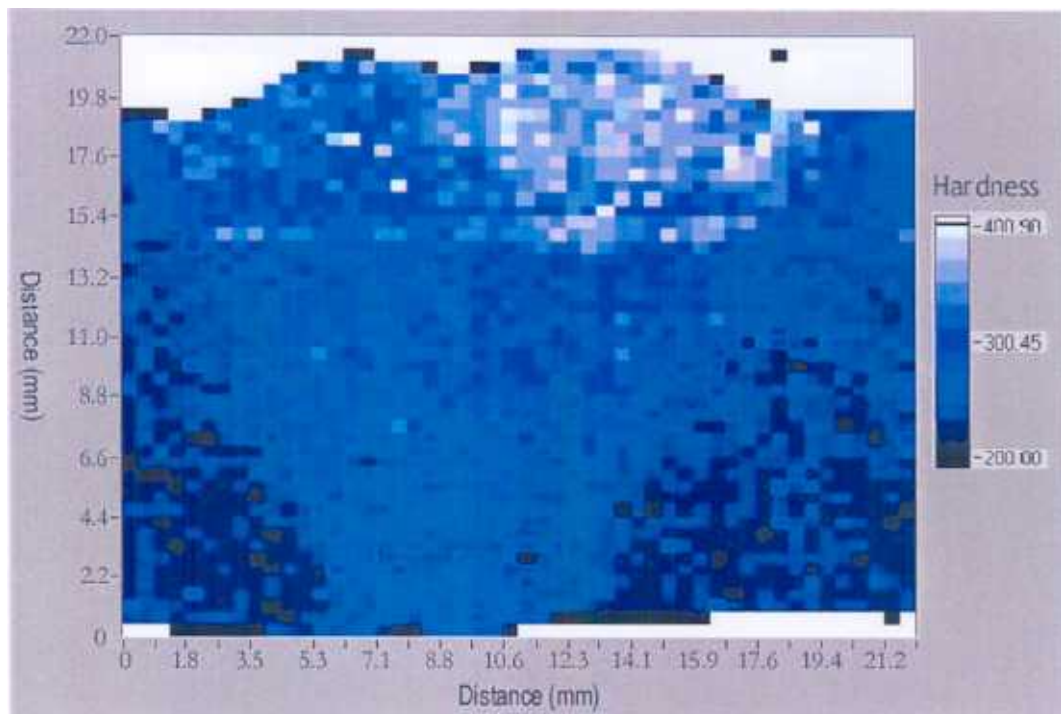


Figure 29. Microhardness scan of Weld Z showing hot spots.

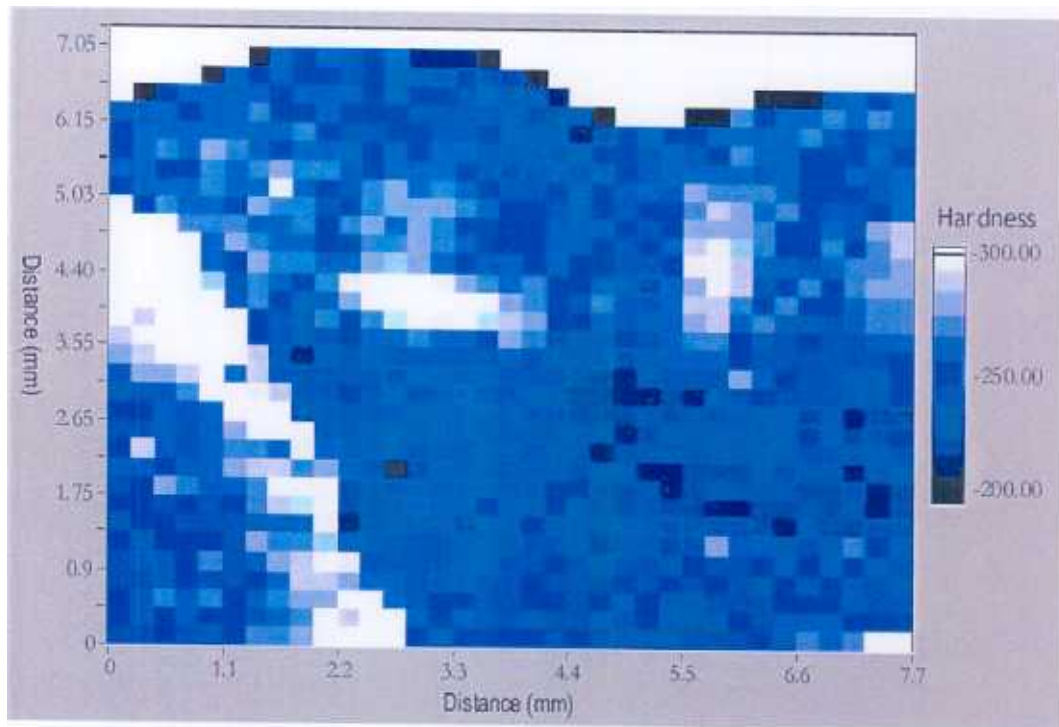


Figure 30. Microhardness scan of weld X showing HAZ near final weld pass.

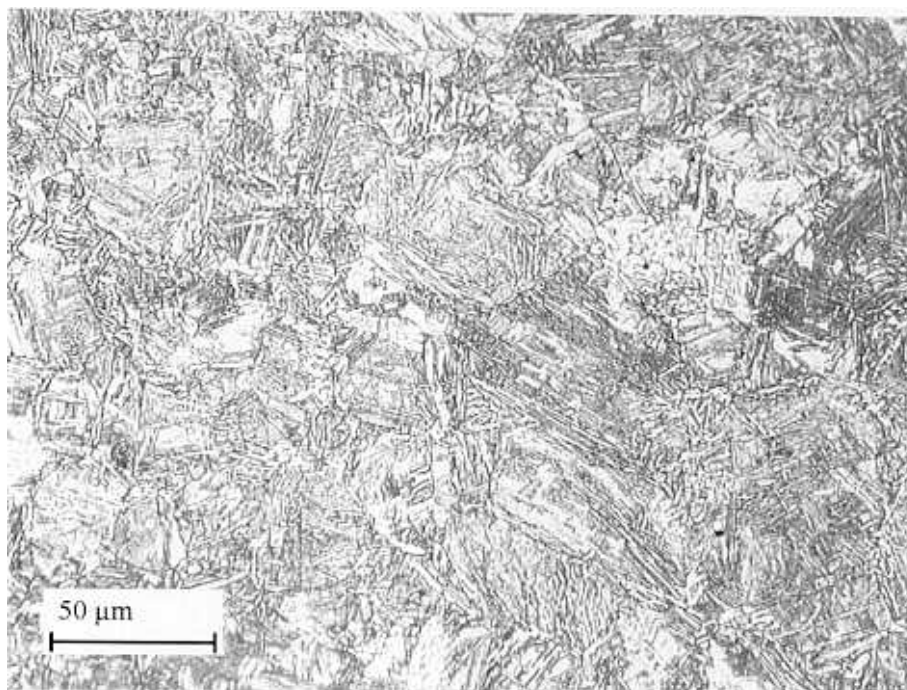


Figure 31. Micrograph of weld X showing martensitic microstructure of HAZ between weld cap and parent plate.