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ANODIC BEHAVIOUR OF MILD STEEL DURING YIELDING IN NITRATE SOLUTIONS*

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Abstract—The anodic behaviour of mild steel during yielding, at constant potential in various hot nitrate solutions, has been studied. The influence of solution composition, pH, strain rate and electrode potential, has been examined. Yielding of oxide-covered steel is accompanied by a large increase in anodic current density. This increase is almost independent of strain rate and is a linear function of percentage strain; the anodic c.d. on the yielding metal bared by rupture of the oxide layer can be as high as $2A/cm^2$. At low strain rates stress corrosion "cracking" can be observed. The rate of "crack" propagation was estimated microscopically as up to ~ 0·25cm/h, which is equivalent to an anodic dissolution of the advancing edge of the "crack" of up to ~ $2A/cm^2$. The stress corrosion "crack" is therefore considered to be a fissure of which the yielding advancing edge is bared metal that can dissolve anodically at up to $2A/cm^2$ while the static sides become oxide-covered so that the anode c.d. there is many times smaller.

Résumé—Une étude a été faite du comportement anodique de l'acier doux pendant le fluage, à un potentiel constant dans différentes solutions nitrées chaudes. On a examiné l'influence de la composition de la solution, du pH, de la vitesse de déformation et du potentiel des électrodes. Le fluage de l'acier à revêtement d'oxyde est accompagné d'une augmentation importante de la densité du courant anodique. Cette augmentation est presque indépendante de la vitesse de déformation et est une fonction linéaire du pourcentage de déformation; la densité de courant anodique au lieu de rupture sur le métal déformé dénudé de la couche d'oxyde peut s'élever jusqu'à $2A/cm^2$. A des vitesses de déformation faibles on peut observer un effet de "déchirure" par suite de l'effort corrosif. La vitesse de propagation de la "déchirure" a été évalué au microscope comme allant jusqu'à ~ 0,25cm/h, qui équi vaut à une dissolution anodique du bord en progression de la "déchirure" allant jusqu'à ~ $2A/cm^2$. La "déchirure" par suite de l'effort corrosif est donc considéré comme étant une fissure dont le bord en progression se déformant est du métal dénudé qui peut se dissoudre anodiquement jusqu'à ~$2A/cm^2$ tandis que les bords statiques se revêtent d'oxyde de sorte que la densité du courant anodique à cet endroit-là est de nombreuses fois plus faible.

Zusammenfassung—Das Anodenverhalten von Flusseisen während Strecken bei konstanter Spannung in verschiedenen heissen Lösungsnitraten ist untersucht worden. Der Einfluss der Lösungszusammensetzung, pH, Dehnungsgeschwindigkeit und der Elektrodenspannung wurde untersucht. Das Strecken von Oxyd-überzogenem Stahl erfolgt mit gleichzeitiger, starker Vergrösserung der Anodenstromdichte. Diese Vergrösserung ist beinahe unabhängig von der Dehnungsgeschwindigkeit und ist eine lineare Funktion der prozentualen Dehnung. Die Anodenstromdichte auf dem dehnenden blanken Metallriss der Oxydschicht kann bis zu $2A/cm^2$ gross sein. Bei niedrigen Dehnungsgeschwindigkeiten kann Spannungskorrosions "Rissbildung" beobachtet werden. Die Geschwindigkeit der "Riss" Fortpflanzung wurde mikroskopisch auf bis zu 0,25cm/Std. geschätzt, was einer anodischen Auflösung des fortschreitenden Randes vom "Riss" bis auf etwa $2A/cm^2$ gleichkommt. Der Spannungskorrosions-"Riss" wird daher als ein Sprung angesehen, dessen fortschreitende Streckkante blankes Metall ist, welches sich anodisch unter bis zu $2A/cm^2$ auflösen kann, während die statischen Seiten sich mit Oxyd bedecken, sodass dort die Anodenstromdichte vielfach kleiner ist.

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INTRODUCTION

THE ANODIC behaviour of 18Cr–8Ni type stainless steels while yielding in 42wt-% aqueous magnesium chloride at 154°C was studied by Hoar and West,[1,2] who discovered marked yield-assisted anodic dissolution, which was confirmed by Hoar and Scully.[3] The experiments were performed at ∼ − 0·15 to − 0·05V(nhe), which is the range of potential in which stress corrosion cracking of the *stressed* 18–8 steel occurs under the same chemical conditions.[4,5] Since the cracks propagate at ∼ 1mm/h and since yielding material was shown to dissolve at ∼ 0·6A/cm^2, equivalent to 0·75mm/h penetration, the earlier hypothesis of Hoar and Hines[4,5] that cracks propagate by anodic dissolution of their yielding advancing edges, their static sides being scarcely affected, received strong support.

The stress corrosion cracking of mild steel in hot nitrate solutions has been examined in several publications.[6–15] Logan[8] proposed that crack propagation is caused by mechanical fracture of the oxide film at the yielding advancing edge, so that rapid anodic dissolution can occur. This was criticized by Parkins[7,16] because it did not take into account the specificity of the media that give stress corrosion cracking. Furthermore, a mechanism of crack propagation by involving anodic dissolution alone would require a high c.d. at the advancing edge. Logan[8,17] pointed out that there should be a high driving force for anodic dissolution when the oxide film is broken, but did not show that the required high anodic c.d. could be sustained. No data have been published for the anodic behaviour of mild steel during yielding in nitrate solutions.

We now report measurements of high anodic c.ds. on mild steel exposed to hot nitrate solutions, simultaneously undergoing traction at high strain rates and anodic dissolution at constant potential. We compare these with microscopic measurements of crack propagation of the same material under the same conditions but at low strain rates, and show that the c.d. available at the *rapidly* yielding *"crack" advancing edge* is sufficient to account for the rate of "crack" propagation.

A difficulty arises in the measurement of anodic c.d. on mild steel in hot nitrate solutions. In experiments in chloride solution, it is simple to study anodic reactions at or just below the "natural" corrosion potential of isolated metal in such solutions exposed to the atmosphere, by removing all dissolved oxygen, the major cathodic reactant; thus Hoar and West[1,2] and Hoar and Scully[3] were able to measure the anodic c.d. at and below the "natural" corrosion potential of 18Cr–8Ni steel in hot magnesium chloride solution by rigorous de-aeration and the use of a separate cathode. But in hot nitrate solutions, the nitrate ion itself is a cathodic reactant; consequently at the corrosion potential of isolated metal in de-aerated solution, there is a local anodic c.d. equal to the cathodic c.d. of nitrate reduction, and below the corrosion potential the measurable c.d. is *cathodic*. Consequently it was necessary in the present work to examine the anodic reaction at potentials sufficiently positive to the corrosion potential so that the cathodic reaction was small compared to the anodic. Fortunately, although the present results refer to potentials more positive than those found in "natural" nitrate cracking, they include actual measurements of the greatly accelerated crack propagation found under these anodic conditions.

EXPERIMENTAL TECHNIQUE

Materials

Experiments were made with 1mm diameter mild steel wire kindly supplied by the British Welding Research Association.* The chemical composition was C, 0·10%; Mn, 0·53%; Si, 1·16%; S, 0·013%; P, 0·013%. The wire, cut into pieces about 40cm long, was degreased, vacuum annealed for 8h at 1100°C, and slowly cooled in the furnace. The final material had a mean grain size of about 0·035mm diameter.

Just before the experiments, the area of the wire to be exposed to the electrolyte solution was cleaned with 4/0 emery paper, etched with dilute nitric acid, washed with distilled water and with industrial methylated spirit, and dried with hot air.

All the solutions were prepared with "AnalaR" grade chemicals, with the exception of calcium nitrate and calcium hydroxide, which were G.P.R. grade. The concentration

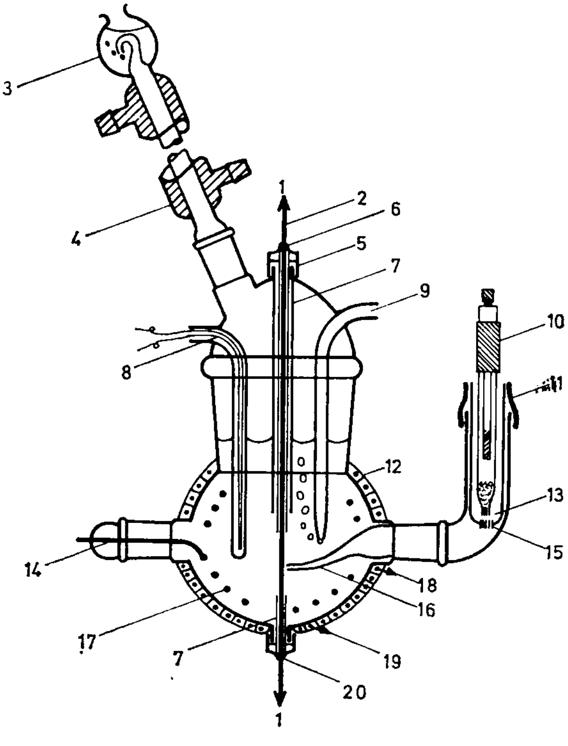

FIG. 1. Cell used for constant experiments at constant strain rate.

1, to Tensometer chuck;
2, specimen;
3, bubbler for egress of nitrogen;
4, water condenser;
5, polyethylene seal;
6, Picien seal;
7, polyethylene sheath;
8, thermocouple leads;
9, nitrogen;
10, saturated calomel reference electrode;
11, p.v.c. tape seal;
12, asbestos insulation;
13, saturated KCl salt bridge;
14, cathode connection;
15, porous plug;
16, Luggin capillary;
17, platinum cathode;
18–19, heater supply;
20, Araldite seal.

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of the nitrate solutions used in all experiments was 4N. The solutions were de-aerated with "White Spot" quality nitrogen further purified by bubbling the gas through a solution of reduced chromium sulphate, by the method of Gilroy and Mayne.[18]

Cell

The cell was a modification of that described by Hoar and West;[2] details are shown in Fig. 1. The top and bottom ends were of polyethylene, and were secured to the cell by a wire fastener. The bottom end was fixed to the specimen with Araldite resin and this end of the specimen was fixed to the moving chuck of a Hounsfield Tensometer. The wire at the top was sealed with Picien wax; this sealing permitted the de-aeration of the cell and did not interfere with the movement of the wire during traction. Cemented to both plastic ends and extending into the cell were two polyethylene capillaries that covered the wire, leaving a definite area of specimen exposed to the solution.

The potential of the specimen was measured via a Haber–Luggin capillary vs. a saturated calomel half-cell at room temperature. The counter-electrode was a helix of platinum wire.

Temperature in the cell was measured with a chromel–alumel thermocouple and was regulated by changing the power supplied to the heating coil, or varying the speed of the bubbling nitrogen. Temperature was controlled to 102° ± 0·5°C.

Apparatus

Potential measurements were made with a Dynacap electrometer millivoltmeter. Current was measured and recorded with a Kipp & Zonen micrograph-BD 2 recorder. The range of the recorder was extended with a range-unit, which allowed recordings from 0·1μA to 500mA (full-scale) in eleven ranges. The error in any of the ranges was 1% of the measured current. As well as the recording pen, a second pen was used to mark on the chart the time of initiation of yielding of the specimens, and of their fracture. Potential was controlled with a Tacussel ASA 4BT potentiostat. Traction was applied to the wires with a modified motor-driven Hounsfield Tensometer.

Procedure

For traction experiments, the wire was fitted in the cell, the cell fixed to the Tensometer, and a stream of purified nitrogen passed into the cell, which was meanwhile slowly heated. After about ¼h, the condenser was partly removed and the boiling nitrate solution was poured into the cell. The condenser was then replaced, the small bubbler was filled with the solution, the salt bridge filled with saturated KCl, and the reference electrode connected to the circuit. After waiting for 5min, to allow the solution to reach the working temperature, the potentiostat was connected and the desired potential was applied to the specimen. After a further 40min, the motor of the Tensometer was switched on, and the wire was pulled. This lapse of 40min was kept constant in all the traction experiments; it allowed a reasonable time for de-aeration of the solution, and for the anodic current on the specimen to fall to an almost stationary value, with the formation of a magnetite film on the surface.

At the end of a run, the cell was dismantled, the specimen was washed with water and alcohol, and dried with hot air. The portion of specimen that had been in contact with the solution was cut and stored in a desiccator, or mounted for observation.

The reported potentials have been converted to the normal hydrogen scale (nhe) by adding 0·242V to the value vs. the saturated calomel electrode, which was at room temperature; no attempt was made to eliminate or measure liquid-junction or thermal emfs.

The reported strain rates are calculated from the total extension rate and the length of heated wire within the cell, which suffers very nearly the whole of the measured extension: the approximations involved will be considered elsewhere.[19]

RESULTS AND INTERPRETATION

Corrosion potential of static mild steel

Preliminary experiments were made to examine the influence of time of exposure and of oxygen content on the "corrosion" potential of isolated and static mild steel in several hot nitrate solutions. Figure 2 shows a typical potential–time curve, and Table 1 collects the results of "rest" potentials after 2h, when they had become approximately constant. During these tests, the specimens became covered with films of oxide, probably magnetite, either thick enough to appear black, or thin enough to show interference colours, except at high pH. If the film is porous to solution, the

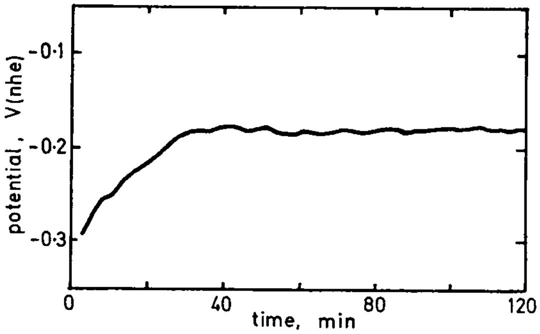


FIG. 2. Typical potential–time curve.
Mild steel in 4N $NaNO_3$, pH 3·4 (at 25°C), 102°C.

TABLE 1. CORROSION POTENTIAL OF STATIC MILD STEEL AFTER 2h EXPOSURE IN HOT NITRATE SOLUTIONS

Solution	Initial pH	Potential (under N_2) [V(nhe)]	Potential (under O_2) [V(nhe)]	Behaviour under stress
4N $NaNO_3$ + HNO_3	3·4	− 0·18	− 0·10	s.c.c.
4N $NaNO_3$	5·2	− 0·25		s.c.c.
4N $NaNO_3$ + NaOH	10·3	− 0·27		Does not crack
4N $Ca(NO_3)_2$	3·7	− 0·12		s.c.c.
4N $Ca(NO_3)_2$ + $Ca(OH)_2$	11·3	− 0·25	− 0·21	Does not crack
4N NH_4NO_3 + NH_4OH	7·4	− 0·12		s.c.c.

corrosion process can be represented schematically by Fig. 3(a), in which the over-all anodic reaction is

$$\tfrac{3}{4}\,\mathrm{Fe} + \mathrm{H_2O} = \tfrac{1}{4}\,\mathrm{Fe_3O_4} + 2\mathrm{H^+} + 2e^-.$$

At the cathode, probable reactions are

$$\mathrm{NO_3^-} + \mathrm{H_2O} + e^- = \mathrm{NO_2} + 2\mathrm{OH^-},$$

$$2\mathrm{NO_2} + \mathrm{H_2O} = \mathrm{NO_3^-} + \mathrm{NO_2^-} + 2\mathrm{H^+},$$

or over-all,

$$\mathrm{NO_3^-} + \mathrm{H_2O} + 2e^- = \mathrm{NO_2^-} + 2\mathrm{OH^-}.$$

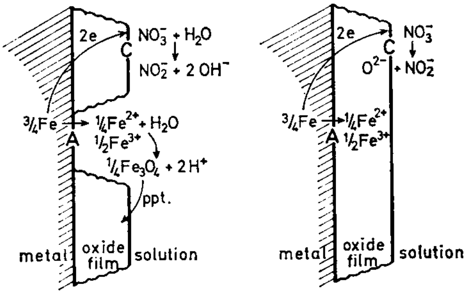
Consequently, the electrolyte solution will tend to become more acid at any points that are especially anodic, and more alkaline at any points that are especially cathodic, although since the film formed is, *when static*, fairly uniform and not very porous, the anode and cathode reactions are very much intermingled and the over-all change in solution pH may not be marked, the main entities produced by corrosion being at all times magnetite and nitrite ion. Indeed, if a *perfect* magnetite film is formed, always in close contact with the metal, the process is as represented schematically in Fig. 3(b), with the anodic reaction

$$\tfrac{3}{4}\,\mathrm{Fe} = \tfrac{1}{4}\,\mathrm{Fe^{2+}_{film}} + \tfrac{1}{2}\,\mathrm{Fe^{3+}_{film}} + 2e^-$$

at the metal/film interface, and the cathodic reaction

$$\mathrm{NO^-_{3\,Sol.}} + 2e^- = \mathrm{NO_2^-} + \mathrm{O^{2-}}_{\mathrm{film}}$$

at the film/solution interface. It is likely that this solid-state process takes place along with the solution process noted in Fig. 3(a).



(a) (b)

FIG. 3. Formation of magnetite by reaction of iron with nitrate solutions: (a) by precipitation process, (b) by solid-state process.

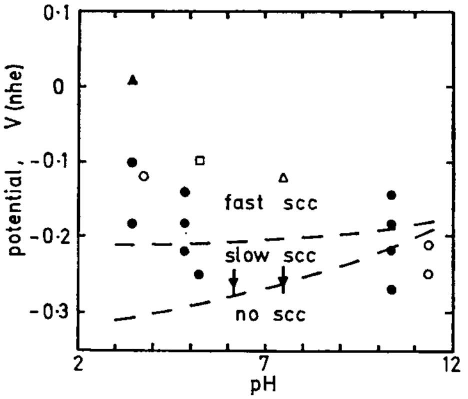


FIG. 4. Behaviour of stressed mild steel in hot nitrate solutions of various initial pH and different potentials.

●, $NaNO_3$ ▼, NH_4NO_3 (Parkins)[10]
○, $Ca(NO_3)_2$ ▲, $LiNO_3$ (Parkins)[10]
△, NH_4NO_3 □, $NaNO_3$ (Parkins)[10]

Figure 4 is a plot of the results of Table 1 as rest potential vs. initial pH at room temperature. Some results of Parkins and Usher[10] are included. We note that the rest potential becomes more positive with decrease of initial pH and in the series of nitrates Na^+—Ca^{2+}—NH_4^+. The rate of crack propagation in nitrate cracking of mild steel is known to increase with decrease of initial pH of the solution and with change of cation in the same series. More positive rest potential indicates a higher c.d. for the anodic process if this remains qualitatively unchanged, or a stimulation of the cathodic process. The results are therefore in harmony with the hypothesis that crack propagation proceeds by anodic dissolution. Stimulation of the cathodic process of NO_3^- reduction by decrease of pH is well known, and the influence of Ca^{2+} and NH_4^+ is probably to limit the rise of pH at the cathode zones.

Interrupted traction experiments

A preliminary series of interrupted traction experiments was made mainly in 4N calcium nitrate solutions of pH 3·7, at a potential of — 0·10V(nhe). Several strain rates were used and the traction was interrupted once or twice before the wire fractured. In each case the variations of the current were recorded. Some experiments were made maintaining the load after interrupting the traction, and in others the load was removed during the interruption. No difference was observed between the results of the two procedures.

Figure 5 shows a typical result. When the potentiostat was switched on, there was a high current flow, which decreased with time; after some 30min the current reached a quasi-stationary, small value. The process is typically one of potentiostatic growth of an oxide layer; at the end of the experiments a black layer was visible on the surface of the specimens. When the passivation condition reached by the specimen was disturbed by traction of the metal, the current increased rapidly. When the traction was stopped, the current decreased again, with the film re-forming just as before

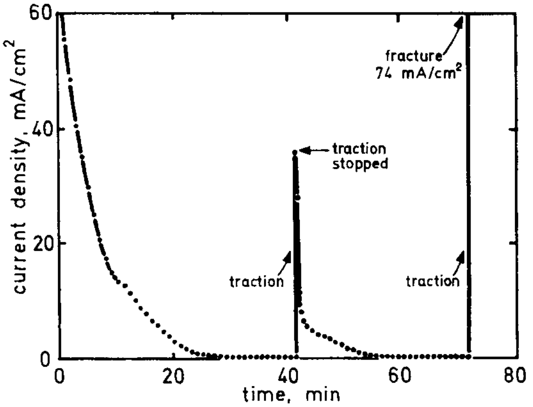


FIG. 5. Potentiostatic formation of magnetite film on mild steel anode in hot calcium nitrate solution, and influence of traction.
4N $Ca(NO_3)_2$, pH 3·7 (at 25°C), 102°C, e_H – 0·10V.
Strain rate 28%/min.

yielding. These results indicate that at the beginning there is oxide-film formation, and that, during traction, the current increases because of the fracture of the film.

The current increase during traction cannot be attributed to the mechanical opening of cracks in the metal, as suggested by Long and Uhlig[14] for a similar case; metallographic examination of wires pulled at high strain rates and showing high anodic c.ds. revealed no detectable cracks—the high c.ds. are found *before* the cracks have had time to grow to visible depths. "Cracks" appeared only when slow strain rates were applied, so that relatively long periods were available for their propagation. They are not the cause of the current increase, but are propagated by the current, concentrated at their rapidly yielding advancing edges.

Constant strain-rate experiments

Figure 6 shows typical current–time curves for mild steel strained in 4N calcium nitrate solutions pH 3·7, at 102°C. The potential was kept constant at — 0·10V(nhe) (about 20mV higher than the rest potential of mild steel in the same solution, Table 1), and four different strain rates were applied. When traction was started the current increased with time, the rate of increase remaining almost constant until the wire broke. The rate of current increase was higher for higher strain rates, and the current density at fracture was almost the same for each strain rate. All the experiments were repeated several times; in each case the current density after passivation before traction was about 0·17mA/cm^2, and it reached nearly 100mA/cm^2 at the time of fracture.

The current-density/strain diagram in Fig. 7 is based upon the data in Fig. 6. The data in the c.d./time diagram approach one common line in the c.d./strain diagram. Thus for the strain rates here used, the c.d. is proportional to the amount of strain that the specimens have undergone. This indicates that once a fissure is formed in the brittle oxide film, and fresh metal is exposed to the solution, the current flowing through the fissure remains constant until the wire breaks; the process of film healing is slow or negligible while the metal is yielding.

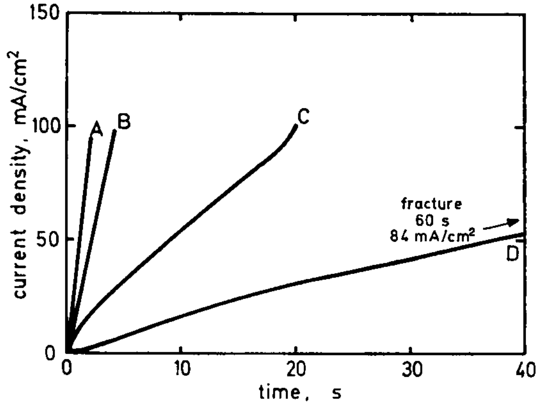


FIG. 6. Potentiostatic current-density/time curves for oxide-covered mild steel yielding at different strain rates in hot calcium nitrate solution.
4N $Ca(NO_3)_2$, pH 3·7 (at 25°C), 102°C, e_H – 0·10V.
Strain rate: A, 307%/min; B, 154%/min; C, 31%/min; D, 8%/min.

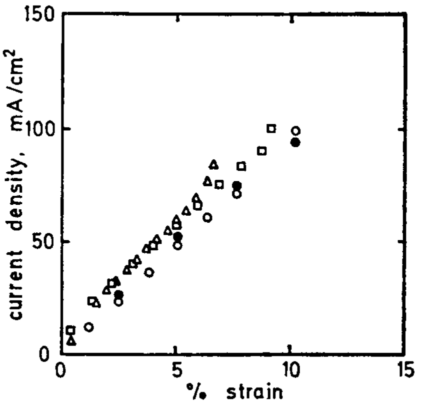


FIG. 7. Variation of current density with % strain (data from Fig. 6.)
4N $Ca(NO_3)_2$, pH 3·7 (at 25°C), 102°C, e_H –0·10V.
Strain rate: ●, 307%/min; ○, 154%/min; □, 31%/min; △, 8%/min.

Similar experiments were performed in sodium nitrate solutions. Figure 8(a–f) shows c.d./time curves for such solutions at two pH values and for several potentials. Figure 9(a–f) shows the corresponding c.d./strain diagrams; again, the data for different strain rates approximate one common line in the c.d./strain diagrams, except in Fig. 9(d, e), which will be considered later.

The potentials used for the data in Figs. 7, 9(a) and 9(d) are slightly more positive than the rest potentials of the same mild steel in the same solutions, Table 1. It is well known that increasing the electrode potential in the range — 0·30 to — 0·15V(nhe) of mild steel in nitrate solutions[8,9] shortens the time to fracture. Correspondingly, Fig. 9(a) and (b) shows that an increase in potential from — 0·22 to — 0·18V(nhe) produces an increase of about four times in the c.d. at equal percentage strain.

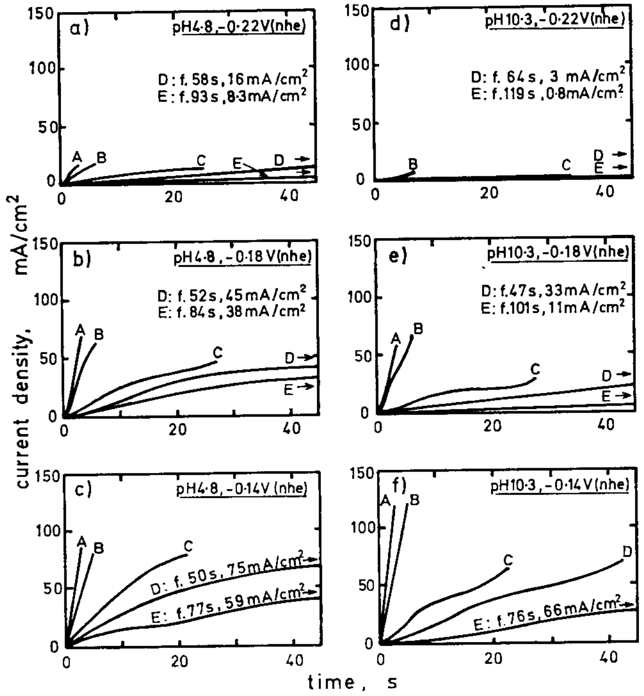


FIG. 8. Potentiostatic c.d./time curves for oxide-covered mild steel yielding at different strain rates in hot sodium nitrate solution.
4N $NaNO_3$, 102°C.
Strain rate: a, 307%/min; b, 154%/min; c, 31%/min; d, 15%/min; e, 8%/min.

For the same amount of deformation, the c.ds. were higher in calcium nitrate than in sodium nitrate solutions, and higher at pH 4·8 than at pH 10·3. These results are in harmony with the classification of stress corrosion cracking aggressiveness of nitrate solutions suggested by Parkins and Usher,[10] if cracking is indeed produced by anodic dissolution.

Figure 9(d) shows that for mild steel in sodium nitrate solutions at pH 10·3 only at the highest strain rates does the yielding affect the current density. It is probable that at pH 10·3, local acidity does not develop at the anodes, and consequently oxide-film healing can occur relatively rapidly even on fresh metal exposed by the fissuring of the oxide film produced by traction. Only at higher potentials will the rate of anodic dissolution increase and thus favour the formation of localized acidity. There will then be competition between the healing process and the dissolution attack, and results such as those given in Fig. 9(e) are not unexpected. Still further increase in potential may well make dissolution predominant over the healing, so that behaviour as shown in Fig. 9(f) occurs. This last figure, compared with Fig. 9(c), indicates that the stress corrosion cracking of mild steel in sodium nitrate solution at pH 10·3 should be as rapid as that at pH 4·8, provided that the potential is raised to — 0·14V(nhe).

From the c.d./strain diagrams an approximate calculation of the c.d. on bare metal, or in the cracks when they occur, can be made. It is assumed that the c.d.

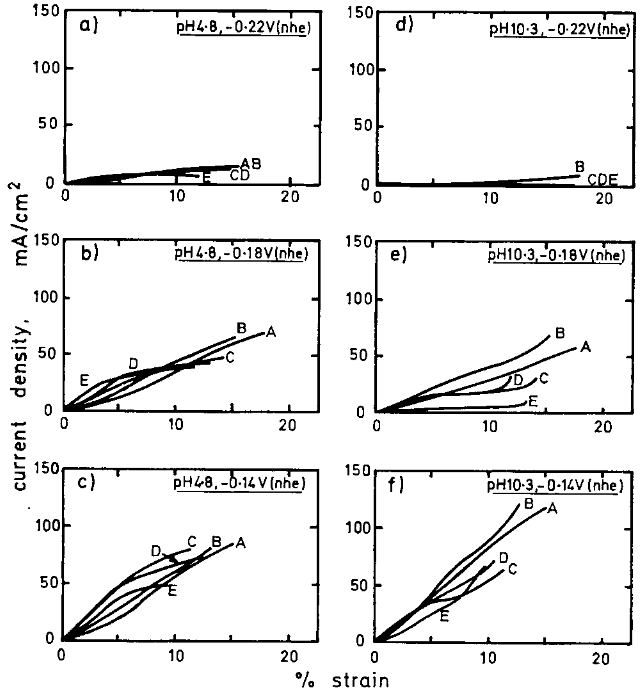


FIG. 9. Variation of c.d. with % strain at different strain rates, pH and potential. 4N $NaNO_3$, 102°C.
Strain rate: a, 307%/min; b, 154%/min; c, 31%/min; d, 15%/min; e, 8%/min.

flowing through the unbroken film or through its pores is not affected by the traction, so that it remains at the low value measured just before traction. Since this initial c.d. is more than two orders of magnitude smaller than the total apparent c.d. measured during traction, it can be ignored. Figure 6 shows that in calcium nitrate solutions after 10 per cent strain, when ~ 5% of the total area is new exposed metal,* the c.d. is 100mA/cm². Thus the c.d. on the fresh metal is of the order of 2000mA/cm². Results of the same calculation for other experiments are collected in Table 2.

Metallographic examination of the yielded specimens showed that the (intergranular) length of the cracks was proportional to the time of traction of the wire. At high strain rates it was difficult to distinguish crack penetration from surface irregularities of the yielded specimen. For slower strain rates, allowing longer exposures, the penetrations could easily be measured; typical micrographs are shown in Fig. 10. Values of the c.d. required to propagate cracks by anodic dissolution were calculated from the penetration rates found in specimens strained at 8%/min, and are given in Table 2. It may be seen that the measured anodic c.ds. are quite sufficient to account for the measured penetration rates.

*When a wire of length l_0 extends to length l, it shrinks circumferentially, so that the net increase in its area is easily shown to be $1 - (l_0/l)^{\frac{1}{2}}$.[20] Thus for small linear strains, %(increase in area) ≈ (½% strain).

TABLE 2. CURRENT DENSITY AT NEW EXPOSED METAL IN FISSURES IN THE OXIDE FILM PRODUCED BY TRACTION, COMPARED WITH CURRENT DENSITY REQUIRED TO ADVANCE "CRACKS" IN THE METAL AT MICROSCOPICALLY MEASURED RATE

Solution	Potential [V(nhe)]	Initial pH	C.D. measured (A/cm^2)	Time to fracture (s)	Average depth of "cracks" at fracture (μm)	C.D. required (A/cm^2)
4N $Ca(NO_3)_2$	− 0·10	3·7	2·01	35	25	2·08
4N $NaNO_3$	− 0·14	4·8	1·48	77	32·5	1·21
4N $NaNO_3$	− 0·18	4·8	0·80	84	20	0·69
4N $NaNO_3$	− 0·22	4·8	0·26	93	5	0·16
4N $NaNO_3$ + NaOH	− 0·14	10·3	1·32	76	19	0·73

DISCUSSION

The present results show that when mild steel anodes are deformed in tension in hot calcium and sodium nitrate solutions, at controlled potentials of up to 100mV above the "natural" corrosion potential, a considerable increase in the anodic c.d. is observed, which is approximately proportional to the amount of strain and independent of the strain rate. The results are different from those obtained by Hoar and Scully[3] for stainless steel in hot chloride solutions, where the measured anodic c.d. shows a very rapid rise on yielding and then remains almost constant, because the whole area of the metal surface at once becomes very active during yielding. In the present case the yield-assisted anodic dissolution results from the fracture of the oxide film over a relatively small area, around 5 per cent of the total.

The correlation between the c.d. at the breaks of the oxide film and the rate of crack propagation strongly indicates that the cracks propagate entirely by electrochemical dissolution, without the contribution of any process of mechanical rupture of the metal. The yield-assisted current increase and the rate of crack propagation are similarly affected by variables such as type of solution, electrode potential and pH; this gives further support to the hypothesis of crack propagation by the anodic dissolution of yielding metal at the crack advancing edge.

In controlled-potential experiments in 5N *ammonium* nitrate solutions, Sklarska-Smialowska[13] found rapid stress corrosion cracking between −0·28 and −0·10V(nhe), but she observed no oxide formation in potential-sweep polarization experiments below "about − 0·1V". However, the rate of the potential sweep towards the positive direction was 20mV in 10s; it is probable that had the potential been maintained at, say, − 0·15V(nhe) for some time, a fall in anodic c.d. accompanied by visible oxide formation would have been observed. As our Fig. 4 shows, even at − 0·10V(nhe) the fall of c.d. and the growth of the oxide layer continues for well over 1000s in 4N calcium nitrate solution. It is of course possible that stress corrosion cracking of mild steel held at − 0·28 to − 0·10V(nhe) in ammonium nitrate solutions occurs without the formation of oxide, but we think it likely that oxide formation begins at potentials around − 0·25V(nhe) (although of course more slowly than at − 0·10V(nhe)). In our experiments in 4N sodium nitrate at pH 10·3, no film could be observed at −0·22V(nhe) and there was no yield-assisted anodic dissolution, Fig. 8(d), or stress

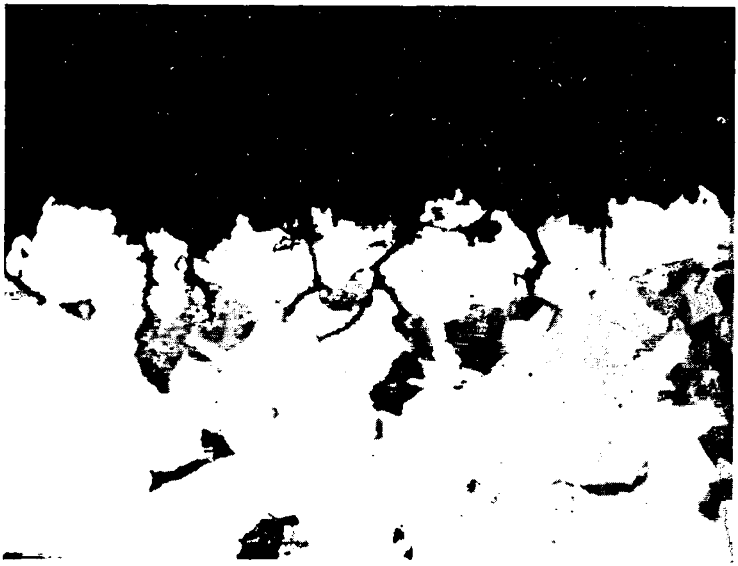


FIG. 10. Stress corrosion cracks (partly transgranular) in mild steel. 4N $Ca(NO_3)_2$, pH 3·7 (at 25°C), 102°C, e_H − 0·10V. (× 400)

corrosion cracking; but at − 0·18 and especially at − 0·14V(nhe), the black film was formed and yield-assisted anodic dissolution, Fig 8(e, f), and stress corrosion cracking, occurred. The transition in this solution appears to be at about − 0·18V(nhe).

We think that the present experiments, and the earlier results of other workers, support a mechanism for the stress corrosion cracking of mild steel in hot nitrate solutions, either under "isolated" conditions or at anode potentials up to some 100mV above the corrosion potential, that can be summarized as follows. It is, of course, based on the early ideas of Logan,[8,17] but constitutes an extension of them.

1. Oxide film grows by anodic action on the metal surface; on isolated metal, the concomitant cathodic process is nitrate reduction, accompanied by oxygen reduction if the solution is aerated. Under sufficient load, brittle fractures appear in the oxide because of local microscopic strain of the ductile metal beneath it.

2. At such a fracture, repair begins by rapid anodic conversion of the exposed metal to fresh oxide. If the fracture is (as is likely) coincident with a grain boundary in the metal, the anodic conversion is especially rapid—Parkins and Usher[10] showed that grain-boundary trenching is a preferential mode of anodic corrosion.

3. At a grain-boundary trench, the stress intensification is sufficient to cause further and more rapid yielding of the exposed metal, so that the new oxide formed is not well adherent and does not stifle further anodic attack.

4. The "crack"—better termed a "fissure"—now propagates by rapid anodic dissolution of its yielding advancing edge, while its static sides become protected by being converted into adherent oxide. Since the fissure thus remains "sharp", it continues to propagate unless either (a) the stress is diminished, (b) the anodic process is prevented by a lowering of the potential, i.e. by cathodic protection.

It is still not possible to be certain whether the greatly enhanced anodic reaction of yielding metal is caused solely by removal of oxide film and inability to reform it rapidly enough or with sufficient adhesion, or whether it is also assisted by a mechanochemical stimulation of the actual anodic process; however, in special experiments we could find no mechanochemical effect in oxide-free mild steel strained in hot nitrate solutions. Moreover, at more positive anode potentials, + 0·2–0·8V(nhe), Sklarska-Smialowska[13] found a region of evident partial anodic passivity, with oxide/ film formation, accompanied again by rapid stress corrosion cracking; whereas at still higher potentials there was almost complete passivation by a *very thin* compact oxide film and little or no stress corrosion cracking, evidently because under such conditions a broken film can reform very rapidly even on yielding metal.

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