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Linearly-increasing-stress testing of carbon steel in 4 N $NaNO_3$ and in Bayer liquor

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This paper reports the application of linearly increasing stress testing (LIST) to the study of stress corrosion cracking (SCC) of carbon steel in 4 N $NaNO_3$ and in Bayer liquor. LIST is similar to the constant extension-rate testing (CERT) methodology with the essential difference that the LIST is load controlled whereas the CERT is displacement controlled. The main conclusion is that LIST is suitable for the study of the SCC of carbon steels in 4 N $NaNO_3$ and in Bayer liquor. The low crack velocity in Bayer liquor and a measured maximum stress close to that of the reference specimen in air both indicate that a low applied stress rate is required to study SCC in this system. © *1998 Chapman & Hall*

1. Introduction

In service, stress corrosion cracking (SCC) [1] is often characterized by slow subcritical crack growth at low applied stresses. This means that a metallic component or structure at stresses otherwise considered to be safe can have a growing crack-like defect. Crack initiation and growth can take long periods of time. During the "initiation" period, there may be no outward indication of any defect in the part or structure, which may perform to specification. Nevertheless, while conditions are appropriate, the small subcritical stress corrosion cracks continue to grow in size at low applied stresses until a critical crack size is reached. When the critical crack size is reached, the combination of the crack plus the applied load causes (macroscopic) brittle fracture. This brittle fracture is sudden, often with little prior warning, and can be catastrophic.

SCC often occurs under corrosive conditions where general corrosion is not a problem. The corrosion resistance of interest is caused by surface films that separate the material from its environment. Such films can cause a low rate of general corrosion despite a large thermodynamic driving force for corrosion. For example, stainless steels are stainless because of a very thin passive surface layer which is essentially Cr_2O_3. Although, this layer is so thin (typically less than 4 nm [2–5]) that it cannot be seen with the naked eye, this layer is nevertheless effective in separating the steel from its environment. The passive films on stainless steels are usually self repairing. The breakdown of such films can be induced chemically (e.g. by chlorides), and pitting corrosion results when the breakdown is localized. Localized film breakdown under the joint action of a stress and an environment is the essence of SCC.

SCC is a complex multistep process [1], in which crack advance occurs by interaction of the applied loading, plastic response of the material at the crack tip, interaction of crack-tip plasticity and surface passive protective films, and localized corrosion in the crack-tip region in a local solution which can be very different from that of the bulk. Crack-tip corrosion can liberate hydrogen which can be involved in the crack advance mechanism by hydrogen embrittlement (HE). Fracture of the surface films can give rise to crack advance by brittle fracture. Alternatively, the crack in a brittle surface layer can provide local environmental conditions at the metal surface which are very conducive to the initiation of SCC in the metal [6]. SCC involves both mechanical factors (such as the stress intensity factor and the crack-tip plasticity) and electrochemistry.

SCC is an ongoing concern for steels in which the susceptibility increases with increasing strength level [7, 8]. Our previous work has dealt extensively with the SCC of steels. A new test method for SCC was developed [9, 10]: linearly-increasing-stress testing (LIST) was applied to high-strength steels [9, 10] and pure copper [11]. Stress rate effects have been shown [9–12] to be an important part of the SCC mechanism and, in particular, crack-tip creep has been shown to be an important part of the SCC mechanism for high-strength steels undergoing SCC in water [9–12], which can provide [12] an explanation for the stationary stress corrosion cracks observed in service. Room-temperature creep has been measured for high-strength steels including AISI 4340 and AerMet 100 [13] and related to crack initiation [14]. A new model was proposed for SCC for quenched-and-tempered steels based on strain assisted dissolution [15]. Crack velocity was related to heat treatment and microstructure [16, 17]. The possible causes for the intergranular crack path for high-strength steels undergoing SCC in water have been explored by microstructural characterization using electron microscopy [18–20], measurements of grain-boundary chemistry [21] and electrochemistry [22]. A precipitation-strengthened duplex stainless steel was developed [23].

This paper reports a study applying LIST [9, 10] to a carbon steel in 4 N $NaNO_3$ and in Bayer liquor. LIST is similar to the constant-extension-rate testing (CERT) methodology [24] with the essential difference that the LIST is load controlled whereas the CERT is displacement controlled. The main aim was to investigate the suitability of this new testing method for the study of the SCC of carbon steels in 4 N $NaNO_3$ and in Bayer liquor.

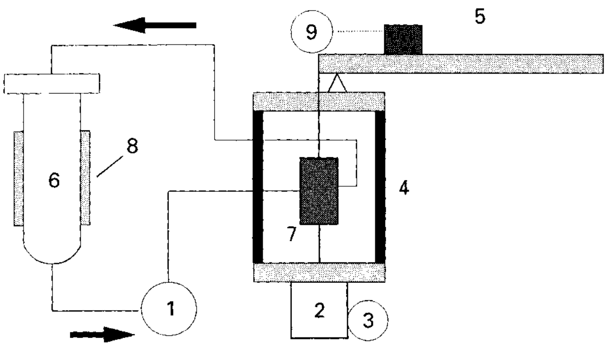

Figure 1 Schematic diagram of the LIST apparatus as used for SCC experiments with Bayer liquor. 1, metering pump; 2, gearbox; 3, servomotor; 4, LIST frame; 5, lever beam with 14 kg weight; 6, reservoir vessel; 7, steel test cell; 8, heating coil; 9, synchronous motor.

2. Experimental procedure

LIST has been described previously in detail [9, 10]. Fig. 1 shows the LIST apparatus adapted for the study of SCC in Bayer liquor. The LIST apparatus allows application of a linearly increasing (engineering) stress to a specimen exposed to the environment of interest. This test is very similar to CERT, except that CERT is controlled by the extension rate whereas LIST is controlled by the loading rate. The LIST apparatus consists of a lever beam balanced at its equilibrium position. One arm of the lever beam is connected to the test specimen and there is a known moveable weight on the other arm. Movement of the weight, driven by a synchronous motor, causes a proportional load to be experienced on the specimen. By using synchronous motors of different speeds, various applied stress rates are achieved. One loading rate was used in this study, 0.142 N s^{-1}, equivalent to an applied (engineering) stress rate of 0.02 MPa s^{-1} or an applied strain rate of 1×10^{-7} s^{-1} in the linear elastic region. This applied strain rate is significantly slower than that used in much CERT where it is common to use an applied strain rate of 1×10^{-6} s^{-1}. There is a servo system to control the arm movement in such a way that the arm should remain horizontal throughout the whole test, despite the specimen elongation due to the slowly increasing load; this has worked well in previous tests with high-strength steels [9, 10], pure copper [11] and pipeline steels [25]. For some specimens a direct-current (d.c.) potential drop method was used to detect SCC initiation. A constant current of 5 A was applied to the specimen by means of two wires soldered onto the specimen ends and the d.c. potential drop across the gauge section was measured. In order to eliminate the influence of applied current fluctuation, a standard resistance was added to measuring circuit. The measured parameter U/U_0 (U is the potential drop from the specimen gauge section and U_0 is that from standard electric resistance) can reflect the deformation of the specimen and the SCC initiation processes. Previous experiments have shown that the onset of SCC is correlated with a significant change of electrical resistance versus time [9–11, 25].

Two different environmental cells were used. Tests in 4 N $NaNO_3$(pH 2) were carried out at the free corrosion potential in a glass cell as described previously [9–11].

Tests in Bayer liquor were carried out in the steel cell, 7, as shown in Fig. 1. The bulk solution was contained in a steel reservoir vessel, 6, heated by means of an electrical heating coil, 8, wrapped around the vessel, controlled by a standard temperature controller to a temperature of 110 °C. Flexible 12.7 mm reinforced Teflon hoses connected the reservoir vessel with the test cell, 7, and the metering pump, 1, which circulated the solution at a constant rate of 400 ml min^{-1}. The test cell had three ports and a continuous air bleed at the top to prevent air from being trapped inside the cell. One of the ports accommodated the Hg/HgO reference electrode and the other two connected the cell with the pump and the reservoir vessel. Two openings, one at the top and one at the bottom of the test cell, allowed the tensile specimen to extend from the cell so that it could be attached to the load string of the LIST apparatus. Teflon rings acted as sealing devices and simultaneously assured electrical insulation between the specimen and the steel test cell. After the experiment was set up, the solution was heated in the reservoir vessel to 110 °C and circulated through the test cell using the metering pump. The potential was controlled at -850 ± 10 mV (Hg/HgO) by a Wenking model PSG 81 potentiostat. Loading was started after allowing 1 h for stabilization of experimental conditions.

The specimen material had the chemical composition given in Table I and was used in the as-received condition (cold rolled). The smooth tensile specimens were machined with a gauge diameter of 3 mm and a gauge length of 16 mm and were abraded with 400 grit paper along the gauge section immediately before testing.

The 4 N $NaNO_3$ was made up of analytic-grade chemicals and distilled water. The Bayer liquor, supplied by Queensland Alumina Limited from their Bayer alumina refinery at Gladstone, Qld, had a total sodium content of 177 g l^{-1} and a free caustic content of 105–110 g l^{-1} [26, 27]. Bayer liquor is essentially a concentrated solution of NaOH containing dissolved alumina (Al_2O_3) as well as some impurities from the bauxite ore. Because Bayer liquor is a concentrated solution of NaOH, the control potential for the tests in Bayer liquor was chosen to be in the middle of the potential range for SCC, between -700 and -1100 mV (Hg/HgO), as measured for SCC in

TABLE I Chemical composition of steel

Element	C	Mn	Si	S	P	Ni	Cr	Mo	Cu	V	Nb	Ti	Al
Amount (wt %)	0.08	1.0	0.01	0.3	0.07	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.004

9 N NaOH by Jones *et al.* [28]. Tests in both 4 N $NaNO_3$ and Bayer liquor were carried out at 95 °C.

3. Experimental results

3.1. Reference test

The results are summarized in Table II. A reference test (specimen LR) in laboratory air at 20 °C in the steel cell gave a maximum stress of 590 MPa (corresponding to the ultimate tensile strength of the steel) and a reduction in area of 51%. The maximum stress corresponded to the beginning of the plastic instability of necking as expected for a load controlled tensile test.

3.2. Tests in 4 N $NaNO_3$

Specimens L1 and L2 were tested in 4 N $NaNO_3$ (pH 2) at 95 °C using the glass environmental cell. Both specimens were covered by a black adherent oxide over the entire immersed part of each specimen, had multiple cracks along the gauge length and failed in a brittle manner as indicated by the low values of reduction in area (4% and 8%, respectively). The fracture surfaces of both specimens had a semicircular stress corrosion crack of average depth of 0.75 mm. Specimen L1 was not subjected to the d.c. potential drop technique; so there was no measurement of stress corrosion crack initiation. The potential drop record for specimen L2 is shown in Fig. 2. The abrupt change in slope suggested an initiation stress of 211 MPa. After 300 min, the specimen elongation due to the multiple cracks had become larger than could be accommodated by the servomechanism of the LIST apparatus; as a consequence the lever arm came to rest at the lower end of its possible travel, stopping further loading of the specimen. Nevertheless, the potential drop record indicates that SCC continued under these constant-displacement conditions. The specimen was completely separated into two parts when it was removed from the LIST apparatus, further indicating that the stress corrosion crack had grown at a constant strain and under conditions of decreasing stress, and that there was sufficient stress remaining on the specimen to cause final rupture by plastic overload. A predominantly intergranular fracture mode is suggested by Fig. 3 which shows part of the fracture surface of specimen L2 although determination of the fracture mode was difficult because there was an appreciable corrosion product film covering large areas of the fracture surface.

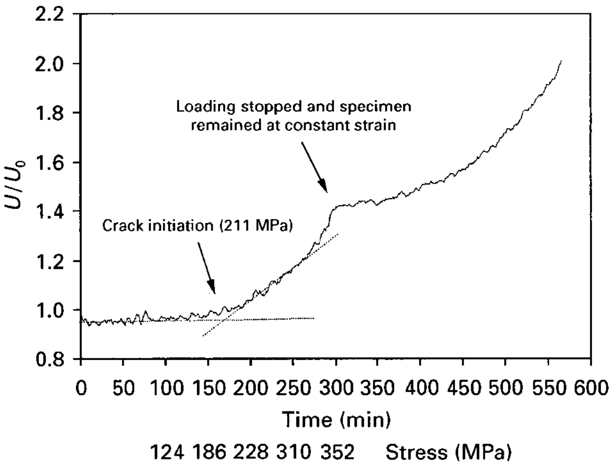

Figure 2 Potential drop as a function of time for specimen L2 tested in 4 N $NaNO_3$ at 95 °C. The corresponding stress values are noted below the test time up to 300 min, after which the load increase stopped.

Specimens L3 and L4 were tested in 4 N $NaNO_3$ (pH 2) at 95 °C using the steel environmental cell. Specimen L3 was not subjected to the d.c. potential drop technique; so there was no measurement of stress corrosion crack initiation. Specimen L3 failed in a brittle manner at 527 MPa and exhibited multiple cracks along the gauge length very similar to those on specimens L1 and L2. Note, however, the higher

TABLE II Results for the reference test (specimen LR) in laboratory air at 20 °C and for tests at 95 °C in 4 N $NaNO_3$ (pH 2) at the corrosion potential and in Bayer liquor at − 850 ± 10 mV (Hg/HgO)

Specimen	Cell type	Environment	Initiation stress (MPa)	Maximum stress (MPa)	Reduction in area (%)
LR	Steel	20 °C, laboratory air	—	590	51
L1	Glass	4 N $NaNO_3$, 95 °C at corrosion potential	No PD[a]	380	4
L2	Glass	4 N $NaNO_3$, 95 °C at corrosion potential	211	375	8
L3	Steel	4 N $NaNO_3$, 95 °C at corrosion potential	No PD[a]	527	14
L4	Steel	4 N $NaNO_3$, 95 °C at corrosion potential	≈ 608	608	39
L5	Steel	Bayer liquor, 95 °C, − 850 ± 10 mV	No PD[a]	602	42
L6	Steel	Bayer liquor, 95 °C, − 850 ± 10 mV	No PD[a]	592	48

[a] No potential drop for measurement of the SCC initiation stress.

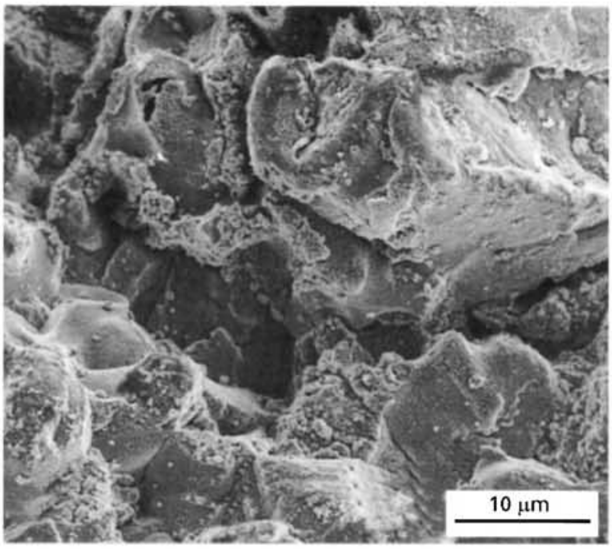

Figure 3 Micrograph showing intergranular fracture for specimen L2 tested in 4 N $NaNO_3$ at 95 °C.

maximum stress and reduction in area, although both quantities are smaller than those for the reference test in air (specimen LR). Specimen L4 was subject to the potential drop technique; the potential drop technique did not indicate crack initiation. Specimen L4 underwent plastic instability at a stress of 608 MPa which is comparable with the maximum stress measured in the reference sample in air (specimen LR). Specimen L4 had a reduction area of 39%, which was significantly lower than that of the reference sample in air (specimen LR). Subsequent examination revealed a few stress corrosion cracks located in the necked region of the gauge section; this was consistent with the low value of the reduction in area.

3.3. Tests in Bayer liquor

Specimens L5 and L6 were tested in Bayer liquor at 95 °C at a potential of -850 ± 10 mV (Hg/HgO). Specimens L5 and L6 failed by the plastic instability of necking at the stresses indicated in Table II; these stresses were comparable with that at failure of the reference specimen in air. Optical microscope examination of specimen L5 indicated SCC along the gauge length whereas specimen L6 showed SCC indications only in the necked region. Fig. 4 presents a representative micrograph of a stress corrosion crack from the gauge length of specimen L5 and Fig. 5 shows a magnified view of this crack. Several very small stress corrosion cracks were visible around this site and all grew in an orientation normal to the tensile stress. There was very little plastic deformation around the crack site, suggested by no distinct change in the abrasion marks on the specimen surface. Examination of the fracture surface was not possible because of a covering by a thick oxide layer.

None of the specimens tested in Bayer liquor had an obvious oxide film; the surfaces were shiny without any sign of corrosion attack. However, a black adherent oxide had developed in a small band below the top Teflon seal.

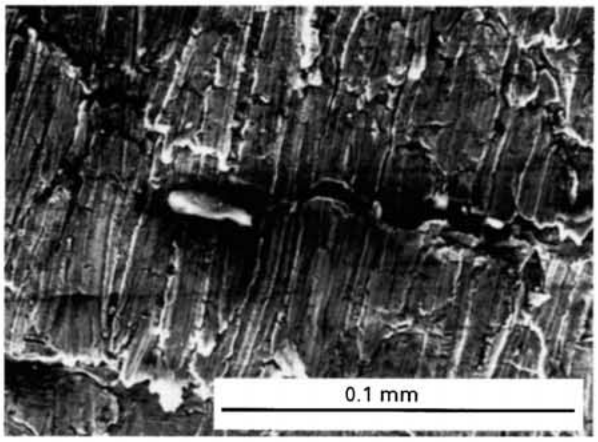

Figure 4 Stress corrosion crack on the gauge section of specimen L5 tested in Bayer liquor at 95 °C and -850 ± 10 mV (Hg/HgO).

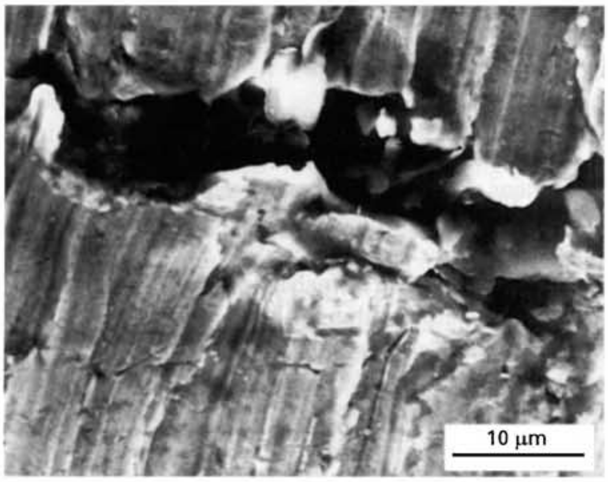

Figure 5 Magnified view of Fig. 4.

4. Discussion

This study has shown that LIST can be used for the evaluation of the SCC susceptibility of carbon steel in 4 N $NaNO_3$ and in Bayer liquor. A loading rate of $0.142\ \mathrm{N\,s^{-1}}$, equivalent to an applied (engineering) stress rate of $0.02\ \mathrm{MPa\,s^{-1}}$ or an applied strain rate of $1 \times 10^{-7}\ \mathrm{s^{-1}}$ in the linear elastic region, produced severe SCC of the mild steel in 4 N $NaNO_3$ for specimens L1 and L2 tested in the glass environmental cell. These observations were in good agreement with the work of Krupowicz *et al.* [29] who used CERT (with an applied strain rate of $1 \times 10^{-6}\ \mathrm{s^{-1}}$) to study a 0.23 wt% C steel in 4 N $NaNO_3$ at 121 °C and measured a fracture stress of 290 MPa and a reduction in area of 10%.

Specimen L3 tested in the steel environmental cell also failed in a brittle manner with a relatively low reduction in area but at a significantly higher stress, whereas specimen L4 exhibited more ductility and a higher fracture stress approaching that of the reference specimen LR. Nevertheless specimens L3 and L4 did show SCC and a reduction in area lower than the reference sample LR. The difference between specimens L1 and L2 and between specimens L3 and L4 is attributed to subtle environmental differences brought about by the difference in test cell (glass and steel, respectively) because all test parameters were maintained constant (specimen material, applied stress rate, $NaNO_3$ concentration and temperature). The most likely consequence of a subtle environmental change is a change in the free corrosion potential which is related to the oxygen concentration of the solution. The glass cell is expected to have no influence on the test solution oxygen concentration whereas the self-corrosion of the steel cell will use up the test solution oxygen content thereby change the free corrosion potential. Mazille and Uhlig [30] showed that a change in the corrosion potential by 50 mV was sufficient to increase the time to fracture by two orders of magnitude in constant-(plastic-)displacement tests. Similar observations that SCC occurs in a narrow potential range corresponding to the active–passive transition have been made by Jones *et al.* [28], Humphries and Parkins [31] and Bohnenkamp [32], and Jones *et al.* [28] have shown that the oxygen content of the solution can shift the SCC region.

LIST also revealed SCC in the Bayer liquor tests (specimens L5 and L6). Specimen L5 had several small stress corrosion cracks along the gauge section. Their depth of penetration was shallow as indicated in Fig. 4, but this is in good agreement with experimental observations in the literature of relatively slow crack propagation in caustic solutions. The work of Parkins [33] has shown that SCC of mild steels in nitrates and hydroxides requires the combination of high stresses (often above yield) and plastic deformation. This is in general agreement with the results of this study.

Estimates can be made for the SCC velocity in these tests from the largest stress corrosion crack on the fracture surface and the total testing time. This estimation method gives a SCC velocity of 5.0×10^{-8} m s^{-1} for tests in the nitrate solution and 3.5×10^{-10} m s^{-1} for tests in the Bayer liquor. The low crack velocity in the Bayer liquor and a measured maximum stress close to that of the reference specimen in air both indicate that a better indication of SCC would be made with a lower applied stress rate. A similar situation was also shown to be applicable for the study of the SCC of pipeline steels in a carbonate–bicarbonate solution [25] where an applied stress rate of 0.002 MPa s^{-1} was found to give good results with LIST. The applied stress rate of 0.002 MPa s^{-1} is an order of magnitude slower than the applied stress rate used in the present study which was 0.02 MPa s^{-1}. The applied stress rate of 0.02 MPa s^{-1} produces an applied strain rate of 1×10^{-7} s^{-1} in the linear elastic region which is much slower than the strain rate often used in CERT (typically 1×10^{-6} s^{-1}). However, above the yield stress, the applied strain rate accelerates in LIST because it is the stress rate which is being increased at a constant rate. In contrast in CERT the extension rate is constant until specimen fracture. This means that LIST and CERT are essentially equivalent up to the yield stress whereas, for the study of SCC initiation above, the yield stress requires lower applied loading rates for LIST. The yield stress is usually considered [1] to be the limit of applied loading in most normal design situations and consequently it is very rare for plant or machinery to be designed to operate at stresses near or above the yield stress. The acceleration of the applied strain rate above the yield stress in LIST is considered to be an advantage as the total test time is shortened after the specimen has exceeded the allowable design limit.

The lack of an oxide film on the specimen surface after testing in Bayer liquor was unexpected as a thin black adherent oxide was reported by Humphries and Parkins [31] and Hoar and Jones [34] in the potential range between −850 and −550 mV (standard hydrogen electrode) and the potential applied in the present work is within this range. The presence of the black oxide on the shoulders of the specimens in the present work, close to the O-ring might suggest an influence of oxygen in the film formation.

5. Conclusion

The main conclusion is that LIST is suitable for the study of the SCC of carbon steels in 4 N $NaNO_3$ and in Bayer liquor.

The low crack velocity in the Bayer liquor and a measured maximum stress close to that of the reference specimen in air both indicate that a better indication of SCC would be made with a lower applied stress rate.

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