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FACTORS CONTROLLING NITRATE CRACKING OF MILD STEEL*

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Abstract

Nitrite and hydroxide ions inhibit the growth of nitrate stress corrosion cracks in mild steel. Crack growth measurements showed that sufficient concentrations of nitrite and hydroxide ions can prevent crack growth; however, insufficient concentrations of these ions did not influence the Stage II growth rate or the threshold stress intensity, but extended the initiation time. Stage III growth was discontinuous.

Oxide formed in the grain boundaries ahead of the crack tip and oxide dissolution (Stage II) and fracture (Stage III) are the proposed mechanisms of nitrate stress corrosion crack growth.

Introduction

Mild steels are susceptible to stress corrosion cracking (SCC) by nitrate solutions, as well as caustic (Lees, 1973) and carbonate (Sutcliffe, 1972) solutions. The cracking mode in these solutions is intergranular (Parkins, 1969) and thought to be due to pre-existing active paths related to the compositional differences at grain boundaries (Parkins, 1972). SCC can be inhibited by adding NO_2^-, OH^-, and some organic chemicals to the bulk solution (Mazille, 1972).

This study included (1) the determination of the concentrations of NO_2^- and OH^- required to inhibit SCC in 5M $NaNO_3$ solutions, (2) an evaluation of relative influences of Ca^{2+}, Na^+, and NH_4^+ ions on crack propagation, and (3) the study of the metallography of crack growth. Results are discussed in terms of crack tip chemistry, role of stress, and intergranular oxides. The suggested mechanism of nitrate stress corrosion is the anodic dissolution and fracture of grain-boundary oxide.

Experimental Procedure

A 285 Grade B mild steel (composition given in Table I) was machined into 1.9-cm (0.75-in.)-thick wedge-opening loaded (WOL) (Novak, 1969) and compact tension (CT) (Wessel, 1969)specimens that were modified with side grooves. Specimens without side grooves were used in early experiments, but deep tunneling of the stress corrosion cracks occurred. Grooves eliminated the tunneling. The stress intensity K is known as a function of the load P and crack size a for both specimens.

The specimens were precracked by fatigue at a maximum stress intensity of 50% of the initial stress intensity that was applied during the test. Most specimens were loaded so that the crack opening displacement was equivalent to an apparent stress intensity of 49.5 MPa $\sqrt{m}$ (45 ksi $\sqrt{in.}$). Due to the large plasticity of mild steel, the load required to achieve an actual stress intensity of 49.5 MPa $\sqrt{m}$ (45 ksi $\sqrt{in.}$) could not be achieved. However, as the crack grows in the WOL specimen, the stress intensity decreases, and the error due to plasticity also decreases. The CT specimens were loaded assuming linear elastic behavior.

Loaded specimens were exposed to the NO_3^- solutions containing various amounts of NO_2^- and OH^- (all prepared from reagent-grade chemicals), at constant temperature. The influence of Na^+, Ca^{2+}, and NH_4^+ ions on crack velocity was also determined. Periodically the WOL specimens were removed from the solution, and crack lengths were measured as a function of time. The crack length in the CT specimen was considered to be approximately proportional to the logarithm of the crack opening (Roberts, 1969).

Results

The presence of NO_2^- and/or OH^- in NO_3^- solutions can prevent SCC growth. Figure 1 maps the concentration zones in which cracks either grow or do not grow within 1000 hours in a 5M $NaNO_3$ solution at 368 K. Sufficient concentration of either ion can prevent crack growth; these concentrations are 1.8M NO_2^- and 1.25M OH^-. NO_2^- and OH^- act synergistically to prevent cracking; that is, if both ions are present, SCC can be prevented by a solution containing less than 1.8M NO_2^- and less than 1.25M OH^- (Figure 1).

Generally, the dependence of SCC velocity on stress intensity proceeds in three stages of crack growth (Wiederhorn, 1966). Crack growth measurements on self-loaded WOL specimens revealed only Stage II growth, and showed that a threshold stress intensity for crack growth, K_{scc}, existed. An initiation period, even though the specimens were precracked, was usually observed (Figure 2). After the initiation period, crack growth was linear with time, and velocity was independent of K, until it stopped abruptly at K_{scc} (Figure 3). Constant load, compact tension specimens had an incubation period and showed more rapid discontinuous crack growth at higher stress intensities (Figure 3). Therefore, nitrate cracking of mild steel shows Stages II and III crack growth and a K_{scc} (Figure 3) but not a well-defined Stage I.

TABLE I

Composition of A 285 Grade B Mild Steel

Element	Wt %
C	0.12
Mn	0.49
P	0.01
S	0.015

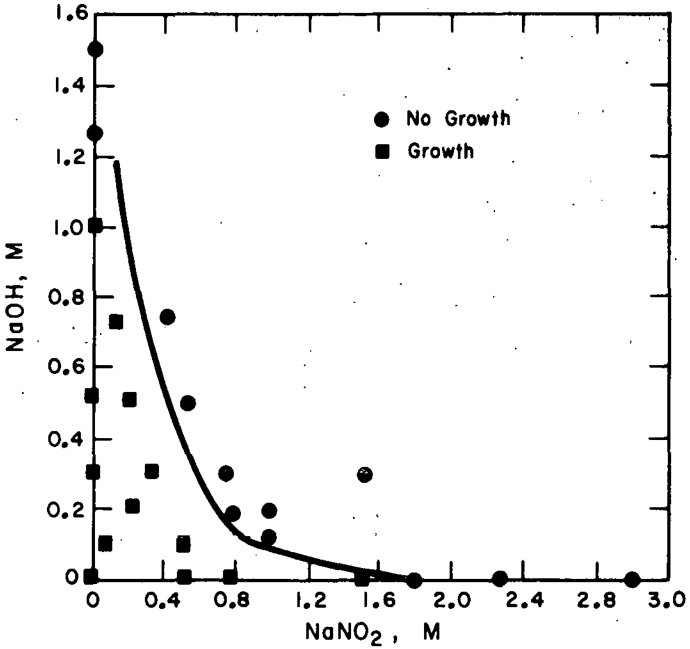


FIGURE 1. Influence of Sodium Nitrate and Sodium Hydroxide on Stress Corrosion Cracking of A 285 B Steel in 5M $NaNO_3$ at 368 K

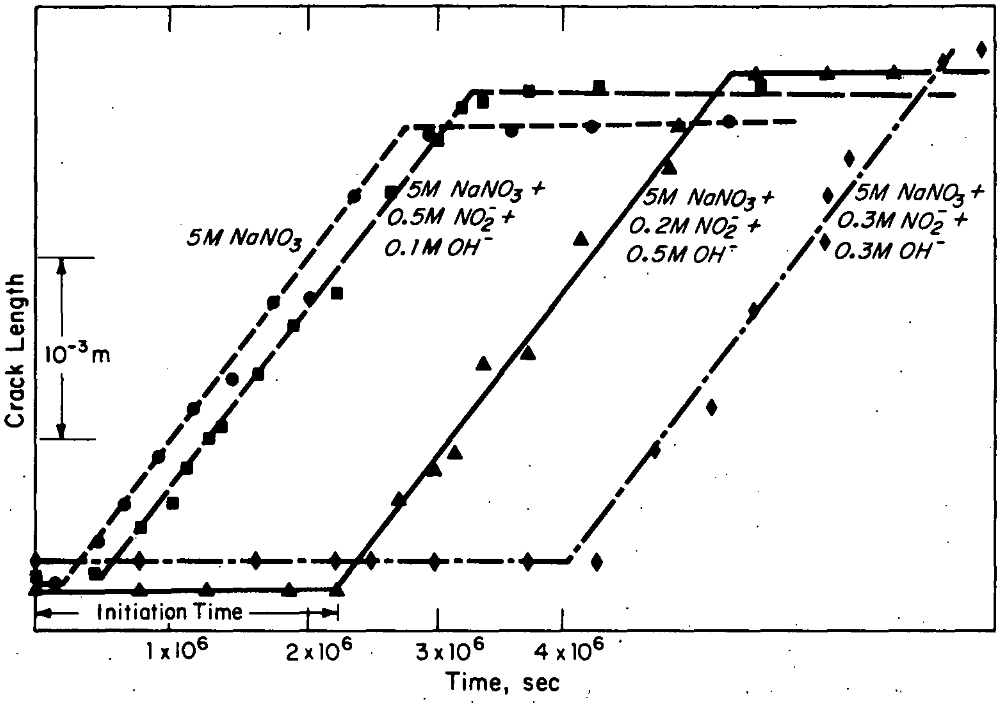


FIGURE 2. Crack Size as a Function of Time for 5M $NaNO_3$ Solutions Containing Various Concentrations of NO_2^- and OH^- Ions

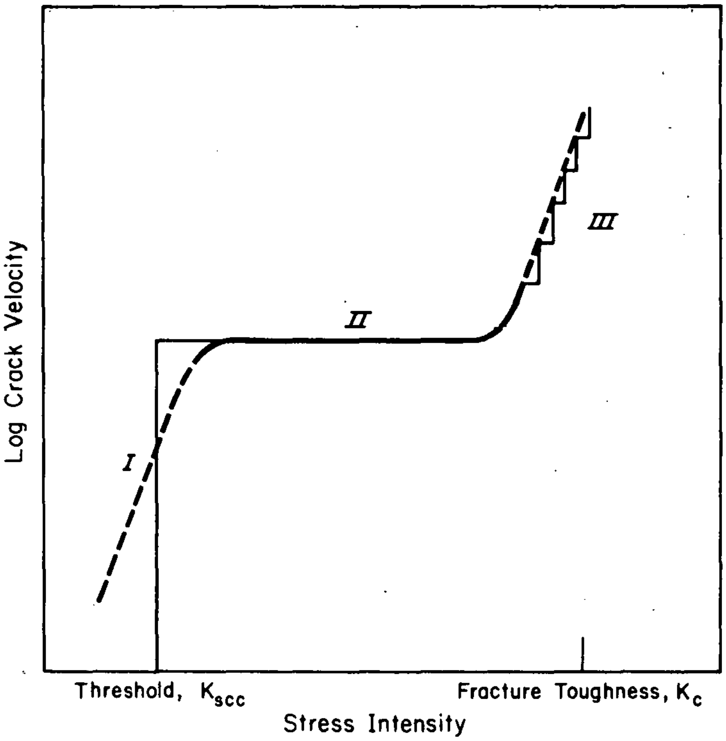


FIGURE 3. Dependence of Nitrate Stress Corrosion Crack Velocity on Stress Intensity

Initiation times for the WOL specimens are listed in Table II for various bulk solution compositions. The data, although scattered, suggest a correlation of initiation time with composition; generally, the greater the concentration of the inhibitor, the longer the initiation time. However, additional data would be required to show a statistically significant dependence of initiation time on bulk solution composition.

Crack velocity was measured in solutions of $Ca(NO_3)_2$, $NaNO_3$ (pH = 6.8), $NaNO_3$ (pH = 3.5), and NH_4NO_3, all 5M in NO_3^- at 368 K (95°C). Except for the NH_4NO_3 solution, all solutions produced the same crack velocity and K_{scc}, within experimental error; crack velocity was independent of the NO_2^- and OH^- concentration. Figure 4 shows the crack growth as a function of time for the $Ca(NO_3)_2$ and the NH_4NO_3 solutions. Table III gives the values of crack velocity, K_{scc}, and initial and final pH of the bulk of the solution for the other cation solutions.

In brief, the SCC velocity is independent of ionic concentrations of either NO_2^- or OH^-, and of Ca^{2+} of Na^+. But crack velocity is different in NH_4NO_3 than in any of the other solutions tested: the initial crack velocity is twice and the second stage is one-half that observed in the Na^+ or Ca^{2+} solutions (Figure 4).

The apparent threshold stress intensity, K_{scc}, for all the compositions that caused crack growth was approximately 32 MPa $\sqrt{m}$ (29 ksi $\sqrt{in.}$). Specific values of K_{scc} for the various solutions are listed in Tables II and III.

Discussion

Crack Growth Inhibition by NO_2^- and OH^-

NO_2^- and OH^- are known to inhibit NO_3^- stress corrosion of mild steel (Parkins, 1969 and Mazille, 1972) and high-strength steel (Baker, 1972). The mechanisms of cracking are thought to be anodic dissolution (stress assisted or not) (Hoar, 1970) in mild steel and hydrogen embrittlement in high-strength steel (Baker, 1972 and Okado, 1976). Even though the mechanisms are probably different, the map of cracking and no-cracking zones is the same for the work of Baker (1972) on high-strength steel and these data on mild steel, Figure 1.

Baker and Singleterry (1972) discuss their results in relation only to the initiation phase, because their smooth U-bend specimens were most sensitive to this phase of SCC. The rough correlation of initiation time with composition (Table II) suggests that the bulk solution composition influences the initiation time. But the insensitivity of crack velocity and K_{scc} to bulk solution composition shows clearly that the NO_2^- and OH^- concentrations determine only whether a stress corrosion crack will

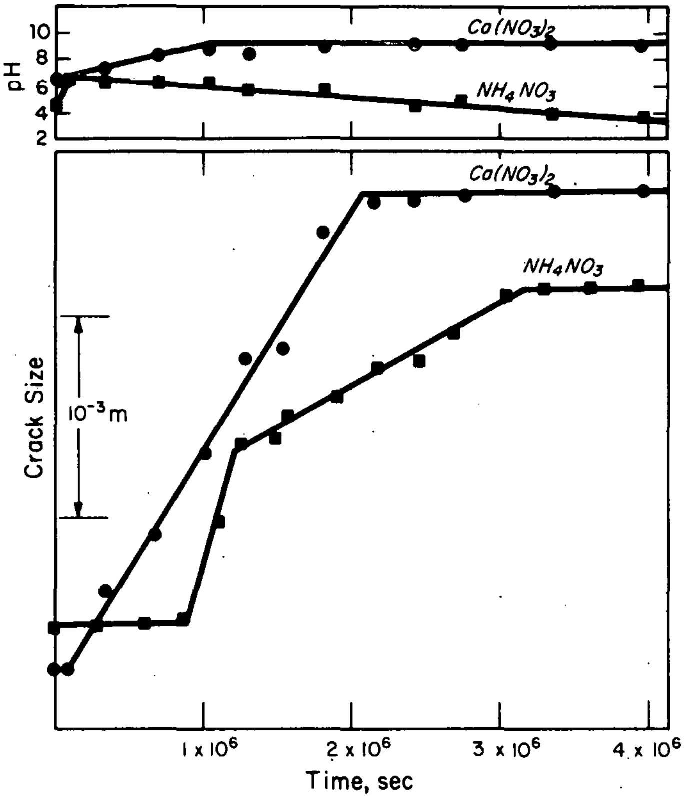


FIGURE 4. Crack Size and pH as a Function of Time in $Ca(NO_3)_2$ and NH_4NO_3 at 368 K, 5M NO_3^-

TABLE II

Initiation Time and Threshold Stress Intensity for Various Amounts of NO_2^- and OH^- in 5M $NaNO_3$ Solutions at 368 K

NO_2^-, M	OH^-, M	Initiation Time, hr	Threshold Stress Intensity (K_{scc}), MPa $\sqrt{m}$
-	-	75-200	31
0.5	-	200	31
0.75	-	400	31
1.5	-	600	36
3.0	-	∞	∞
-	0.3	75	27
-	0.5	400	33
-	1.0	350	30
-	1.2	∞	∞
0.2	0.5	615	30
0.2	0.2	525	33
0.3	0.3	1100	35
0.5	0.1	150	29

TABLE III

Initiation Time, Threshold Stress Intensity, Initial and Final pH of Bulk Solution, and Crack Velocity for 5M NO_3^-

Cation	Initiation Time (t_i), hr	Threshold Stress Intensity (K_{scc}), MPa $\sqrt{m}$	pH		Crack Velocity (da/dt), m/sec
			Initial	Final	
Na^+	25-200	31	3.6	9.8	8.4×10^{-6}
Ca^{2+}	25	31	6.0	8.8	10.5×10^{-6}
NH_4^+	24-225	33	4.2	6-3.6[a]	3.5×10^{-6}

a. See Figure 4.

initiate or not; these ion concentrations do not affect the kinetics of propagation. Therefore, since the growth mechanism is unaffected by bulk solution composition, local crack tip conditions must control growth.

The initiation phase of crack growth no doubt involves a balance between two anodic reactions that can occur on the crack surfaces. The possible reactions are dissolution of iron and the formation of iron oxide. Therefore, to act as inhibitors, the NO_2^- and OH^- must influence the formation of oxide. That OH^- decreases the aggressiveness of solutions toward the oxide on steel is well known. Therefore, since the crack tip solution must be the same as the bulk solution, at least initially, NO_3^- solutions containing OH^- would be less aggressive towards the oxide than only NO_3^- solutions. When NO_2^- is present, a strong protective oxide forms faster than when it is not present (Ambrose 1972).

Another possible mechanism of cracking inhibition is that the cathodic reaction(s) would be inhibited by OH^- and NO_2^-. Hoar and Galvele (1970) suggested that for dissolution of iron the cathodic reaction would be

$$NO_3^- + H_2O + 2e \rightleftarrows NO_2^- + 2OH^- \qquad (1)$$

Therefore, both NO_2^- and OH^- would inhibit the cathodic reaction and therefore the anodic one also. For the solid-state formation of iron oxide they suggested the reaction

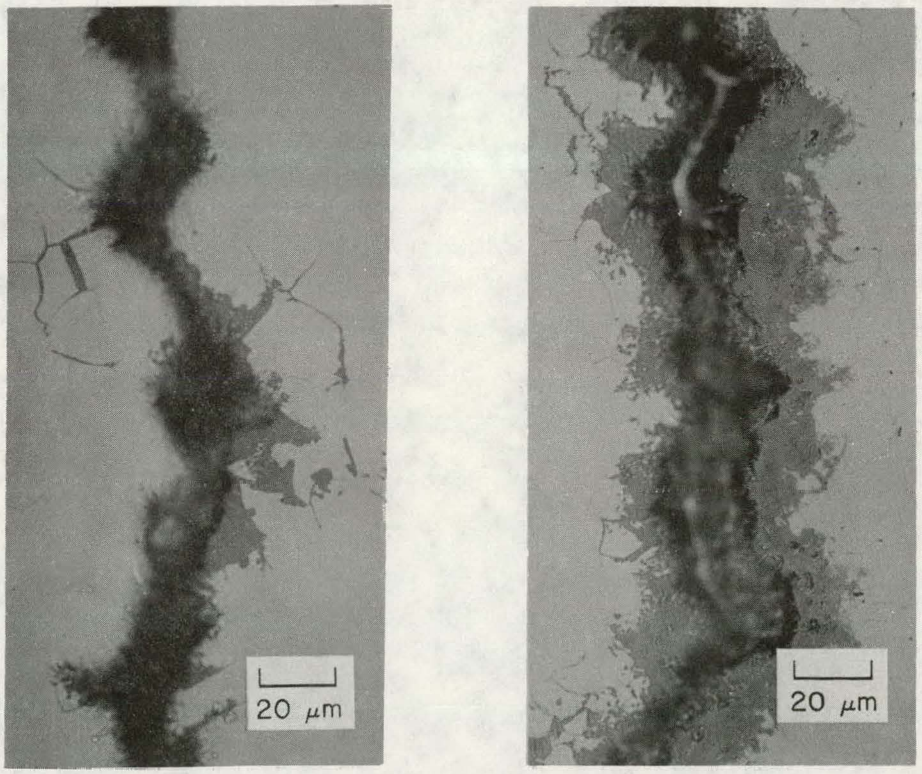
$$NO_3^- + 2e^- \rightleftarrows NO_2^- + O^{2-} \qquad (2)$$

and the inhibition of this reaction by the prior presence of NO_2^- is obvious.

Influence of Cation on Crack Growth

Parkins (1969) concluded in a recent review that the aggressiveness of nitrate SCC depended on the pH of the solution. Thus, nitrate salts with the more acid cations would be more aggressive than those of high pH. Solutions of $Ca(NO_3)_2$ caused the same crack velocity as did $NaNO_3$ (initial pH 6.8 or pH 3.6). The pH of bulk solutions changed relatively quickly (Figure 4). And, as in the case of solutions containing NO_2^- or OH^-, the crack velocity is unaffected by the particular cation in the bulk solution. In spite of the observed insensitivity of crack kinetics to pH or cationic species, Parkins' conclusion is probably still correct for smooth specimens that require initiation of a crack because the bulk solution would affect the kinetics of pit or crack nucleation.

However, the results obtained with NH_4NO_3 were significantly different (Figure 4) than those obtained with Na^+ or Ca^{2+}. The initial crack velocity in NH_4^+ solutions was twice that in the Na^+ or Ca^{2+} solutions, but after 100 hours it was only one-half that in the Na^+ and Ca^{2+} solutions. These results are analogous to those of Lees and Lockington (1970) who found that NH_4NO_3 causes intergranular corrosion, while nitrates of Ca^{2+} and Na^+ do not unless assisted by stress or by an imposed potential (Parkins, 1962). The initial high velocity may be related to the ability of NH_4NO_3 to cause intergranular corrosion. During the first 100 hours, high crack velocity probably results from the NH_4^+ - Fe complex formation (Parkins, 1972; Smialowski, 1964); after about 100 hours, the large quantity of oxide, Figure 5, possibly decreases the rate of anodic dissolution.



a. b.

FIGURE 5. Comparison of Oxide Formed in the Crack due to (a) $NaNO_3$ and (b) NH_4NO_3

The insensitivity of crack velocity to concentrations of Ca^{2+}, Na^+, NO_2^-, and OH^- emphasizes the role of the crack tip solution chemistry in the process of nitrate SCC. Hoar (1961) suggested in 1937 that the conditions within a crack or crevice may reduce the pH within the crack. Brown and co-workers (Sandoz 1970) were the first to show that the pH of the crack tip solution was indeed very different from that of the bulk solution.

The insensitivity of K_{scc} to bulk solution chemistry follows if the crack tip chemistry is independent of the bulk solution and controls crack growth.

The Role of Stress

The role of stress in nitrate cracking has not been clear. But, since the stress is applied to the WOL specimens before exposure to the nitrate solution, most of the plastic strain occurs prior to exposure. Exposure of CT specimens before or after application of the load made no difference in initiation times. The initiation times were up to hundreds of hours during which active strain was not occurring. Therefore, fracture of the oxide film by deformation to expose new metal that corrodes more rapidly does not seem necessary.

Apparently, the initiation time is the time required for the crack tip chemistry to be established (become acid), and for oxide to form and penetrate the grain boundaries. Then the role of stress is to cause the crack opening that allows the critical crack tip solution to be established.

Straining-electrode tests (Donovan, 1977) showed that dissolution was not strain assisted. The results were similar to those of Hoar and Galvele (1970) who could find no mechanochemical effect due to straining iron in nitrate solutions. Therefore, stress maintains an active crevice but does not appear to be necessary to fracture the oxide nor enhance the dissolution process.

Intergranular and Crack-Wall Oxide

That NO_3^- stress corrosion failure is intergranular, and that the walls of the cracks are covered with a layer of oxide, Fe_3O_4 (Flis, 1975), is well known; however, formation of oxide in the grain boundary prior to fracture is not (Figure 6). In both WOL (K decreasing with crack growth and CT (K increasing with crack growth) specimens, the grain boundaries ahead of the crack tip contain oxide. Also, grain boundaries along the crack contain oxides that have not cracked. Therefore, oxide is formed by grain-boundary diffusion of oxygen prior to cracking, rather than by cathodic oxidation of crack walls.

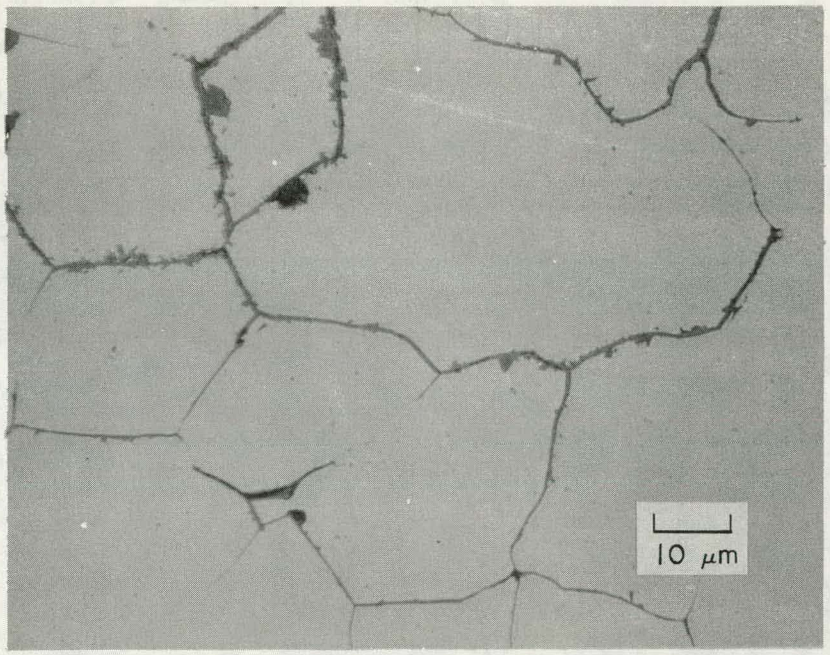


FIGURE 6. Intergranular Oxide Ahead of the Crack Tip

Proposed Mechanisms of Nitrate Cracking

In summary, the significant observations of this study are:

1. Prolonged incubation time is required, even in precracked specimens.
2. K_{scc} and crack growth rate are independent of bulk solution composition.
3. Grain-boundary oxide forms ahead of the crack.
4. Stage III crack growth is discontinuous.

These results are best explained by a new mechanism for nitrate cracking based on the solid-state formation of grain-boundary oxide and its dissolution or fracture as the means of crack propagation.

The existence of an incubation time in precracked specimens, WOL or CT, that is related to the concentration of inhibitor suggests that this time is required to establish the critical crack tip chemistry and/or oxide in the grain boundaries. Its existence in a pH 3.5 nitrate solution suggests that the formation of the grain-boundary oxide is controlling.

In Stage II cracking, the composition of the bulk solution did not influence the crack velocity. The activation energy for Stage II cracking, 27 kJ/mole (Donovan, 1977), agrees reasonably well with the activation energy for dissolution (Smialowski, 1962, and Alexander, 1975), suggesting that the controlling mechanism is the anodic dissolution of the oxide or passing layer preferentially along grain boundaries. The rate of disintegration of this oxide determines the corrosion rate (Hauffe, 1965) and, in this case, the crack growth rate in Stage II. Okada (1976) showed by acoustic emission that nitrate cracking of low strength steel was "quiet" and therefore occurred by anodic dissolution of active paths, specifically grain boundaries.

The existence of oxide in the grain boundaries ahead of the crack tip, with good metal-oxide bonds, indicates that the oxide has grown into the grain boundary before cracking occurs. The oxide penetrates the grain boundaries in the plastic zone of the crack in both WOL and CT specimens.

Stage III cracking is a discontinuous process, with brittle jumps in the crack length, Figure 2. This discontinuity appears to be the rupture of the oxide or the oxide-metal interface. The apparent activation energy for this process was 54 kJ/mole (Donovan, 1977). This activation energy is similar to that for oxygen diffusion down an interface or grain boundary. At low temperatures, the ratio of grain-boundary diffusion to lattice diffusion may be 10^5 - 10^6, and the activation energy for diffusion in a grain boundary is about half that for lattice diffusion. The activation energy of the anion is about the same as that of the cation, which is 108 kJ/mole (Kofstad, 1966). Therefore, the rate-controlling process of Stage III cracking appears to be grain-boundary diffusion of oxygen. This oxide rupture mechanism is similar to that suggested by Forty (1963), McEvily (1965), and Pugh (1971) for the stress corrosion cracking of brass in tarnishing solutions. But, Pugh (1975) no longer supports this view primarily because of evidence (Pinchback, 1975) in brass that suggests the thick tarnish film does not exist at the crack tip.

Conclusion

A mechanism of nitrate stress corrosion cracking of mild steel is proposed that includes: (1) oxide formation in grain boundaries due to a solid-state anodic reaction; and (2) dissolution (Stage II) or fracture (Stage III) leading to stress corrosion crack growth. Existing data do not unequivocally demonstrate that this is the mechanism of nitrate cracking. Additional experiments are necessary to verify these observations and improve our understanding of nitrate cracking.

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References

1. Alexander, B. J., and Foley, R. T., (1975), "Dissolution of Fe," Corrosion, vol. 31, p. 148.
2. Ambrose, J. R., and Kruger, J., (1972), "Tribo-Ellipsometry: A New Technique to Study the Relationship of Repassivation Kinetics to Stress Corrosion," Corrosion, vol. 28, p. 30.
3. Baker, H. R., and Singleterry, C. R., (1972), "Inhibition of Stress Corrosion Cracking of AIST 4340 Steel," Corrosion, vol. 28, p. 385.
4. Donovan, J. A., (1977), "Temperature Dependence of Nitrate Stress Corrosion Cracking of Mild Steel," to be presented at Symposium "Environment-Sensitive Fracture of Engineering Materials," sponsored TMS-AIME Chicago, October 24-27, 1977.
5. Forty, A. J. and Humble, P., (1963), "Influence of Surface Tarnish on the Stress-Corrosion of α-Brass," Philosophical Magazine, vol. 8, p. 247.
6. Flis, J., (1975), "Role of Oxide films in Stress Corrosion Cracking of Mild Steel in Nitrate Solution," Corrosion Science, vol. 15, p. 553.
7. Hauffe, K., (1954), <u>Oxidation of Metals</u>, Plenum, New York, p. 423.
8. Hoar, T. P., (1961), <u>Electrode Processes</u>, Butterworths, London, p. 299.
9. Hoar, T. P., and Galvele, J. R., (1970), "Anoidic Behavior of Mild Steel during Yielding in Nitrate Solutions," Corrosion Science, vol. 10, p. 211.
10. Kofstad, P., (1966), <u>High Temperature Oxidation of Metals</u>, Wiley, New York, p. 140.
11. Lees, D. J., Ford, F. P., and Hoar, T. P., (1973), "Some Guidelines to the Development of Stress Corrosion Resistant Alloys," Metals and Materials, vol. 7, p. 231.
12. Lees, D. J., and Lockington, N. A., (1970), "Influence of the Cation on the Mode of Stress Corrosion Failures of Iron in Nitrate Solutions," British Corrosion Journal, vol. 5, p. 167.
13. Mazille, A., and Uhlig, A. H., (1972), "Effect of Temperature and Some Inhibitors on Stress Corrosion Cracking of Carbon Steels in Nitrate and Alkaline Solution," Corrosion, vol. 28, p. 427.
14. McEvily, A. J., and Bond, A. P., (1965), "On the Initiation and Stress Corrosion Cracks in Tarnished Brass," Journal of Electrochemical Society, vol. 112, p. 131.

15. Novak, S. R., and Rolfe, S. T., (1969), "Modified WOL specimen for K_{ISCC} Environmental Testing," Journal of Materials, vol. 4, p. 701.

16. Okada, H., Yukawa, K., and Tamura, A., (1976), "Transition of Cracking Mechanisms from Active Path Corrosion to Hydrogen Embrittlement in High-Strength Steels in a Boiling Nitrate Solution," Corrosion, vol. 32, p. 201.

17. Parkins, R. N., (1969), "Stress Corrosion Cracking of Low Carbon Steels," Proceedings Conference on Fundamental Aspects of Stress Corrosion Cracking, (R. W. Staehle, A. J. Forty, and D. Van Rooyen, Editors), NACE, Houston, p. 351.

18. Parkins, R. N., (1972), "Stress Corrosion Spectrum," British Corrosion Journal, vol. 7, p. 15.

19. Parkins, R. N., and Usher, R., (1962), "The Effect of Nitrate Solutions in Producing Stress Corrosion Cracking in Mild Steel," First International Congress on Metallic Corrosion, Butterworths, London, p. 289.

20. Pinchback, T. R., Clough, S. P., and Heldt, L. A., (1975), "Stress Corrosion Cracking of Alpha Brass in Tarnishing Ammoniacal Environments: Fractography and Chemical Analysis," Metallurgical Transactions, vol. 6A, p. 1479.

21. Pugh, E. N., (1971), "The Mechanism of Stress Corrosion Cracking of Alpha-Brass in Aqueous Ammonia," The Theory of Stress Corrosion Cracking in Alloys (J. C. Scully, Editor), NATO, Brussels, p. 418.

22. Pugh, E. N., (1975), "The Stress-Corrosion Cracking of Copper Alloys," Presented at the NATO Advanced Study Institute on Stress Corrosion Cracking, Copenhagen. To be published.

23. Roberts, E., (1969), "Elastic Crack-Edge Displacements for the Compact Tension Specimen," Material Research and Standards, vol. 9, No. 2, p. 27.

24. Sandoz, G., Fujii, C. T., and Brown, B. F., (1970), "Solution Chemistry Within Stress Corrosion Cracks in Alloy Steels," Corrosion Science, vol. 10, p. 839.

25. Smialowski, M., (1962), "Corrosion of Iron and Mild Steel in Nitrate Solutions," First International Congress on Metallic Corrosion, Butterworths, London, p. 296.

26. Sutcliffe, J. M., Fesseler, R. R., Boyd, W. K., and Parkins, R. N., (1972), "Stress Corrosion Cracking of Carbon Steel in Carbonate Solution," Corrosion, vol. 28, p. 313.

27. Smialowski, M., (1964), "Effects of Potential of Mild Steel on Stress Corrosion Cracking in Ammonium Nitrate Solutions," Corrosion, vol. 20, p. 198t.

28. Wessel, E. T., (1969), "State of the Art of the WOL Specimen for K_{IC} Fracture Toughness Testing," Engineering Fracture Mechanics vol. 1, p. 77.

29. Wiederhorn, S. M., (1967), "Influence of Water Vapor on Crack Propagation in Soda-Lime Glass," Journal of American Ceramic Society, p. 407.