

**Effect of Oxygen and
Chloride on Pitting and
Stress Corrosion
Cracking of Steam
Turbine Disc Steel**

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ABSTRACT

Long term exposure tests, up to 1 year, have been carried out on a 3% NiCrMoV steam turbine disc steel in the form of cylindrical tensile test specimens self-loaded to 90% of $\sigma_{0.2}$ and exposed to three environmental conditions, viz. deaerated pure water, aerated pure water, and aerated water containing 1.5 ppm of chloride ion. The distribution of pit depths was analysed and where appropriate the length of initiated cracks. Pitting occurred in all environments but the density and depth of pits in the chloride-containing medium was markedly greater. The aerated pure water gave rise to a somewhat higher density of pits than the deaerated pure water but the maximum depths did not vary so much. Stress corrosion cracking was observed in the chloride-containing water but only above a critical pit depth of between 60 μm and 70 μm . In contrast, no cracking was observed for the aerated or deaerated pure water despite pit depths up to 200 μm .

Keywords: Steam turbine, disc steel, pitting, stress corrosion cracking

INTRODUCTION

Stress corrosion cracking of steam turbine disc steel most commonly originates from corrosion pits, except perhaps at high stresses for which the role of pits may be less significant (because there is strain localisation to disrupt the surface film and there is no need for stress concentration). When pitting is the precursor to stress corrosion cracking, the fundamental steps in the overall process of crack development include: pit initiation; pit growth; transition from pit to a crack; short crack growth; long crack growth. Whilst there are considerable data for the growth rate of long cracks in various simulated environments¹, there is comparatively little information on the growth rate of pits and the early stages of crack growth. Key external factors affecting pit initiation and growth include oxygen concentration, chloride concentration, nature and concentration of other anions, temperature and dynamic strain. Inclusion density, size and distribution would be key material parameters.

As part of a larger programme designed to provide a framework for predicting the stress corrosion cracking of turbine disc steels, long-term exposure tests have been conducted to investigate the evolution of pits and cracks on self-loaded tensile specimens under conditions nominally expected to represent service exposure in a conventional coal-fired power station. Typically, on-load, a thin liquid film will form from the steam at temperatures below about 90 °C. Recent evaluation¹ suggests that the liquid film will contain usually about 300 ppb chloride ion under normal operating conditions with well-controlled water chemistry, with perhaps up to 1.5 ppm chloride if the chloride in the inlet steam is not controlled tightly. On-load, the oxygen concentration of the liquid film will be negligible. Off-load, the liquid film on the discs will be aerated and at a temperature of 70 °C but the chloride ion concentration will be very low. During start-up, the chemistry is less well understood but a transient combination of oxygen in solution with some chloride is possible.

EXPERIMENTAL

MATERIAL

The material used in this work was a disc steel (3% NiCrMoV), cut from an ex-service steam turbine disc supplied by PowerGen. The chemical composition is listed in Table 1.

Table 1. Chemical composition of the 3% NiCrMoV disc steel (mass %)

C	Si	Mn	P	S	Cr	Mo	Ni	V	N	Fe
0.30	0.28	0.45	0.017	0.013	0.69	0.27	2.89	0.091	0.21	bal

SPECIMENS

Self-loaded cylindrical specimens of the disc steel were manufactured according to ASTM E8² with the longitudinal axis perpendicular to the radius of the turbine disc. The overall length was 100.0 mm, the shoulder diameter 16.0 mm, the gauge length 25.4 mm and the diameter 6.4 mm. The specimen and the loading frame are shown in Figure 1.



Figure 1. Photograph of the specimen and the loading frame for pitting and SCC tests.

To avoid galvanic corrosion, the loading frames and the nuts were also made of the disc steel. The specimen surface was dry ground using P2400 grinding paper (1200 SiC grit finish). The surface profile³ was measured using a laser profilometer. Measurements were made at eighteen locations on two specimens. The length of profile for each individual measurement was 2 mm. The arithmetical mean deviation of the assessed profile, R_a , was $0.50 \pm 0.28 \mu\text{m}$. The corresponding maximum height of the profile, R_z , was $3.13 \pm 0.91 \mu\text{m}$. The final grinding direction, and hence any grinding marks, were parallel to the length of the specimen.

STRESS RELIEF

To avoid an uncontrolled influence of residual stress resulting from machining or from grinding, all specimens, after final grinding, were stress-relieved in vacuum for 2 hours at 625 °C. The mechanical properties at ambient temperature and at the test temperature are listed in Table 2.

Table 2. Mechanical properties of the disc steel (mass %)

Condition	T /°C	E /GPa	$\sigma_{0.2}$ /MPa	UTS /MPa	Elongation /%
As received	23	208 ± 2	747 ± 9	882 ± 5	23 ± 1
Stress relieved	23	206 ± 1	734 ± 4	870 ± 2	20 ± 0
Stress relieved	90	210 ± 4	705 ± 4	827 ± 13	20 ± 0

It can be seen that the stress relief had no effect on the mechanical properties. Since the specimens were cut from an ex-service disc, there was a concern that the mechanical properties may vary at the different locations of the disc. Therefore, the hardness of the steel was measured on ten randomly selected specimens. There was no significant variation in the hardness measured; the average value being 28.5 (Rockwell C), with a standard deviation of

1.5. The microstructure of the materials after stress relief is shown in Figure 2. The mean grain size was $26 \pm 8 \mu\text{m}$.

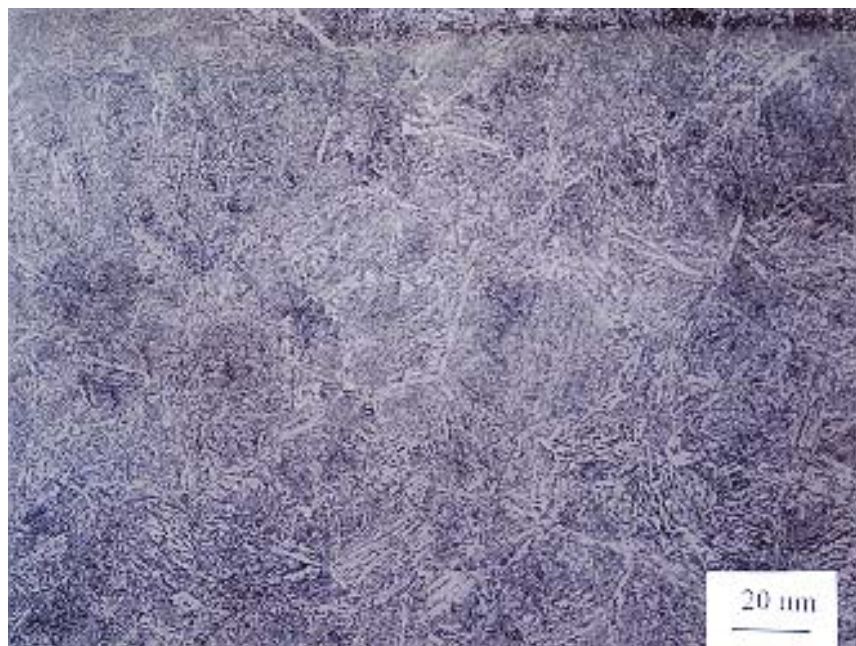


Figure 2. Microstructure of 3% NiCrMoV disc steel.

PRE-PITTING

Some of the cylindrical specimens were pre-pitted to produce single pits, or occasionally a few pits using the procedure developed at NPL⁴. The anticipation was that the single pits would grow preferentially and the cracks might initiate readily at these locations. Should this be the case then crack measurement probes could then be located accordingly in future tests. The use of pre-pits also might be expected to give insight as to the subsequent likely growth rate of pits should their initiation and early development be accelerated by a water chemistry excursion.

The pre-pitting procedure established for cylindrical tensile specimens of 3% NiCrMoV disc steel is summarised as follows. A solution of 0.02 M $\text{Na}_2\text{B}_4\text{O}_7$ + 0.01 M NaCl (pH 9.2) was used. The test temperature was $23 \pm 1^\circ\text{C}$. A test cell with a flushed-port seal adapted for cylindrical specimens was used to prevent crevice corrosion at the seals between the cell and the specimen. After the specimen was immersed in the test solution for one hour, a constant anodic current of $10 \mu\text{A}$ was applied to the exposed area of approximately 9.6 cm^2 . This tends to lead to development of a single dominant pit. To minimise corrosion on the periphery of the pit, the solution was gently stirred but the stirring was applied only after the pit had just initiated as indicated by the decrease in potential. If the applied current were increased to $20 \mu\text{A}$, more than one pit (usually less than 5) was produced on the specimen surface.

TEST ENVIRONMENT

The environments used for the pitting and SCC tests are listed in Table 3.

Table 3. The environments and test temperatures for pitting and SCC tests

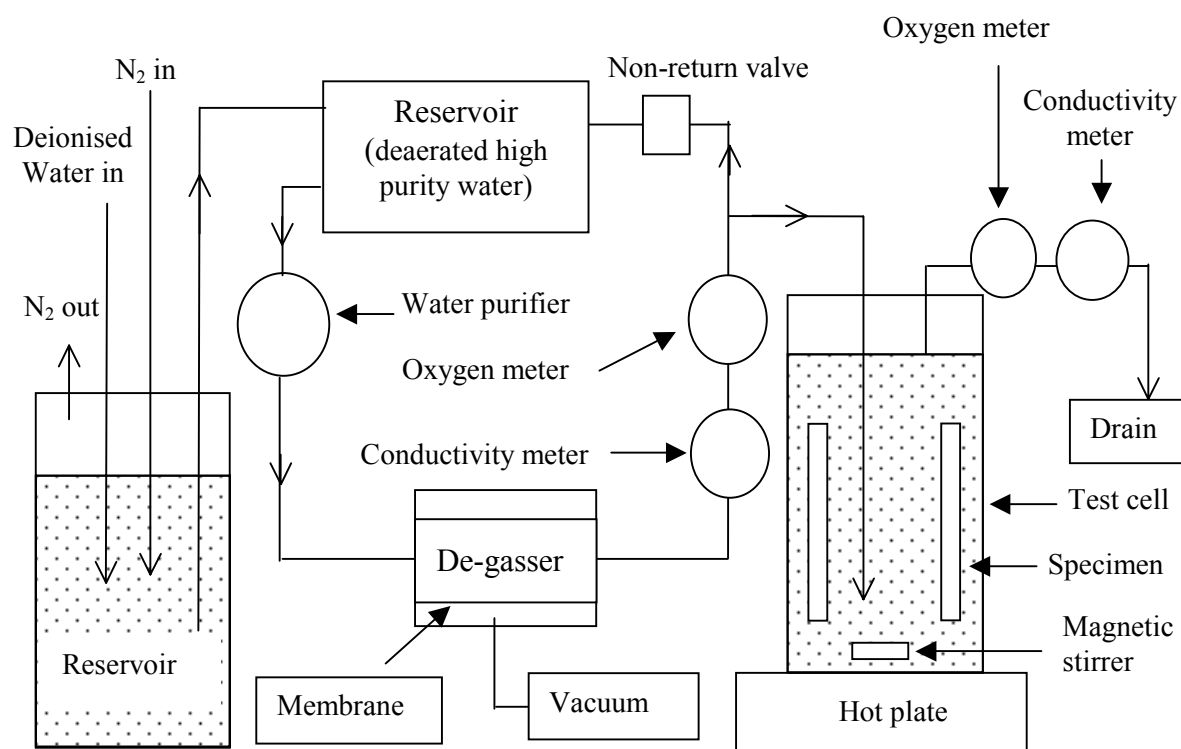
Environment	Test temperature (°C)	Simulation
Deaerated high purity water*	90	Inlet steam chemistry during on-loading operation conditions.
Aerated high purity water	90	Inlet steam chemistry during starting-up
Aerated water + 1.5 ppm Cl ⁻	90	Liquid film chemistry during major system upset.

* Prior to the detailed review and analysis of reference 1 which evaluated the chloride content of the liquid film on-load, there was an indication in several papers on stress corrosion cracking that on-load conditions were best represented by laboratory tests in high purity water. This was the basis for this environment when initiating these long-term tests. It is now realised that 300 ppb Cl⁻ is likely in the liquid film whilst on-load.

WATER SUPPLY/CIRCULATION SYSTEMS

Deaerated high purity water at 90 °C

The quality of the deaerated high purity water was maintained by using a *once-through* system, as shown schematically in Figure 3.

**Figure 3.** Schematic diagram showing the test cell and high purity water supply system

The deaeration was achieved initially by continually passing nitrogen into a 20-litre reservoir containing the feed-in deionised water. Further water purification and deaeration were achieved and maintained by continually circulating the feed-in deaerated deionised water in a loop containing a second deionising cartridge (purifier) and three de-gasser cylinders. The main component of the de-gasser is a membrane that allows only the gas (oxygen) to pass through (Figure 3). The conductivity and oxygen level of the inlet and outlet water were

monitored using on-line probes. The low conductivity and oxygen level were achieved using a once-through water flow system in which the water flows from the above circulation line to the test vessels and then to drainage. The flow rate was approximately 15 mL/min and hence the water in the 1 litre test cell was replenished about once an hour. The slow rate of input of solution into the test cell allowed the temperature to be maintained within $\pm 1^\circ \text{C}$ without the need for a pre-heater.

Aerated high purity water at 90 °C

A *once-through* system, similar to that shown in Figure 3, was also used for tests in aerated high purity water but in this case the inlet water was aerated using an air pump. The flow rate was also approximately 15 mL/min.

Aerated water containing 1.5 ppm Cl^- at 90 °C

The solution circulation loop for aerated water containing 1.5 ppm Cl^- was slightly different from that in Figure 3. In this case the aerated feed-in solution was re-circulated from a 40-litre reservoir, again at a flow rate of approximately 15 mL/min. The solution in the 40-litre reservoir was refreshed every week and the conductivity and pH were measured before and after the solution change.

CORROSION POTENTIAL MEASUREMENT

The corrosion potential was measured using an external 0.01N Ag/AgCl reference electrode designed specially with an extremely low chloride diffusion rate. The reference electrode was connected to the test cell through a glass bridge filled with the test solution. The reference electrode chamber and the test cell were separated with a glass valve, which was closed except when a measurement was taken. The solution conductivity was monitored to ensure that there was no significant chloride contamination due to the diffusion of chloride from the reference electrode chamber to the test cell during the potential measurement. For the potential measurement in deaerated high purity water, the reference electrode chamber was sealed. The reference electrode remained at ambient temperature. All potentials quoted are with reference to the saturated calomel electrode (SCE) at 25 °C.

TEST PROCEDURE

35 self-loaded cylindrical tensile specimens of disc steel were used; 16 of the specimens were smooth (without pre-pitting), 7 specimens had a single pre-pit and 12 specimens had multiple pre-pits. The depth and the surface width of the pit (the mouth of the pit was not always ideally circular) were measured using a travelling microscope (resolution 1 μm). In the latter case, the maximum width in one direction was measured and the width perpendicular to this was measured also. The average value was used later in calculating the aspect ratio. The location of the pre-pits was mapped out before testing so that the surface of the tested specimen could subsequently be examined to determine the growth characteristics of the pre-pits.

All specimens were loaded to 634.5 MPa, i.e. 90% of the $\sigma_{0.2}$ at the test temperature (90 °C). In order to prevent possible stress relaxation as the specimen and the loading frame were heated to the test temperature, all specimens were loaded at 90 ± 1 °C with the specimen and the loading frame placed in a temperature-controlled oven. The loaded specimens were then cooled down and stored in a dessicator for at least 24 hours before placing in the test cell. For each environment, the specimens were distributed in two or three different test cells of 1 litre capacity so that specimens could be removed and examined at different test intervals without affecting the remaining specimens. After placing the specimens in the cells, the test solution was introduced and the test temperature increased gradually to 90 °C in about three hours. For deaerated high purity water, the test cells were purged with nitrogen for 4 hours before the solution was introduced. The specimen details in the three environments are summarised in Table 4.

Table 4. Summary of self-loaded cylindrical tensile specimens being tested
(initial stress: 90% $\sigma_{0.2}$)

Environment	Cell no.	Specimen no.	Number of pre-pits	Maximum pre-pit depth / μm	Test duration / hours	Final stress (% $\sigma_{0.2}$)
Deaerated high purity water (90 °C)	1	3*	0	N/A	On-going	N/A
		4*	0	N/A		
		2	4	131		
		6	5	101		
	2	7*	0	N/A	8322	80
		8*	0	N/A		
		13	2	89		
		21	4	111		
Aerated high purity water (90 °C)	3	38	1	100	5107	90
		11*	0	N/A		
		12*	0	N/A		
		23	1	107		
	4	25	5	128	9138	77
		14*	0	N/A		
		16*	0	N/A		
		39	2	130		
	5	41	8	103	On-going	N/A
		17*	0	N/A		
		22*	0	N/A		
		43	4	96		
Aerated water with 1.5 ppm Cl^- (90 °C)	6	44	1	134	5107	82
		46	1	105		
		24	0	N/A		
		29	0	N/A		
	7	37	4	113	7173	79
		45	5	109		
		30*	0	N/A		
		31*	0	N/A		
	8	32*	0	N/A	9187	71
		47	2	72		
		10*	0	N/A		
		34*	0	N/A		
		1	1	102		
		33	1	98		
		48	3	97		

*Smooth specimens without pre-pitting

During the test, the water chemistry, i.e. conductivity, pH and oxygen concentration, and the corrosion potential were monitored at weekly intervals. The temperature was controlled at 90 ± 1 °C and monitored hourly.

WATER CHEMISTRY CONTROL

The conductivity, oxygen level and pH were measured throughout the tests and the results are summarised in Table 5. In the case of the re-circulated chloride solution, the pH and conductivity were measured immediately after refreshment ('new' solution) and after testing for 7 days, just prior to refreshment ('old' solution).

Table 5 indicates that the conductivity of the inlet deaerated high purity water is almost the same as the theoretical value of pure water ($0.055 \mu\text{S}/\text{cm}$)⁵. The conductivity of the outlet deaerated high purity water is much higher but this is mainly due to the fact that the conductivity of the outlet is measured at 50 °C (the conductivity of pure water at 50 °C is about $0.2 \mu\text{S}/\text{cm}$)⁵. The oxygen content in the deaerated pure water (0.7 ppb) was controlled at less than 1 ppb, except during one excursion in one corrosion cell (see below).

The measured conductivity of the aerated pure water of about $1 \mu\text{S}/\text{cm}$ reflects the effect of dissociation of dissolved carbon dioxide. There was only very modest change in the pH and conductivity of the outlet aerated high purity water and chloride-contaminated solution compared to that of the inlet, highlighting the effectiveness of the water chemistry control. It should be noted that the oxygen concentration of the aerated water and of the 1.5 ppm Cl^- solution was measured at the outlet at a lower temperature (50 °C) than the test temperature. Nevertheless, the oxygen concentration in the test cell at 90 °C can be assumed to be the equilibrium value (1.4 ppm at 90 °C)⁵, since air bubbling was continuous in the reservoir solution.

Table 5. Control of environmental conditions (all data were obtained at ambient temperature (23 ± 1 °C)), unless stated otherwise.

Environments	Test Temp. /°C	Solution into cell			Solution out of cell		
		Cond'ty / $\mu\text{S}/\text{cm}$	O ₂ / ppm	pH	Cond'ty / $\mu\text{S}/\text{cm}$	O ₂ / ppm	pH
Deaerated high purity water	90	0.056	<.0001	nm ^a	0.34 ^b	<0.001 ^b	nm ^a
Aerated high purity water	90	1.1	nm ^a	5.8	1.2	4.4 ^b	5.8
Aerated water + 1.5 ppm Cl^-	90	6.8 ^c	nm ^a	5.9 ^c	8.0 ^d	2.8 ^b	6.3 ^d

Note: a. nm: not measured; b. measured at 50 °C; c. 'new' solution; d. 'old' solution

A concern for long-term tests using glass reaction vessels is the inhibiting effect on corrosion of dissolved silica-containing species from the glass.^{6,7} To minimise this, all glassware was pre-exposed to water at 90 °C for a month, as previous work⁷ had showed that using borosilicate glass treated in this way for corrosion tests gave equivalent results to a quartz glass vessel in terms of dissolved silica and corrosion rate. The impact of dissolved silica is not a

problem for tests in deaerated and aerated water, as the water was continuously refreshed at a rate of approximately 1 L/hour. To ensure that the accumulated silica level in the test cell was not high with the re-circulated aerated 1.5 ppm Cl^- solution, the silica content in the ‘new’ solution and the “old” solution (before being refreshed after one week of testing) was analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS). The silicon content was less than 200 ppb for the fresh solution and 700 ± 200 ppb for the “old” solution. Previous work at NPL has demonstrated that silica species at these levels do not affect the corrosion rate of mild steel in distilled water⁷.

RESULTS AND DISCUSSION

EFFECT OF OXYGEN AND CHLORIDE ION ON THE CORROSION POTENTIAL

The corrosion potential of all specimens was measured. There was little variation for the same type of specimens in the same cell, with the spread being less than 0.05 V. The average potential of the specimens in each cell is shown in Figures 4 a,b,c. This corrosion potential reflects not only the specimen but also the self-loading frame, which is of the same material.

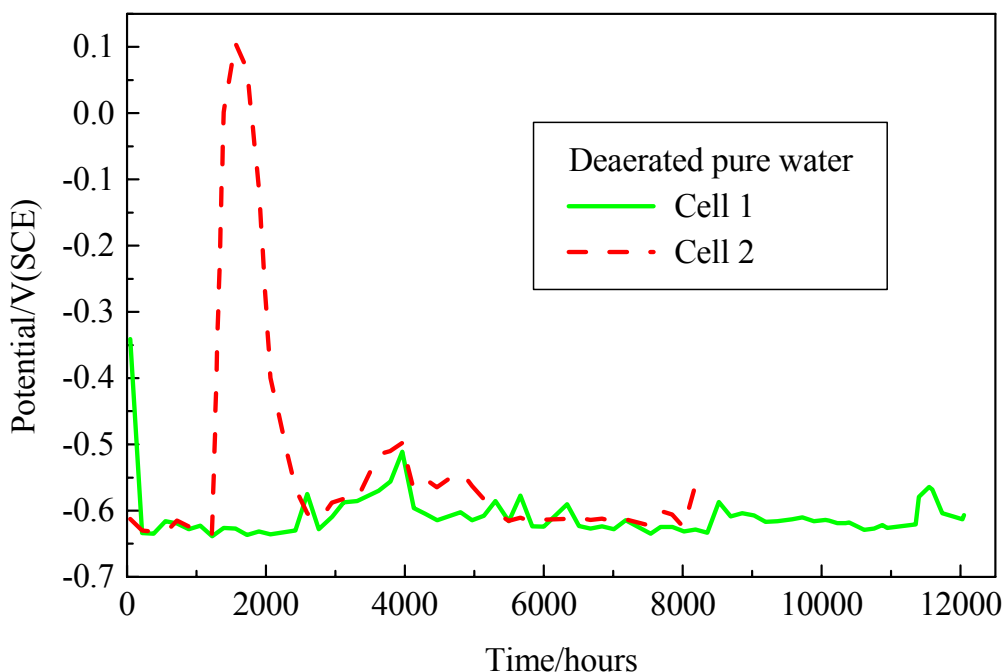
The corrosion potential of the disc steel in deaerated high purity water stabilised relatively quickly, at approximately -0.60 V (SCE). Such a potential in deaerated solution indicates film formation. In separate electrochemical measurements in deaerated 0.1M NaCl at 90°C passivity was sustained despite the high chloride, but with a corrosion potential of -0.76 V (SCE). Unfortunately, in Cell 2, an excursion in oxygen concentration occurred due to an air leak, which was not identified for about 14 days. The potential rose to a high value during this period (Figure 4a). Re-establishing the seal restored the oxygen concentration quickly to a very low level (the peak in potential) and the potential started to decrease. However, the rate of decrease of the potential was slow, taking several weeks to re-establish the surface film characteristic of the initial low potential of -0.60 V SCE. This is an important observation since it would suggest that the variation of the corrosion potential occurring during two-shifting (daily transition from aerated off-load to deaerated on-load)) may be quite complex. Whilst oxygen-free conditions in the liquid film may occur readily, the extent and rate of change of the corrosion potential is less clear. Corrosion tests to simulate this would be of value.

In aerated pure water, the potential rose in a few days to quite noble values, eventually fluctuating in the range $+0.05$ V SCE to $+0.10$ V SCE. When chloride was present in the aerated solution, the corrosion potential increased more slowly and attained a lower potential than the chloride-free environment. It was noted in a similar test that movement of the specimen caused the potential to drop instantly. This transient disturbance of the potential to a lower value suggest that the film is not a coherent passive film but at least partially comprises a loosely adherent corrosion product, providing a transport barrier to metal dissolution.

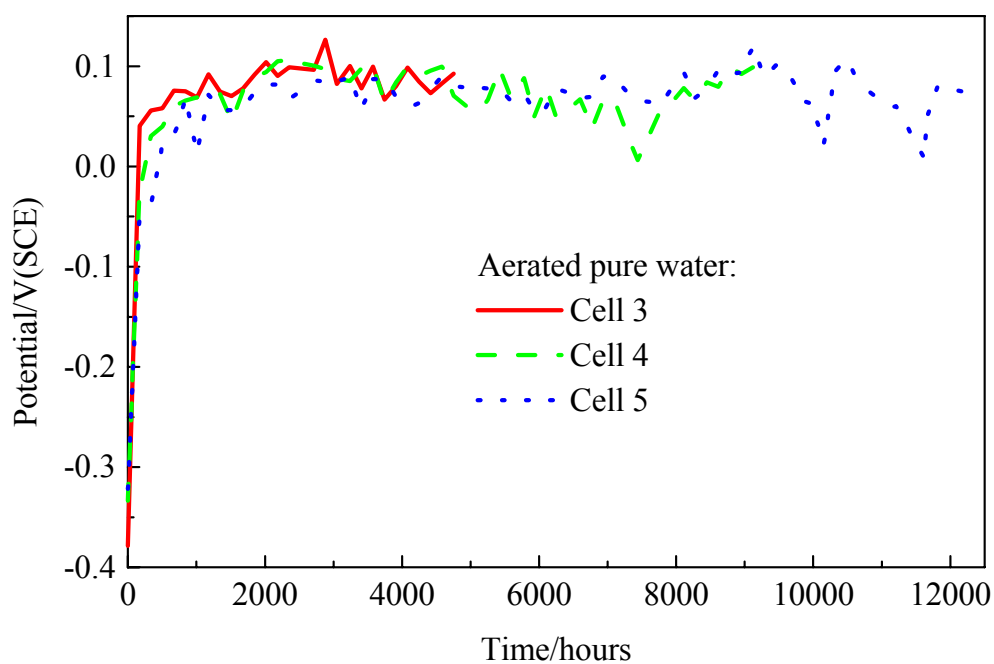
The slow gradual increase of the corrosion potential over a long period of time in the chloride solution has implications for testing, as the electrochemical driving force will be changing with time. This may have an influence on crack initiation, which is likely to be potential dependent, and possibly also on the propagation rate in the short crack regime.

As indicated below, all the specimens had pitted, in the case of the chloride-containing solution, very extensively. In that context, the concept of a free corrosion potential in low conductivity water requires some thought. In conducting solutions, the development of pits often leads to a *decrease* in potential because the pit current introduced, which would be net anodic, has to be supported by an increased cathodic current. Here, even in aerated chloride solution, the potential drifts positive with time despite the observation (see later) that the total pit area must be increasing with time. It would seem that the pit current in the aerated chloride solution is being satisfied very locally to the pit mouth so that there will be significant local gradients in potential but these may not have a significant influence on the potential when measured remotely. The increasing drift toward more noble values can only be explained readily by an increased stability of the surface film. In all cases, the potential does show fluctuations, which may reflect pitting behaviour. Indeed, it is feasible that some parts of the surface are at the high potential associated with tests in aerated chloride-free solution whilst the rest of the surface is pitted and at a low potential; thus, the measured value is some complex average.

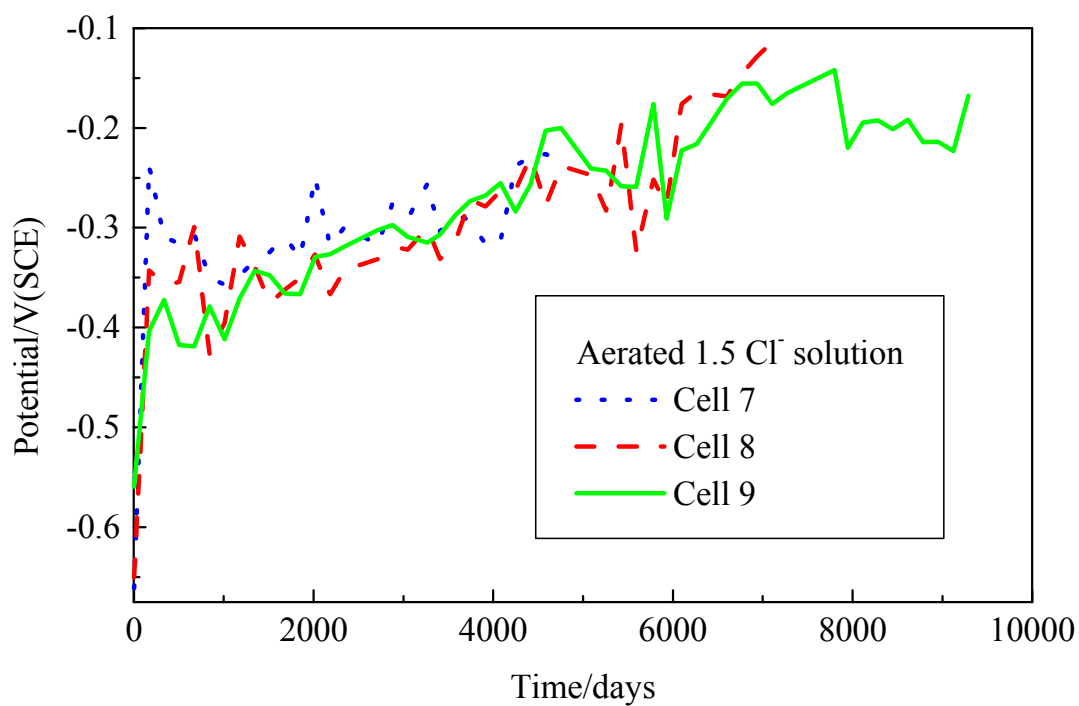
In the case of aerated pure water, the conductivity would be too low for the external surface to provide a supporting cathode once a pit of significant size is produced. In this case, the pits are simply growing at the free corrosion potential in the pit solution, with an internal cathodic reaction of water reduction or reduction of sulphide species from MnS inclusion dissolution. It would be expected that the potential in the pit would be low with very large gradients in potential at the pit mouth but not reflected in the measurement of potential remotely.



(a)



(b)



(c)

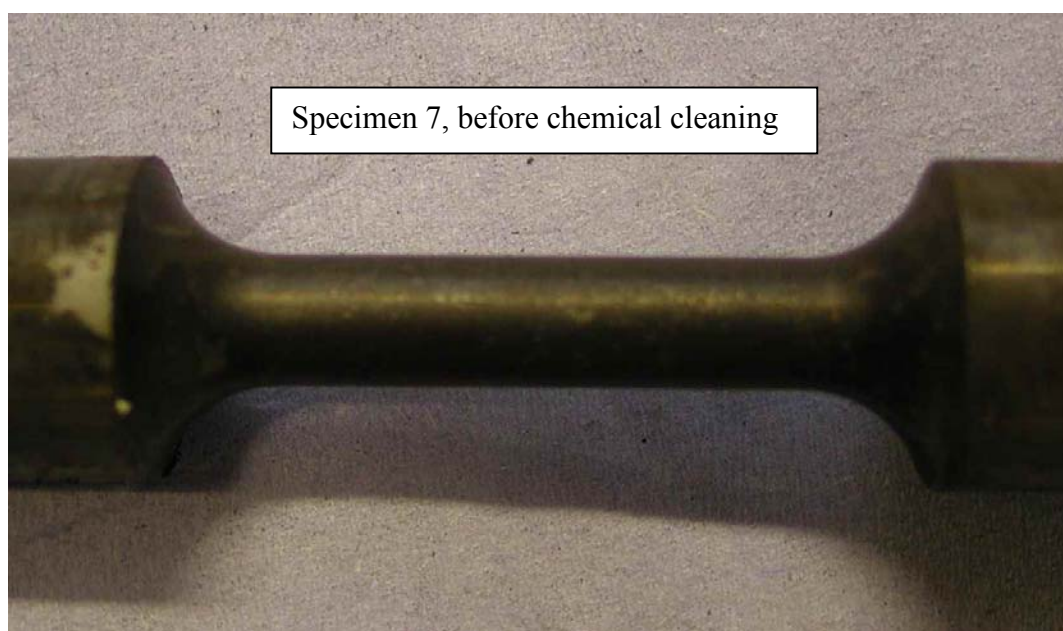
Figure 4. Effect of oxygen and chloride ion on the corrosion potential of disc steel, (a) deaerated pure water, (b) aerated pure water, and (c) aerated 1.5 ppm Cl^- solution.

STRESS REDUCTION DUE TO SPECIMEN RELAXATION

On completion of the tests, the specimens were removed from the solutions approximately 1 hour after the heater was switched off; when the solution temperature had decreased to below 50 °C. The specimens with their loading frames were washed immediately with high purity water, ethanol and acetone. Unloading was then undertaken on a mechanical test machine. The reduced stress, resulting from specimen relaxation, was estimated from the value of the load at which the nut of the loading frame could be readily unscrewed. The estimated final stress of the self-loaded tensile specimens is listed in Table 4, from which it can be observed that the final applied stress had decreased somewhat with test duration, most notably in the aerated 1.5 ppm Cl⁻ solution. In this case, the formation of multiple pits and cracks (see below) would be a factor as the change in average cross-section was only 1%. However, the relaxation in the chloride-free environments, with much reduced pitting and no cracking, suggests that creep must be a factor.

VISUAL EXAMINATION OF THE SPECIMEN SURFACE

After unloading the specimen surface was carefully examined and photographed before and after chemical cleaning. The latter was carried out using “Super Clarke’s” solution (10g/l of 1,3-Di-n-butyl-2-thiourea (DBT) in 37.5% HCl). It had been established previously that this cleaning solution has negligible effect on the general corrosion of the bare disc steel and that there was no measurable change in the size of pits during the cleaning processes (the measurement resolution of the pit dimension was 1 µm). Figures 5 – 7 show the typical surface appearance of the self-loaded cylindrical tensile specimens tested in respectively deaerated pure water, aerated pure water, and aerated 1.5 ppm solution at 90 °C. The higher magnification for the specimen removed from the chloride exposure allows ready observation of the cracks on this specimen. No cracks were detectable, at any magnification, on the specimens tested without chloride.



(a)

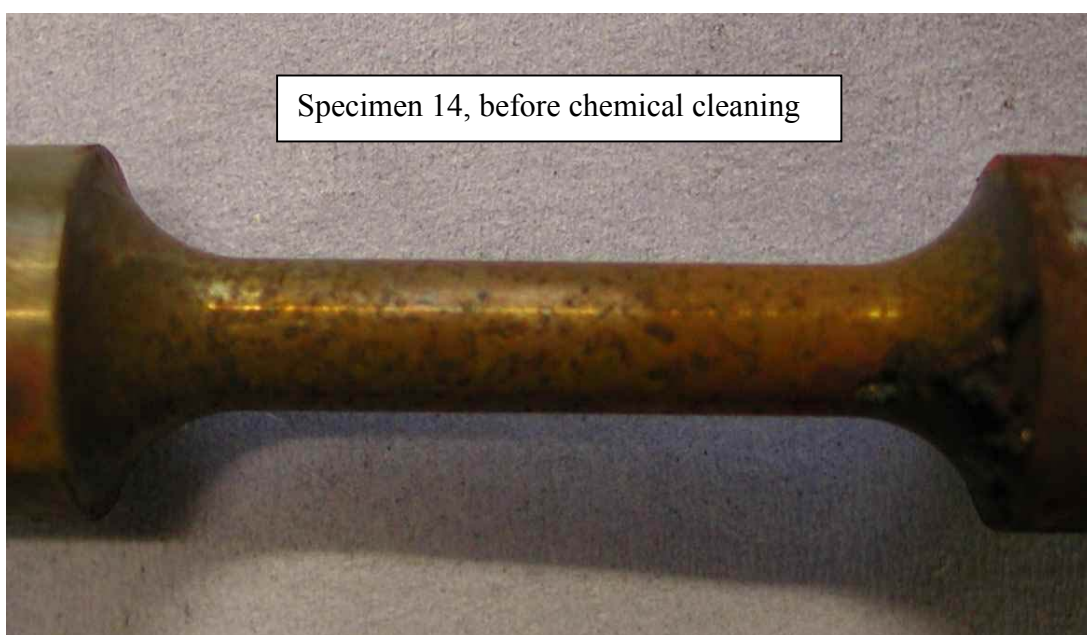


(b)

Figure 5. Surface appearance of a self-loaded cylindrical tensile specimen tested in deaerated pure water at 90 °C for 8322 hours.

In the deaerated pure water at 90 °C, a shiny black film had formed on the specimen surface and pits were readily visible after chemical cleaning. Although this specimen (Figure 5) had experienced an oxygen excursion (Figure 4a), removal of a compact tension specimen from parallel testing under these same conditions indicated a similar appearance with pitting.

In aerated pure water at 90 °C a brownish film was apparent on the surface and pits were readily visible. Also, there was also evidence of crevice attack in the contact area between the specimen and the loading frame.



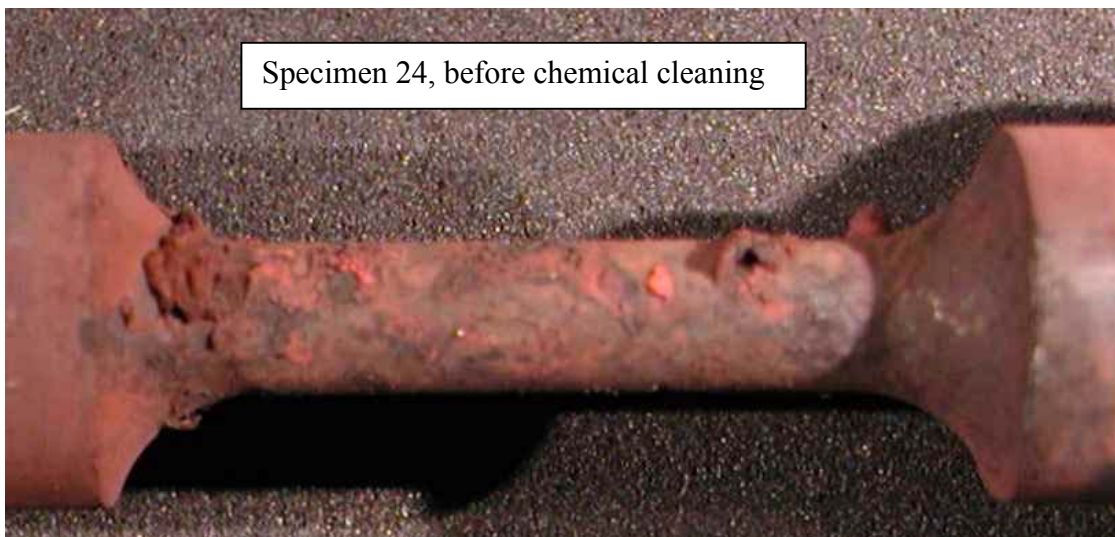
(a)



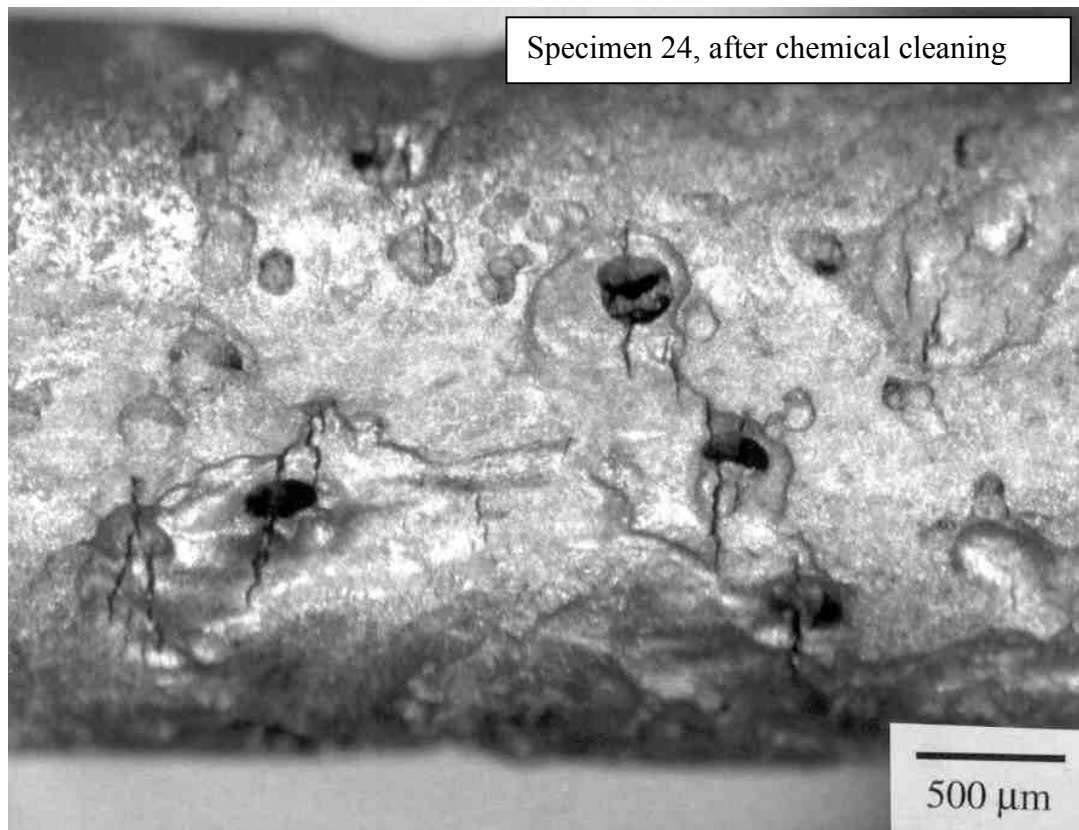
(b)

Figure 6. Surface appearance of a self-loaded cylindrical tensile specimen tested in aerated pure water at 90 °C for 9138 hours.

In aerated 1.5 ppm Cl^- solution at 90 °C, severe general corrosion was evident with a thick reddish-brown corrosion product covering the surface. Large pits and multiple cracks could be discerned. In some cases, the tips of cracks from adjacent pits had turned towards each other and many cracks had coalesced.



(a)



(b)

Figure 7. Surface appearance of a self-loaded cylindrical tensile specimen tested in aerated 1.5 ppm Cl^- solution at 90 °C for 5107 hours.

DISTRIBUTION OF THE SURFACE WIDTHS AND DEPTHS OF PITS

The surface width (w) and depth of pits (a) in the gauge section were measured using the same measurement procedure for pre-pits, as described earlier. Only pits of depths greater than 25 μm were measured. Since the primary interest was in the evolution of pits to cracks, small pits depths were less relevant and their measurement added to the measurement burden unnecessarily. The widths and depths of pits were only measured on selected specimens.

The results for the three environmental exposure conditions in terms of the variation of aspect ratio with pit depth are shown in Figures 8-10.

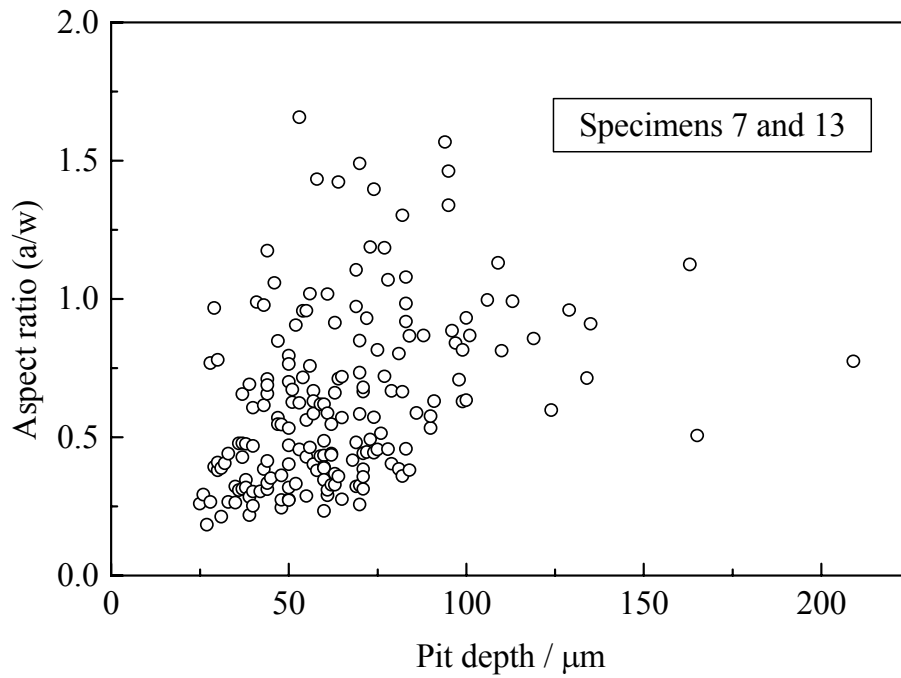


Figure 8. Aspect ratio of pits as a function of pit depth in the self-loaded specimens in deaerated pure water at 90 °C for 8322 hours (no cracks initiated from pits).

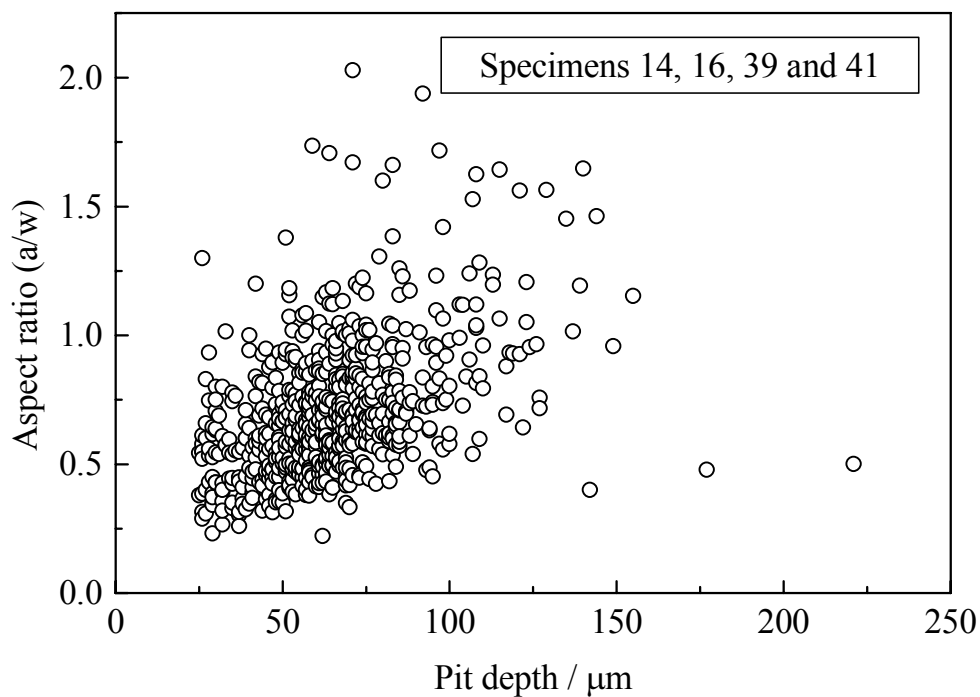


Figure 9. Aspect ratio of pits as a function of pit depth in the self-loaded specimens tested in aerated pure water at 90 °C for 9138 hours (no cracks initiated from pits).

For comparison of the three exposure conditions, the results for the longest duration only are shown here. Also, because of the very high density of pits in the chloride-containing solution, the results for only one specimen are shown in this case. Nevertheless, the data for other

specimens are included in the Appendix, and these confirm the representative nature of this particular dataset.

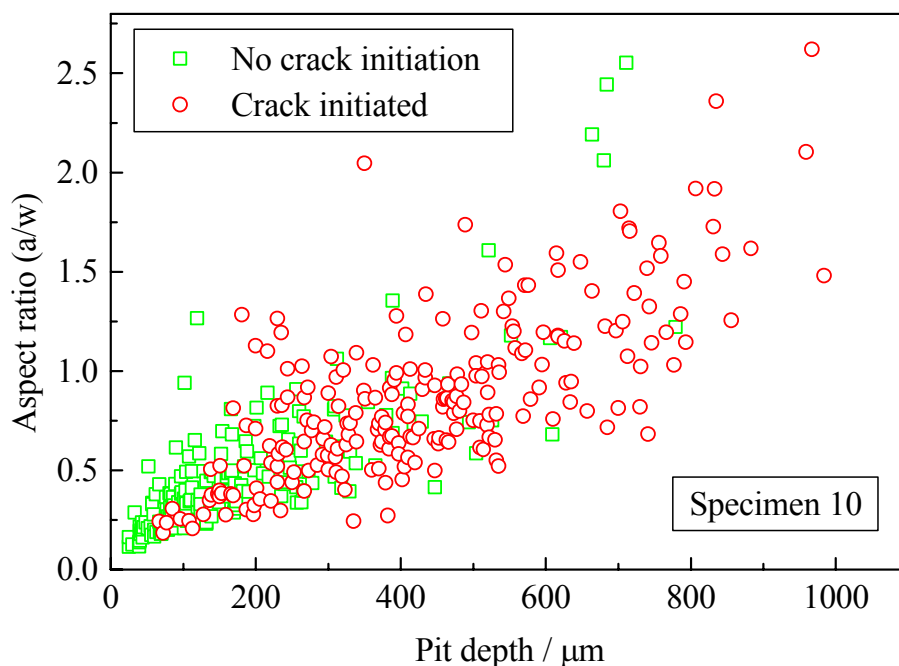


Figure 10. Aspect ratio of pits as a function of pit depth on the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 9187 hours.

In deaerated pure water the exposure period was 8322 h rather than about 9000 h because of a system failure near the end of the test, so comparison with the other test conditions is not ideal. Also, the test cell was aerated for a period. Having said that, the summary of key results in Table 6 (see later) for this test condition compares reasonably well with results from analysis of pits in a separate test on a CT specimen, suggesting that the transient aeration had only a modest effect if at all.

The comparison of the variation of the aspect ratio (note a value of 0.5 would be expected for a hemispherical pit) with crack depth shows that for the chloride-free environments, the aspect ratio increases with pit depth much more significantly than for the chloride-containing pits. In the latter case, it is only when the pit depth exceeds the range 200-250 μm that the mean aspect ratio exceeds 0.5. In chloride-free environments, the depth is of the order of 75 μm. In other words, the pits tend to be “sharper” for the same depth, extending in depth relative to opening much more than for the chloride-containing environment. The broadening of the mouth of the chloride-containing pits may reflect the greater impact of the cathodic reaction externally and the more noble potential near the mouth, relative to the pit base. This would enable greater lateral dissolution because of the higher potential and perhaps also due to the more acidic pit environment (albeit expected to be between pH 5 and 6) than for either the aerated or deaerated chloride-free environment, for which pH values of order 7 or slightly more alkaline in the pit would be expected⁸.

There is still a basic question as to why a pit once started in the chloride-free water should grow faster at the base relative to the walls. If it were simply a case of corrosion of a film-free surface in a neutral to alkaline local environment with internal water reduction, in other words

simply corroding at a low rate in a film-free condition with no “connection” to the outside conditions, it would be hard to explain. However, one possible factor is dissolution of MnS inclusions. In that context, it may be envisaged that the tighter pit is favoured because it enhances retention of the local chemistry associated with this inclusion dissolution.

PIT DENSITY-DEPTH RELATIONSHIP

The relationship between of the pit density and depth for the three exposure conditions at the longest duration is shown in Figures 11-14.

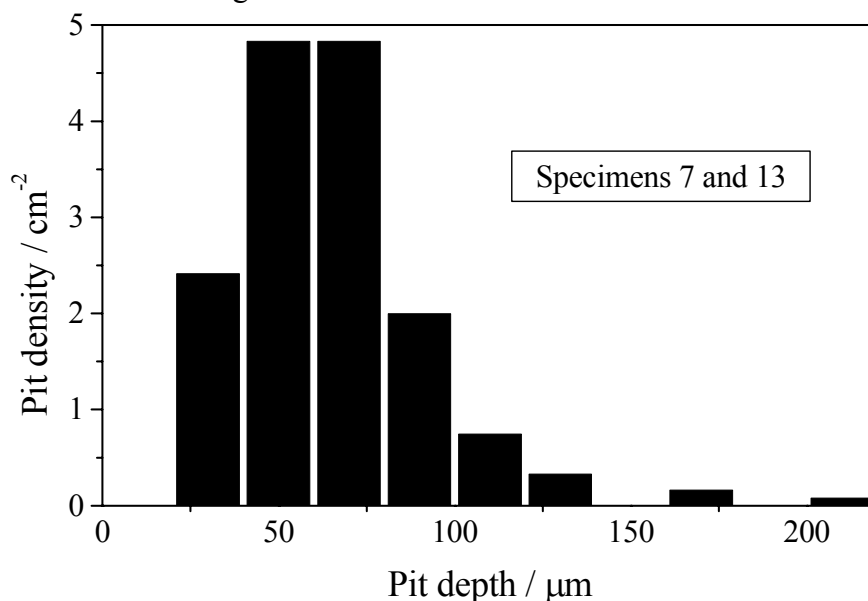


Figure 11. Distribution of pit depths on the self-loaded specimens tested in deaerated pure water at 90 °C for 8322 hours.

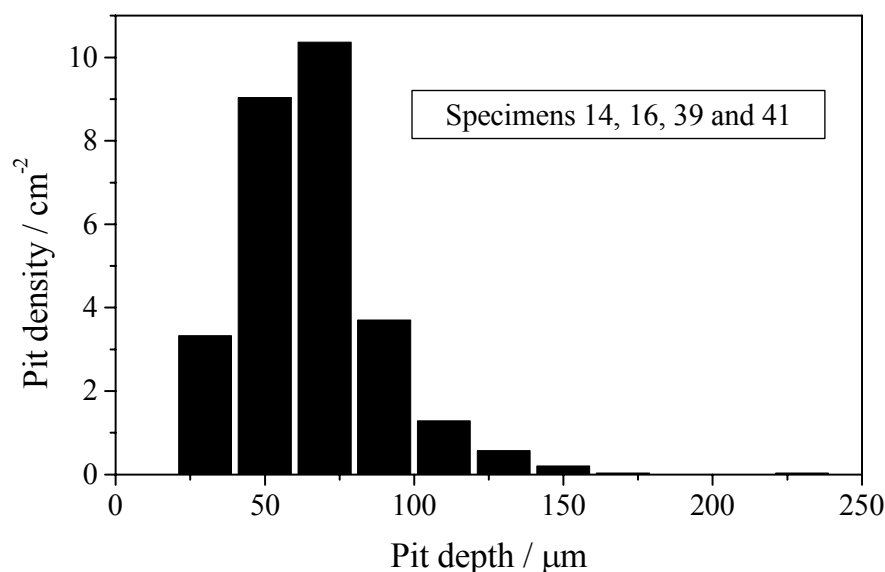


Figure 12. Distribution of pit depths on the self-loaded specimens tested in aerated pure water at 90 °C for 9138 hours.

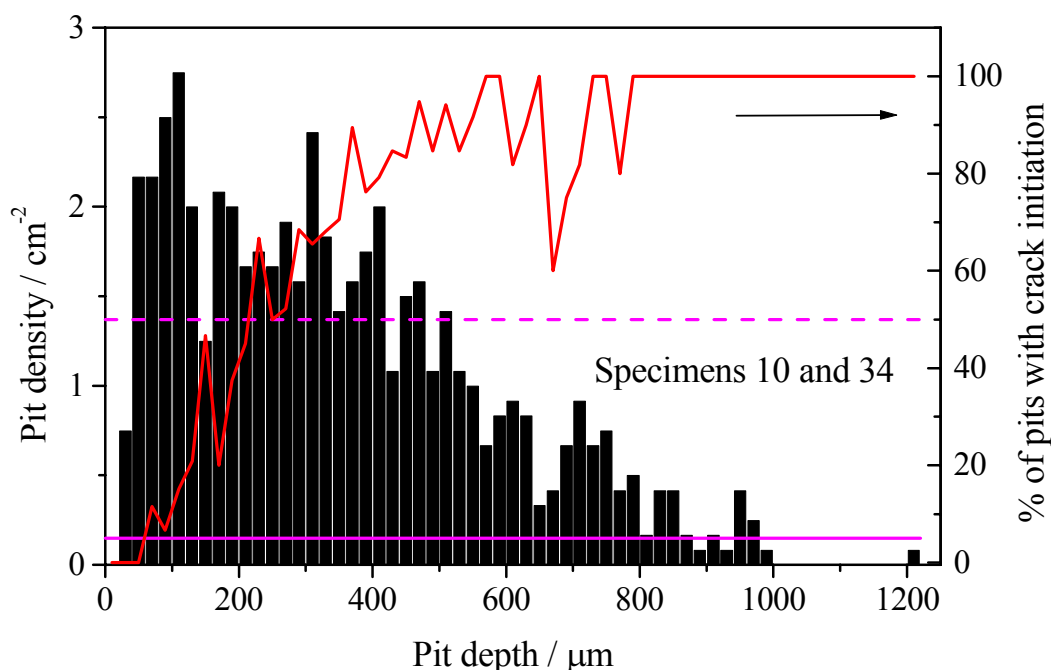


Figure 13. Distribution of pit depths in the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 9187 hours.

The density of pits clearly increases in the order: deaerated, aerated pure water and aerated 1.5 ppm water with the density very high indeed in the last case and with depths up to about 1 mm. In contrast, maximum pit depths for the aerated and deaerated solutions were about 200 μm .

The observation of deep pits in chloride-free water is not confined to this study. Similar observations have been made by Gabetta and Caretta⁹. However, David et al¹⁰ and Speidel et al¹¹⁻¹³ reported no pitting in high purity water, aerated or deaerated. The temperatures were similar to the present test. Also, a 25-year old conventionally smelted steel was used by David et al, suggesting that steel composition does not provide a simple resolution of these different results.

PIT GROWTH RATES

The key parameters from all the test specimens have been analysed and are summarised in Tables 6-8. There is one particular “anomaly” with respect to the results in aerated pure water insofar (Table 7) as the pits depths at 5107 hours were consistently greater than for results at 9138. The test conditions were well controlled throughout and the potentials were similar. There is no explanation for this unusual result.

The evolution of pit depth (a) with time is often described by a relationship of the form:

$$a = \alpha t^\beta. \quad (1)$$

where α and β are system specific constants. The measurement intervals in this study make analysis meaningful only for the 1.5 ppm solution and even here the absence of data at short times is limiting. Nevertheless, using this relationship and fitting to the data for the average of the 10 deepest pits for each specimen gives values of $\beta = 0.376$ and $\alpha = 1.56 \times 10^{-6}$ with t expressed in seconds and a in m.

Table 6. Statistics of pits in disc steels in deaerated pure water at 90 °C (the specimens were loaded nominally to 90% $\sigma_{0.2}$).

Test time /hour	Specimen No	Pit density ^a /cm ⁻²	Maximum pit depth / μ m	Average depth of 10 deepest pits / μ m	Average pit growth rate ^b /10 ⁻¹² m/s
8322	7	14.2	163	121	4.04
	8	**	**	**	**
	13	16.7	209	139	4.64
	21	**	**	**	**
	38	**	**	**	**
	Average	15.5	186	130	4.34
9979	3CT***	16.5	211	172	4.78
*	2, 3, 4, 6	*	*	*	*

a. Specimen surface area: 6.0 cm²

b. Average pit growth rate of 10 deepest pits assuming that the pit initiation time is negligible

* Tests are on-going, ** Not measured, *** Compact tension specimen in parallel test set-up

Table 7. Statistics of pits in disc steels in aerated pure water at 90 °C (The specimens were loaded nominally to 90% of YS).

Test time /hours	Specimen No	Pit density ^a /cm ⁻²	Maximum pit depth / μ m	Average depth of 10 deepest pits / μ m	Average pit growth rate ^b /10 ⁻¹² m/s
5107	11	12.2	194	157	8.54
	12	**	**	**	**
	23	5.2	261	180	9.79
	25	2.3	209	155	8.58
	Average	6.6	221	164	8.97
9138	14	35.3	117	105	3.19
	16	13.2	155	135	4.10
	39	32.7	177	123	3.74
	41	33.3	221	133	4.04
	Average	28.6	168	124	3.77
*	17, 22, 43, 44, 46	*	*	*	*

a. Specimen surface area: 6.0 cm²

b. Average pit growth rate of 10 deepest pits assuming that the pit initiation time is negligible

* Tests are on-going, ** Not measured

Table 8. Statistics of pits in disc steels in aerated 1.5 ppm Cl⁻ at 90 °C (The specimens were loaded nominally to 90% of YS).

Test time /hour	Specimen No	Pit density ^a /cm ⁻²	Maximum pit depth /μm	Average depth of 10 deepest pits /μm	Average pit growth rate ^b /10 ⁻¹¹ m/s	Pit growth rate ^c /10 ⁻¹¹ m/s
5107	24	47.1	825	668	3.63	
	29	46.7	999	814	4.43	
	37	54.0	792	744	4.05	
	45	65.4	829	761	4.14	
	Average	53.3	861	747	4.06	1.5
7173	30	42.8	925	813	3.15	
	31	*	*	*	*	
	32	42.5	939	813	3.15	
	47	*	*	*	*	
	Average	42.7	932	813	3.15	1.2
9187	1	*	*	*	*	
	10	69.3	1024	902	2.73	
	33	*	*	*	*	
	34	43.5	1209	970	2.93	
	48	*	*	*	*	
	Average	56.4	1117	936	2.83	1.0

a Specimen surface area: 6.0 cm²

b Average pit growth rate of 10 deepest pits assuming that the pit initiation time is negligible and dividing by the full exposure time.

c Pit growth rate calculated using Equation 1 and based on average depth of 10 deepest pits for each specimen.

** not measured*

With these parameters, pit growth rates were then estimated at each of the exposure times for the 1.5 ppm chloride solution and are included in Table 8. The values of course are smaller than the average values, which is to be expected as the latter incorporates the faster growth rates at shorter times. The average values were calculated only for comparison with Tables 6 and 7 for which data were limited. On this basis, the chloride-containing environment generated pit growth rates about 4-6 times faster. Comparison of the growth rates of the aerated and deaerated solutions is compromised to an extent by the variability in the results for the aerated case. Using only the long-term data for both cases, the difference in pit growth rate is modest. This is not unexpected. The presence of oxygen in pure water might be expected to enhance the initiation of pits, and thus should give a higher pit density, but because of the very large potential drop in such high purity water, the growth rate would proceed independent of conditions of the bulk and should be comparable to that for the deaerated solution.

EXTENSION OF PRE-PITS

Since multiple pits developed readily from the smooth specimens in all environments pre-pitting to achieve reasonable depths turned out not to be a necessary requirement. Nevertheless, the final depth of the pits that had evolved from the pre-pits was measured, and the maximum depths are shown in Table 9. Comparing Table 9 with Tables 6-8, it would appear that the growth rate of the pre-pits is lower than those of the pits developed from a smooth surface, especially in aerated 1.5 ppm Cl^- solution. However, the comparison is valid only with respect to the same range of pit depths (i.e. between the initial pre-pit depth and the final depth from the pre-pit), as the pit growth rate is known to decrease with time. In that context, the difference in growth rate for the deaerated solution does not seem significant. Also, when account is taken for the distribution of pit depths in Figure 13, rather than considering just the maximum value, it really is not possible to suggest any special features associated with the pre-pit.

In pursuing this pre-pitting approach, the hope was that the pre-pits would grow preferentially and cracks might initiate more readily at these locations because of the greater depth. Crack measurement probes could then be located accordingly in future tests. However, not only did the pre-pits have a modest growth rate in aerated 1.5 ppm Cl^- solutions but cracks did not develop from these sites. For this environment, about 40% of pits had cracks at the depth corresponding to the extended pre-pit depths. It is feasible that with less than one or two pre-pits on these specimens, the statistics were just not favourable enough.

Table 9. Depths of pre-pits on the disc steel before and after testing at 90 °C (initial stress: 90% $\sigma_{0.2}$).

Environment	Test duration / hours	Specimen no.	Pit depth / μm		Pit growth rate / 10^{-12}m/s
			Before	After	
Deaerated high purity water	8322	13	89	182	3.14
Aerated high purity water	9138	41	103	140	1.12
Aerated water with 1.5 ppm Cl^-	7173	47	72	133	2.36
	9187	1	102	193	2.75

PIT-TO-CRACK TRANSITION

The generally accepted phenomenological criteria for a pit to crack transition are that the threshold K value has to be exceeded (the pit has to exceed a minimum depth) and the growth rate of the crack must exceed that of the pit¹⁴.

No cracks were observed at all in the tests without chloride. This may reflect a much lower potential at the pit base and dissolution rate because of the potential drop in the solution or a direct role for chloride in the crack development process. For the tests with chloride, Figures 10 and 13 are representative examples (other data are in the Appendix) indicating the pit depth at which a crack had initiated. Analysis of the data from all the tests is summarised in Table 10.

Table 10. Statistics of cracks and pits (from which cracks initiated) in disc steels in aerated 1.5 ppm Cl⁻ at 90 °C (the specimens were loaded to 90% of YS).

Test time /hour	Specimen No	Crack density ^a /cm ⁻²	Average crack length /μm	Average surface crack growth rate/ 10 ⁻¹⁰ m s ⁻¹	Maximum crack length /μm	Maximum surface crack growth rate/ 10 ⁻¹⁰ m s ⁻¹
5107	24	11.5	1157		2397	
	29	21.3	1085		2230	
	37	28.7	985		2591	
	45	21.0	1075		3421	
	Average	20.6	1076	0.6	2660	1.4
7173	30	27.7	>1479	>0.5	>3662	>1.4
	31					
	32	22.7	>1792	>0.7	>4528	>1.7
	47					
	Average	25.2				
9187	1					
	10	38.3	>1684	>0.5	>4362	>1.3
	33					
	34	28.2	>2110	>0.6	>5240	>1.6
	48					
	Average	33.3				

a. Specimen surface area: 6.0 cm²

In the case of very long cracks the curvature of the specimen made reliable estimation of the crack length problematic using the normal optical methods of focusing on the specimen and adjusting the position laterally to measure the length – some controlled angular rotation will have to be adopted. Thus, in Table 10, the true value will be greater than the quoted value.

As the pit depth increases, eventually almost every pit has an associated crack. However, there is clearly a threshold pit depth for the transition to a crack for these stress conditions. The values (smallest for all the specimens at the test duration) are summarised in Table 11 and are reasonably consistent for the different exposure periods, with a depth of about 60-70 μm.

The corresponding threshold K value, treating the pit like a crack of equivalent depth¹⁵ but ignoring short crack effects is about 6 MPa m^{1/2}, close to values estimated by Lyle¹⁶. However, this assumes that the crack initiates at the base of the pit and this has not yet been determined. Indeed, conceivably, initiation may be close to the pit mouth. At this depth, the mouth opening would be about 250 μm. In calculating the K value, the nominal stress was used. The relaxation observed (Table 4) means that this may overestimate the value by as much as 20%.

Table 11. The critical depth of pits from which cracks initiate on the disc steel specimens loaded nominally to 90% $\sigma_{0.2}$ and tested in aerated 1.5 ppm Cl^- solution at 90 °C and the corresponding estimated stress intensity factor, K.

Test duration /hours	Percentages of pits from which cracks initiate (%)							
	0		5		50		95	
	Depth / μm	K / $\text{MPa m}^{1/2}$	Depth / μm	K / $\text{MPa m}^{1/2}$	Depth / μm	K / $\text{MPa m}^{1/2}$	Depth / μm	K / $\text{MPa m}^{1/2}$
5107	60	5.8	90	7.2	220	11.2	570	18.0
7173	70	6.3	80	6.7	220	11.2	790	21.2
9187	60	5.8	70	6.3	220	11.2	790	21.2

The second criterion for a pit to crack transition also needs to be fulfilled, namely, that the growth rate of the crack should be greater than that of the pit. Evaluation of the distribution of crack depths at different times is required before a meaningful comparison can be made and this is being undertaken. The crack growth rate would have to be in well in excess of 10^{-11} m/s simply on the basis of the estimated pit growth rates for deep pits. Using Equation 1 to calculate the growth rate for a shallow pit of 60 μm is far from reliable but perhaps useful in providing a ballpark figure. On this basis, the crack growth rate would have to exceed 1.4×10^{-9} m/s (the estimated exposure time corresponding to 60 μm is 16423 s, i.e. 4.6 hours). Whilst this may overestimate it, it is likely that the crack growth rate has to be relatively fast compared with long crack growth rates¹, which are between 1×10^{-11} m/s and 5×10^{-11} m/s.

The surface growth rates, Table 9, are relatively very fast, of order of 1×10^{-10} m s⁻¹ despite assuming the crack initiated at time zero rather than when the pit attained a threshold depth of 60-70 μm . Of course, from a mechanics viewpoint, the crack depth is of most significance.

Further work is ongoing to measure the crack depths at different exposure times. The possibility that a crack could be growing near the mouth of a pit whilst the pit is growing in depth is an intriguing possibility and evidence for this will be sought.

It should be recognised that this combination of aeration with 1.5 ppm chloride is an extreme condition which should it occur in service would be for a transient period only.

MNS INCLUSIONS

It is evident that anionic species in solution are not required to cause pitting attack in this steel. By implication, inclusions must be involved of which the most “aggressive” and plentiful is MnS. The MnS inclusion distribution in the disc steel was analysed by sectioning a cylindrical specimen longitudinally. This was then mounted in phenolic resin such that the curved surface of the gauge length was visible. The surface was then ground and polished such that a plane surface was obtained in which the MnS inclusions could be clearly seen using optical microscopy.

For analysis of the MnS size and size distribution, 56 digital images were obtained using a camera attached to an optical microscope. Each image covered an area of 0.021 mm^2 . The area of each inclusion was measured and the diameter of the inclusion was estimated by fitting it to a circle (the diameter of the equivalent circle). The size distribution obtained from these images is shown in Figure 15 and Table 12. The density for this rather old steel is very high indeed and would provide plentiful sites for initiation of pitting and indeed for perhaps continuing to influence the propagation rate and shape for the reasons articulated above.

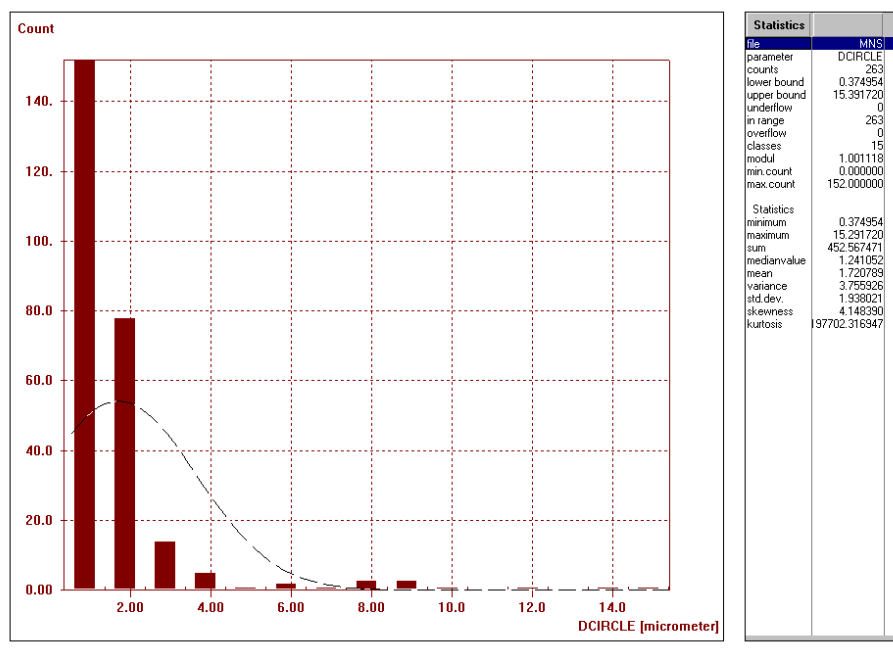


Figure 15. The distribution of the equivalent circle diameter of MnS inclusion in 3% NiCrMnV disc steel.

Table 12. Statistics of MnS inclusions in the 3 NiCrMnV disc steel

Diameter of the equivalent circle / μm			Density / cm^{-2}
Maximum	Minimum	Average	
15.3	0.37	1.72 ± 1.94	2.24×10^4

CONCLUSIONS

- During an exposure test of a disc steel in deaerated pure water, an unplanned ingress of oxygen caused a 0.7 V positive shift in potential, but the important feature was that the recovery of the normal low potential of about -0.6 V SCE took a period of weeks after restoration of deaerated conditions. This raises an issue of the rate of variation of the corrosion potential following start-up and shut-down procedures in service, particularly in two-shifting situations, and requires further investigation.

- Pitting was observed under all exposure conditions with the pit density increasing in the order: deaerated pure water; aerated pure water, and aerated 1.5 ppm chloride-containing water.
- Pits formed in the pure water tended to be “tighter” with a higher depth to mouth opening ratio than for the chloride-containing water. This is rationalised on the basis of retention of local pit solution chemistry influenced by MnS for the pure water bulk solution and by potential drop considerations in the chloride-containing solution.
- The average pit growth rate was 4-6 times faster in the chloride solution with pit depths of 1 mm or so after 1 year exposure. The maximum pit depth obtained in pure water was about 200 μm . Whilst the pit density was greater in aerated pure water than deaerated pure water, the growth rates were similar, which can be explained by the large potential drop (and hence decoupling from the external cathodic current) as the pit propagates.
- Extensive stress corrosion cracking from pits was observed in the chloride-containing solution. A minimum pit size of 60-70 μm for initiation of cracks was identified. There was no cracking in pure water despite pit depths of up to 200 μm . Longer-term exposure tests are ongoing to assess whether the transition to stress corrosion cracking may occur in pure water at a greater pit depth.
- Surface crack growth rates were relatively fast, of the order of $1 \times 10^{-10} \text{ m s}^{-1}$. Evaluation of the distribution of crack depths with exposure time is in progress.
- Further work to evaluate the role of chloride in deaerated solution is required to establish whether its primary function is simply to lower the potential drop and thence to enable a more significant impact of the higher potential external to the pit or whether it has a more direct role in crack development.

ACKNOWLEDGEMENTS

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APPENDIX

Supplementary data

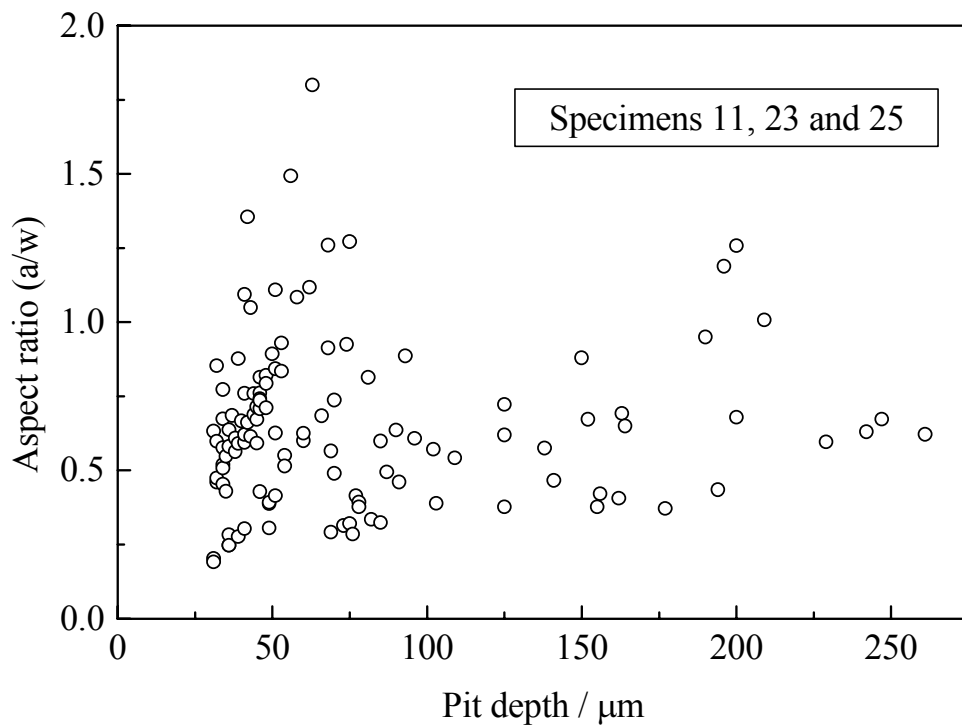


Figure A1. Aspect ratio of pits as a function of pit depth on the self-loaded specimens tested in aerated pure water at 90 °C for 5107 hours (no cracks initiate from pits).

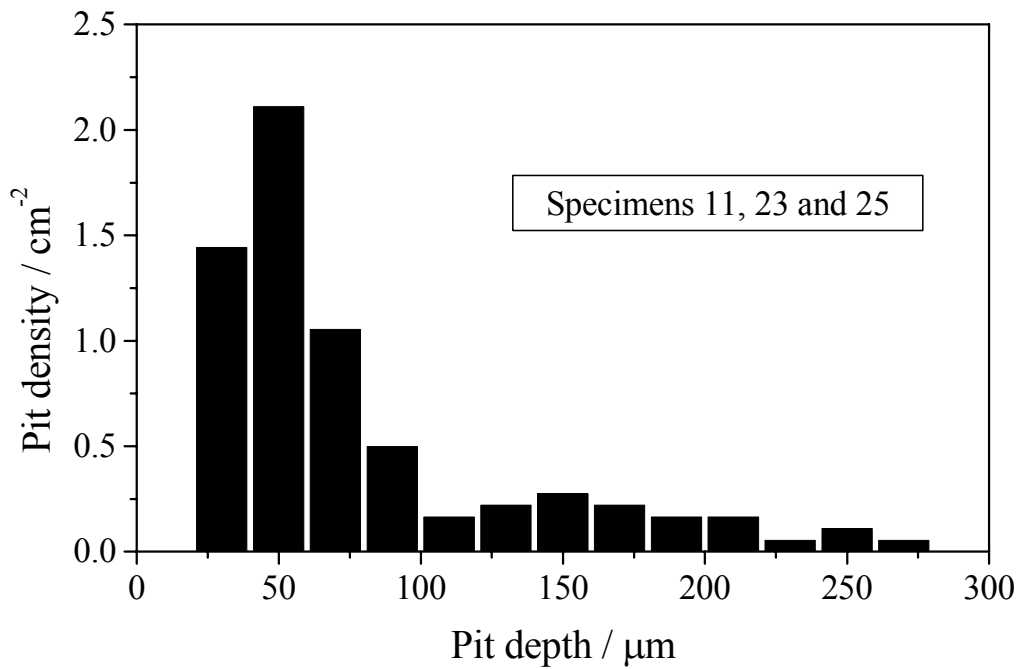
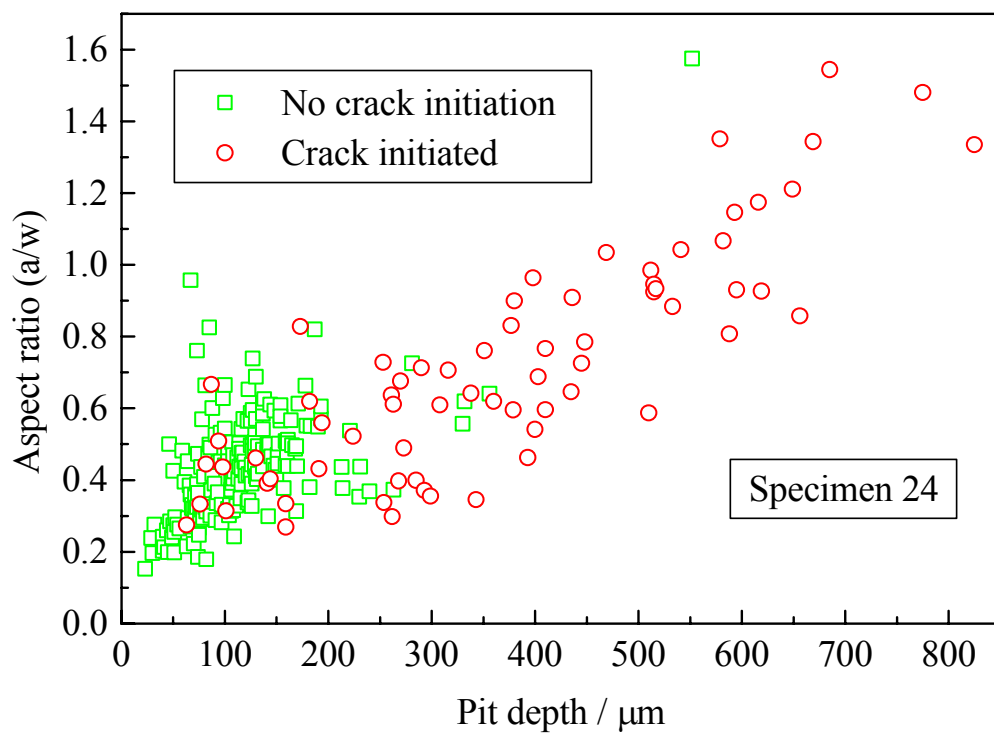
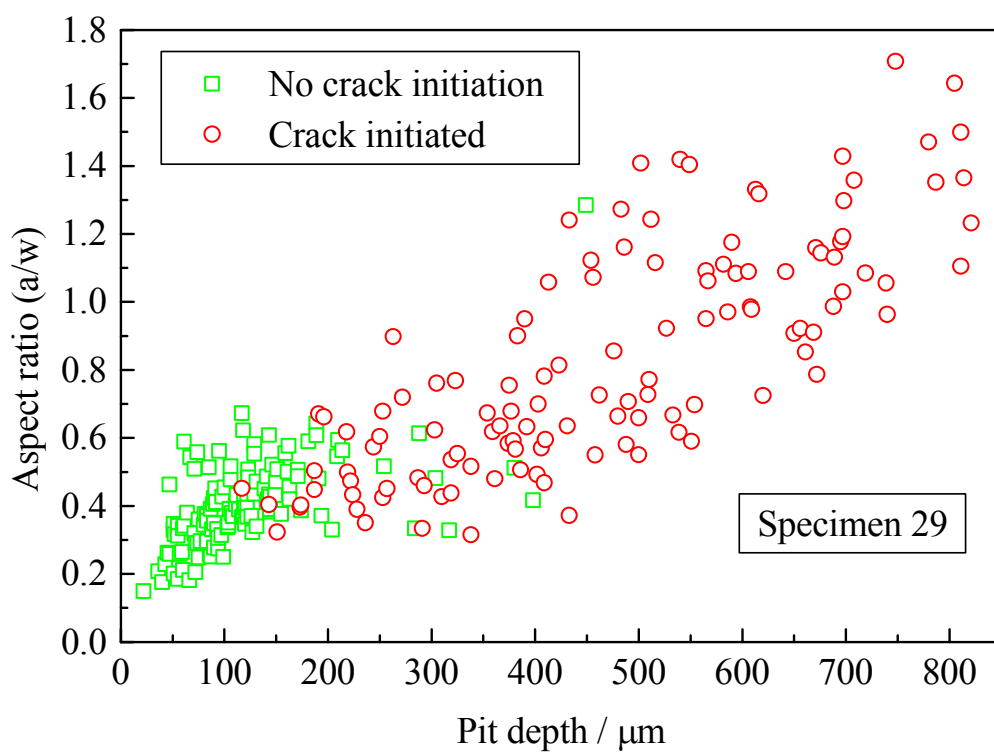


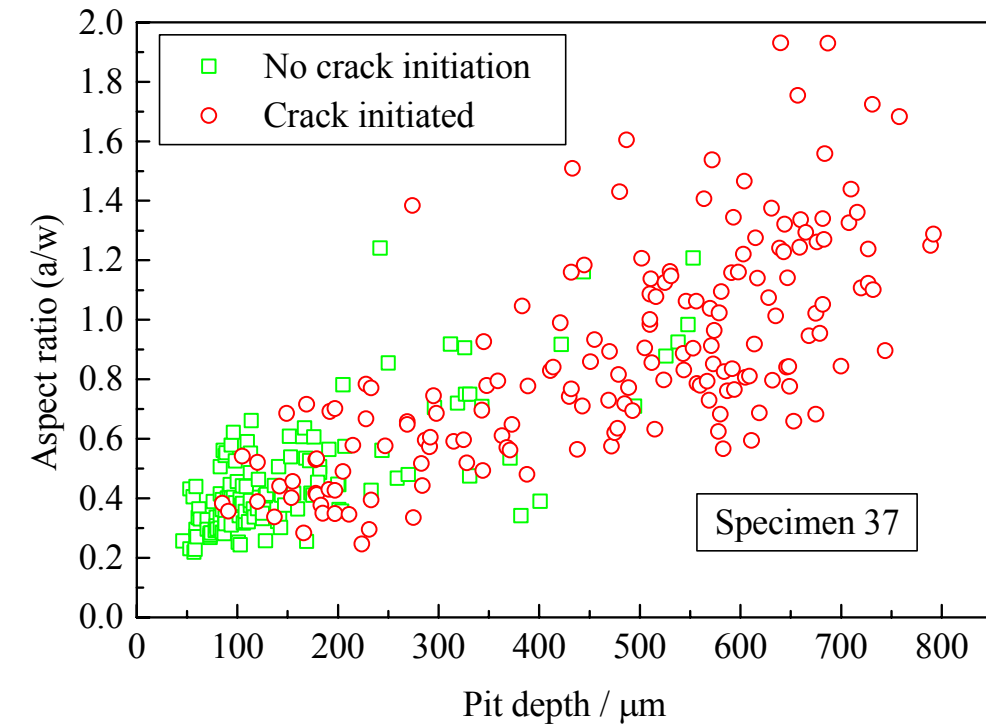
Figure A2. Distribution of pit depth on the self-loaded specimens tested in aerated pure water at 90 °C for 5107 hours.



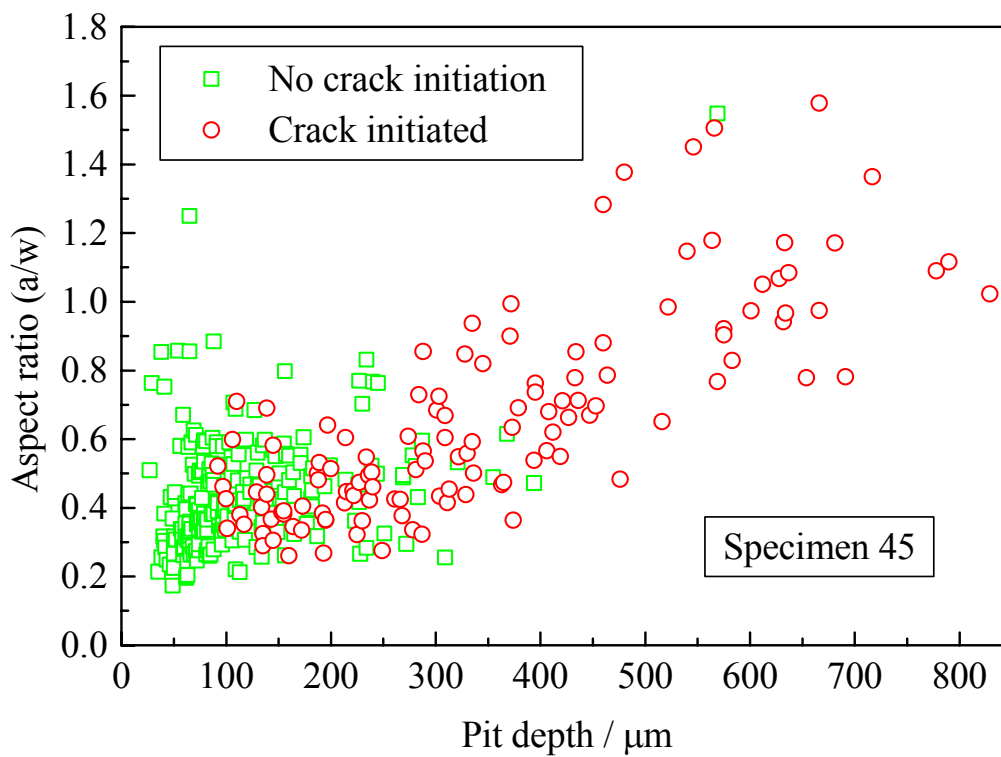
(a)



(b)



(c)



(d)

Figure A3. Aspect ratio of pits as a function of the pit depth on the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 5107 hours.

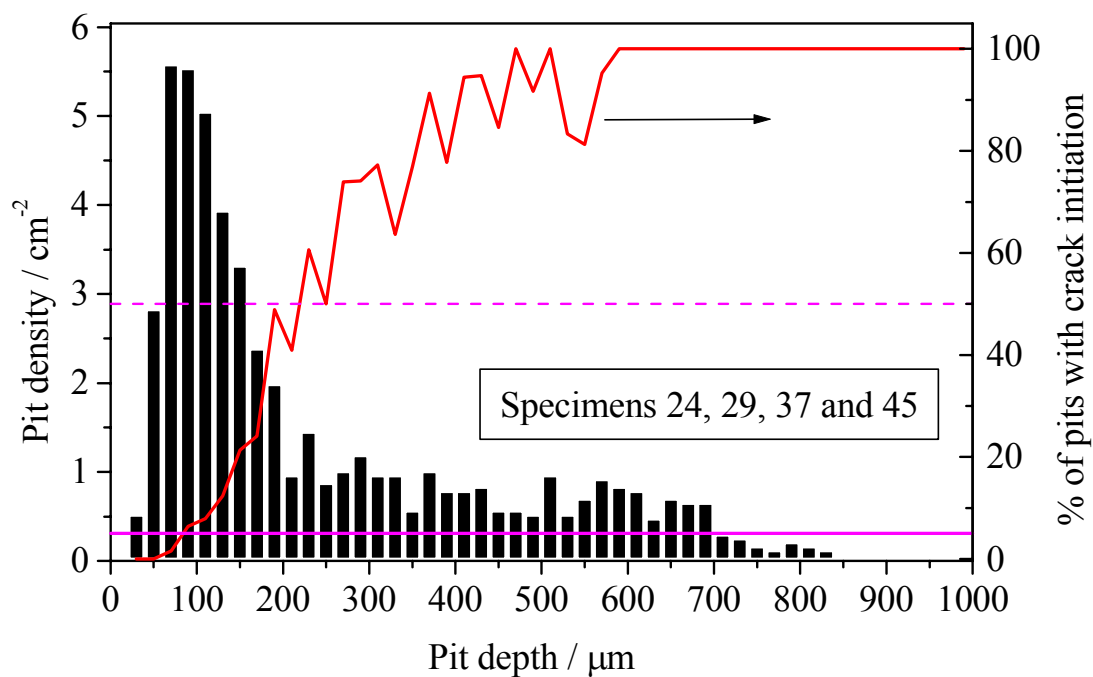


Figure A4. Distribution of pit depths on the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 5107 hours.

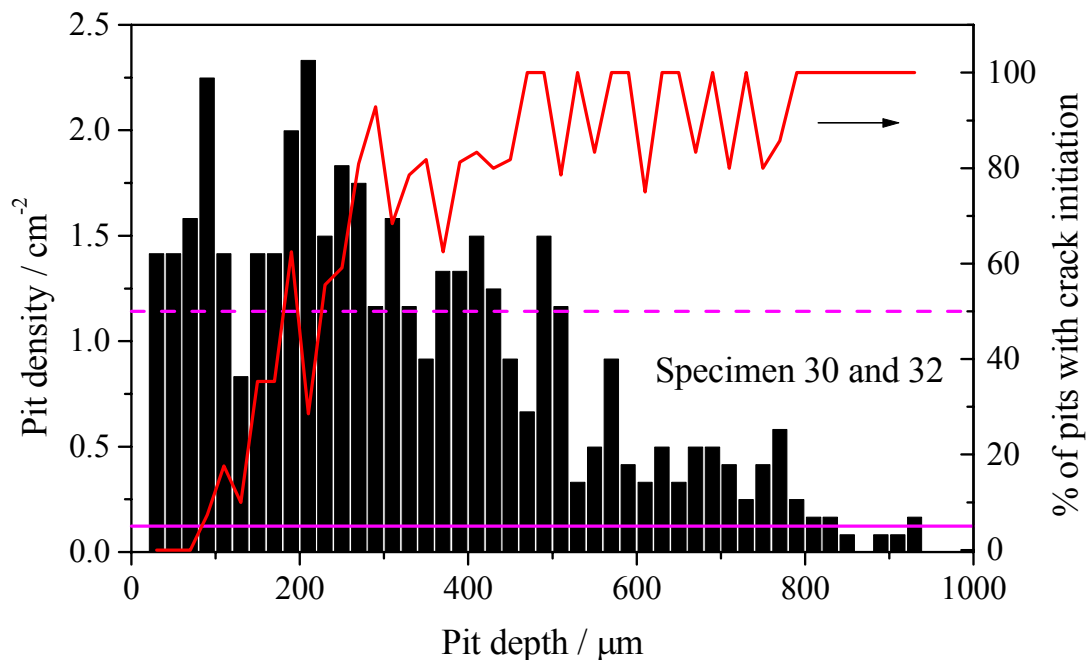
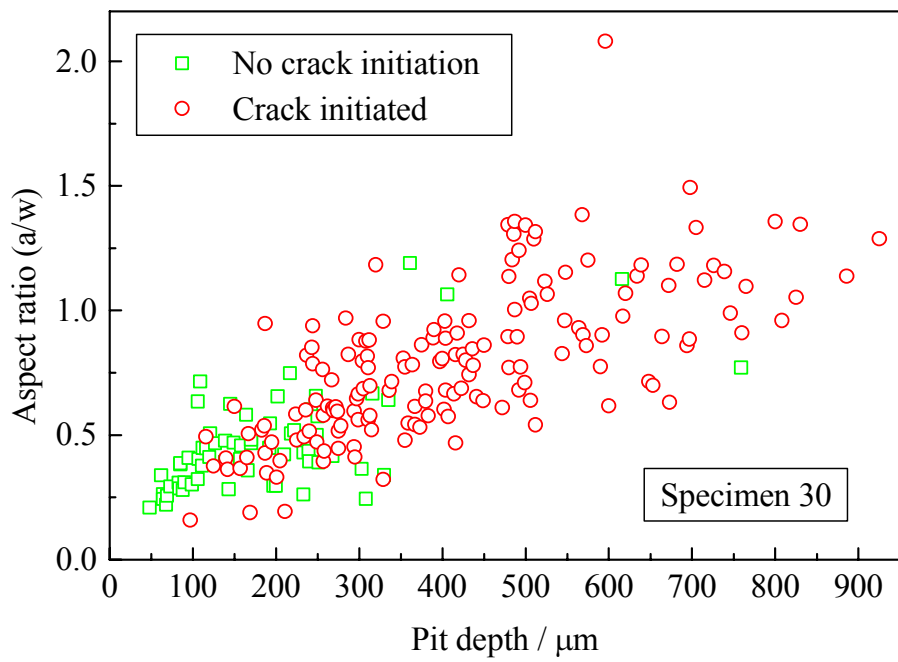
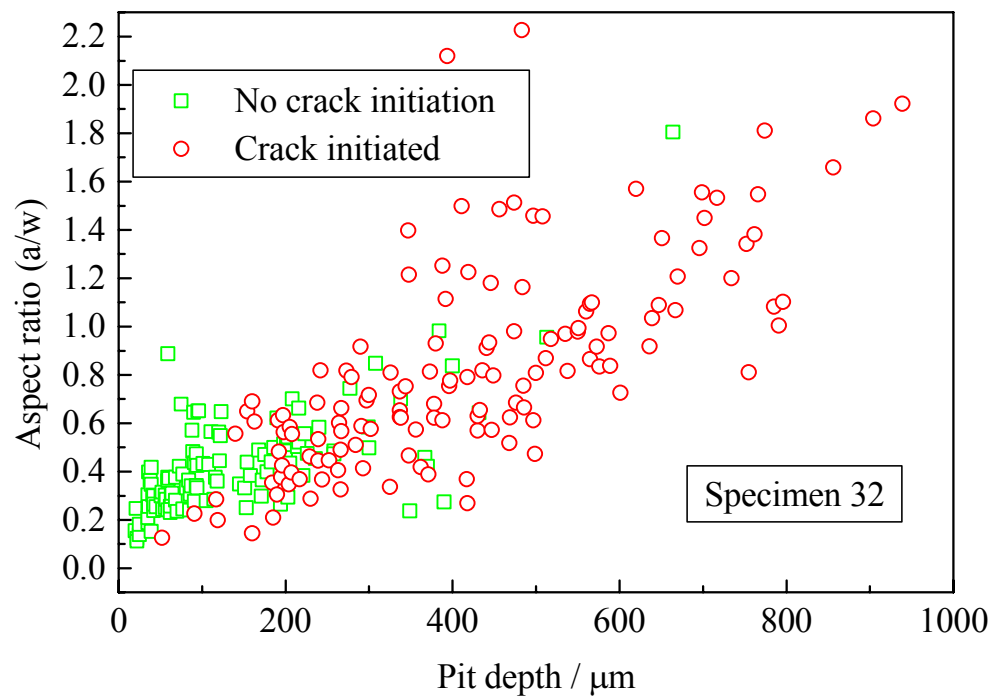


Figure A5. Distribution of pit depths on the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 7173 hours.



(a)



(b)

Figure A6. Aspect ratio of pits as a function of pit depth on the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 7173 hours.

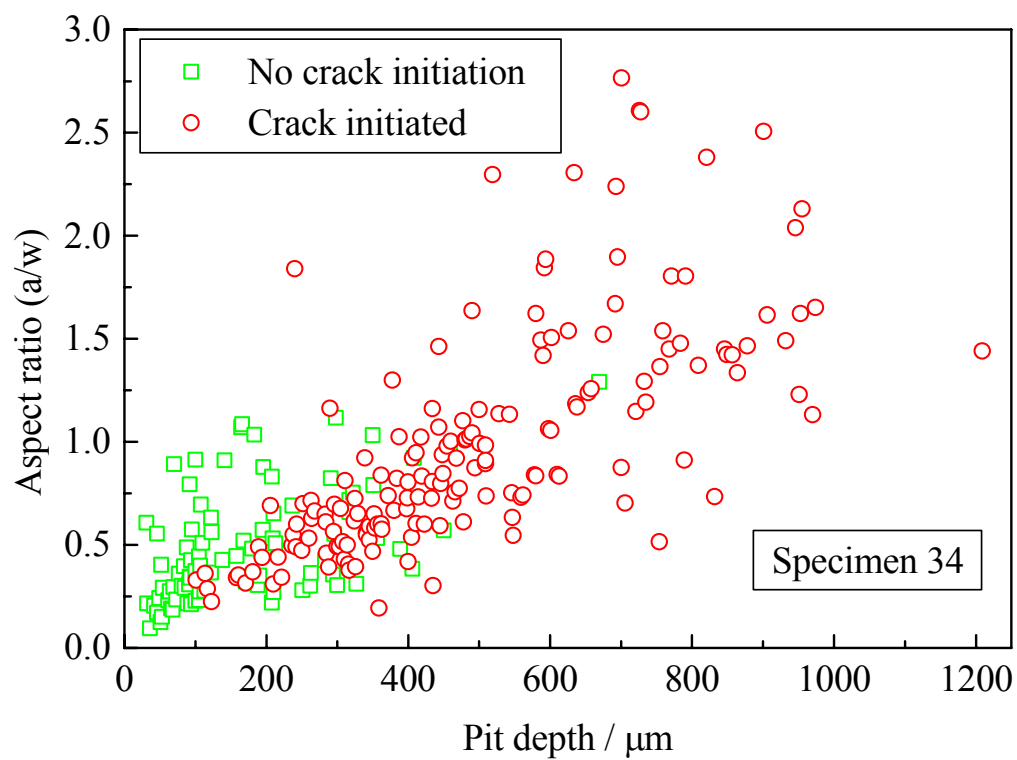


Figure A7. Aspect ratio of pits as a function of pit depth on the self-loaded specimens tested in aerated 1.5 ppm Cl^- solution at 90 °C for 9187 hours.