NBSIR 74-583

The Role of Passive Film Growth Kinetics and Properties in Stress Corrosion and Crevice Corrosion Susceptibility

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

PART I

To be submitted for publication in Corrosion

Effect of Molybdenum Alloying on the Repassivation and Depassivation of Ferritic Stainless Steels

by

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ABSTRACT

A study of the effect of alloying chromium and molybdenum in ferritic stainless steels has been made using techniques to study repassivation kinetics (tribo-ellipsometry) and depassivation kinetics (a recently developed ellipsometry technique for studying optical changes occurring within a crevice). Results indicate that chromium additions affect both repassivation and depassivation processes while molybdenum appears to affect only the repassivation processes. A discussion is given of a generalized mechanism for localized corrosion which postulates that susceptibility to attack is determined by the competititon between depassivation and repassivation processes.

Effect of Molybdenum Alloying on the Repassivation and Depassivation of Ferritic Stainless Steels

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Although additions of molybdenum to ferritic stainless steels have been known for some time to enhance resistance to pitting and crevice corrosion (1,2), attempts to determine the origins of this increased resistance have, for the most part, been limited to electrochemical measurements of corrosion potentials and anodic currents under applied potential on various alloys. Molybdenum concentration in the alloy was found to be directly proportional to the corrosion and the critical pitting potential, and inversely proportional to the peak current density required for passivation (3). What these results do not show is how these variations in electrochemical behavior are affected by the presence of molybdenum in the metal. It would seem that if corrosion resistance were attributable to the presence of a protective film, then perhaps incorporation of molybdenum in the film is a factor, but Auger spectroscopy measurements actually reveal a surface depletion of the element (4). If molybdenum is indeed not in the passive film, its ability to impart to an alloy a greater resistance to localized corrosion must tie in with a mechanism more subtle in origin than the production of more protective film.

This paper explores the role that molybdenum plays in concert with the chromium in ferritic stainless steels in the dynamic interplay of two processes proposed to control localized corrosion: depassivation and repassivation. The broader term "depassivation" is used rather than "breakdown" because it includes any process that removes a protective film from a surface. Thus, film rupture under the influence of external stress, which leads in some cases to stress corrosion, would be covered by the more inclusive term.

EXPERIMENTAL

The materials used in this study were a series of Fe-Cr-Mo alloys with approximately 14, 17, and 25 percent chromium and 0, 2, and 5 percent molybdenum by weight. Compositions of all alloys are given in Table I. One cm square specimens were cut from the received material and cemented to aluminum plates with silver epoxy. The assembly was mounted in clear lucite, then drilled and tapped through the aluminum for electrode assembly. Specimens were polished on silicon carbide papers and rotary polished with 1 μm diamond paste. Specimens were degreased with spectro grade methanol and dried in a jet of compressed air. All experiments were performed in 1.0 N NaCl solution prepared from reagent grade chemical and distilled water (7×10^{-7} ohm^{-1} cm^{-1}).

The two experimental techniques employed in this study were selected in order to measure the rates of the two competing processes affecting corrosion resistance.

Repassivation Kinetics

Repassivation kinetics were studied using tribo-ellipsometry, the apparatus and techniques of which have been described elsewhere (5,6). Here depassivation is caused by *in situ* mechanical abrasion, and film growth rates are measured with an ellipsometer while potentiostatic current transients are simultaneously being recorded.

Although the limiting film thickness on this series of ferritic stainless steels can, depending upon applied potential, exceed 1 nm, the film that forms during the repassivation transient and which is responsible for reducing the anodic current density following film removal to less than 50% of its maximum value, is on the order of 0.1 nm and forms quite rapidly, in less than 15 ms. Since no ellipsometer intensity measurements were obtainable in the early stages of film growth, the oscilloscope scale was expanded to include current and ellipsometer parameter transients up to 100 ms. However, within this range, changes in film thickness were small, barely detectable above background photomultiplier noise levels, and could not be associated with molybdenum content of the alloys studied (Fig. 1). The rate of current decay, on the other hand, was dependent upon alloy composition for all alloys studied, and it is this result that will be presented here. The ellipsometer photo detection system is being modified to include a thermo-cooled gallium arsenide photomultiplier tube which is reported to reduce background noise by some three orders of magnitude. This system, when combined with a high voltage tungsten filament light source, might offer sufficient sensitivity to measure film thickness variations during this time interval.

Depassivation Studies

Depassivation presumed to occur during crevice corrosion was studied using a new technique also utilizing the ellipsometer (7). Using a glass plate to create a crevice, measurements of optical changes occurring during breakdown could be made, and these results correlated with electrochemical measurements.

Table I.

Alloy Composition

Cr	Mo	C	N	Ni	Si	P	S
13.68	0.08	0.003	0.004	NA	NA	NA	NA
13.60	1.88	0.002	0.004	NA	NA	NA	NA
17.35	<0.01	0.002	0.003	NA	NA	NA	NA
17.61	2.02	0.004	0.004	NA	NA	NA	NA
17.38	4.75	0.004	0.004	NA	NA	NA	NA
25.66	0.002	0.002	B	0.13	B	B	B
25.26	2.05	0.002	0.017	0.13	B	B	B
25.25	5.24	0.002	0.013	0.13	0.19	0.12	0.002

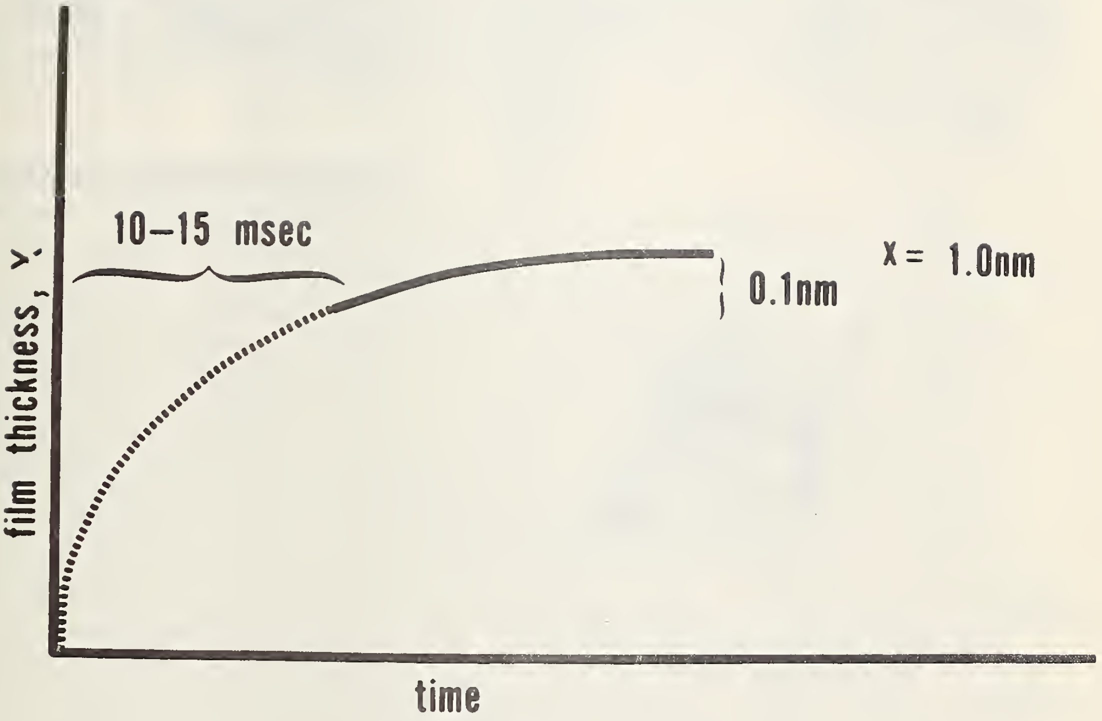

Fig. 1. Schematic representation of film growth measurement using tribo-ellipsometry. Majority of film growth complete before ellipsometer measurement made (10-15 ms).

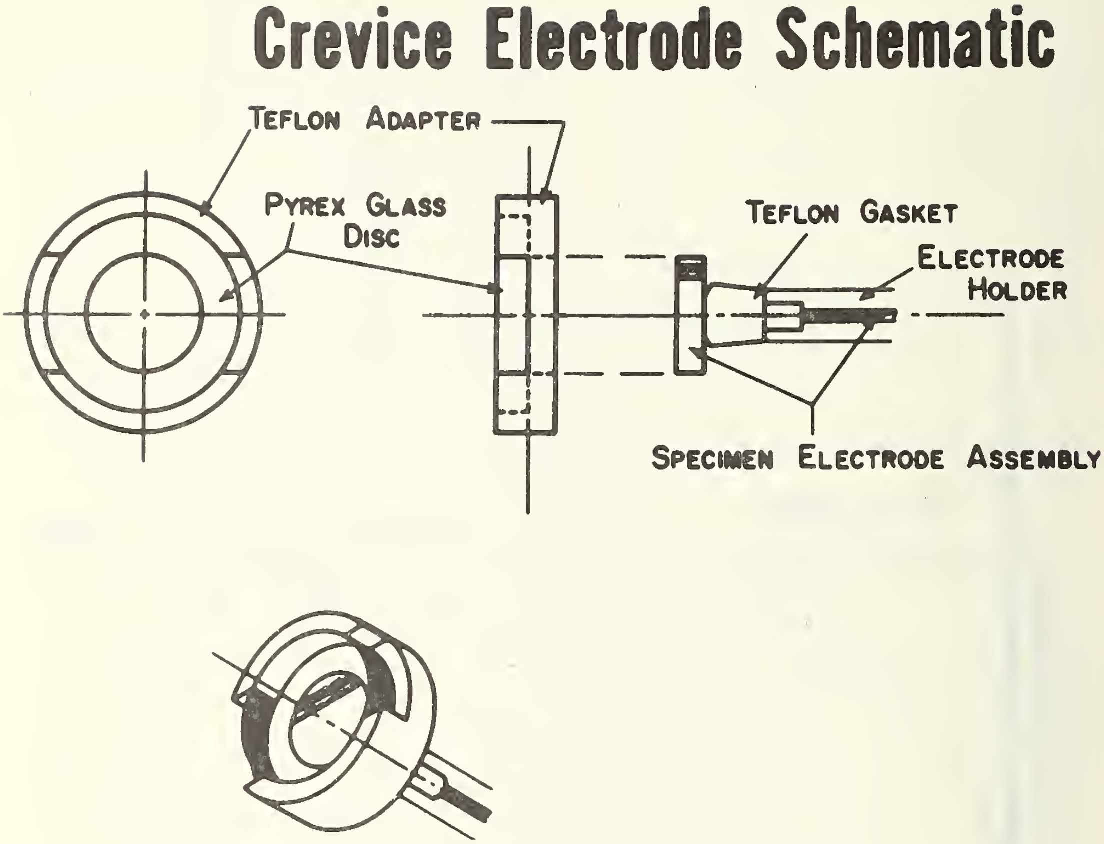

Fig. 2. Schematic of crevice assembly used in depassivation kinetics studies.

The crevice assembly is the same as described earlier (7) with a quartz glass plate substituted for the pyrex (Fig. 2). All crevices were 10^{-2} cm wide. The same alloys and solutions were used in this phase as in the repassivation kinetics studies. Each specimen was potentiostatted at its previously determined open circuit corrosion potential immediately after creation of the crevice (7). Ellipsometric and current measurements were then made over about a 1000 minute time span.

RESULTS

Repassivation Kinetics

Log log plots of anodic current versus time following cessation of abrasion for the Fe-14 Cr with 0 and 2 percent molybdenum are shown in Fig. 3. The linear nature of the plot suggests the relationship:

$$i = At^{-k} \qquad [1]$$

where k is the slope of the decay plot and a function of, among other things, the molybdenum concentration in the alloy. The quantity A in equation [1] is related to the maximum current density for exposed bare metal and is more or less dependent upon the abrasion efficiency (amount of surface area exposed by the carbide paper) of the tribo-ellipsometer system. Since the maximum current level was not particularly reproducible, attention will not be placed on it. The k values, however, were extremely reproducible, varying by no more than ± 1%. The experimental results shown here are based on the second abrasion cycle of a fresh carbide paper and A values for different alloys can be compared on an empirical basis. From Fig. 3 it can be seen that the addition of 2% molybdenum to the Fe-14 Cr slightly decreases the rate of current decay. The effect is much more pronounced in the higher chromium containing alloys Fe-17 Cr (Fig. 4) and Fe-25 Cr (Fig. 5). The values of k varied from 0.42 for the Fe-14 Cr alloy to about 1.2 for the Fe-25 Cr-2 Mo alloy. Values of k plotted as a function of molybdenum concentration are shown in Fig. 6. It is interesting to note that additions of molybdenum raise k to a limiting value quite near that found by Nagayama and Cohen (8) for iron passivation in borate buffer solution, whose current efficiency for film formation was essentially 100%. Secondly, the fact that k is linearly dependent upon molybdenum concentrations is consistent with the results of Rockel (3) who, for similar alloys in H_2SO_4 solution, also found a linear dependence for critical peak current density on percent molybdenum in the alloy. The slope of this linear relationship is clearly a function of chromium content (Fig. 7).

When the potential of the surface was changed, the Fe-Cr alloys containing no molybdenum showed no variation in k with an increase in potential (Fig. 8). When molybdenum was added, however, Fig. 9 shows that k increased with an increase in potential.

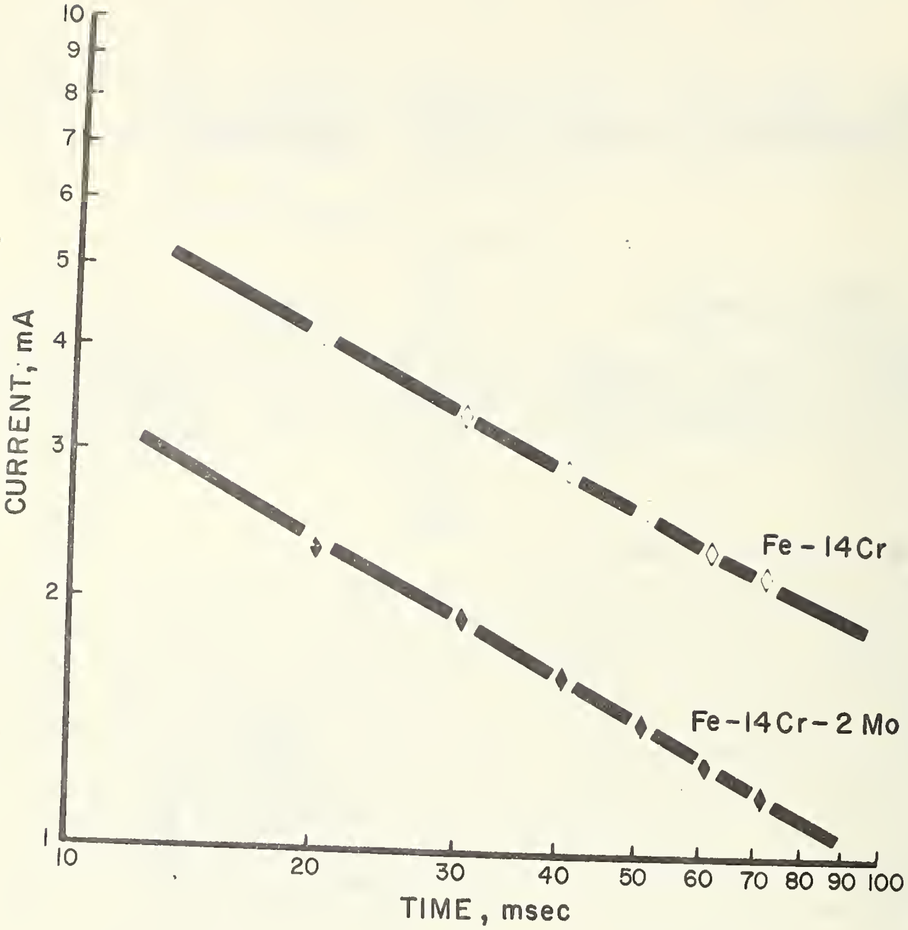

Fig. 3. $\log_{10}$ i versus $\log_{10}$ t during repassivation for Fe-14 Cr (-049 mV SHE) and Fe-14 Cr-2 Mo (-008 mV SHE) in 1.0N NaCl solution.

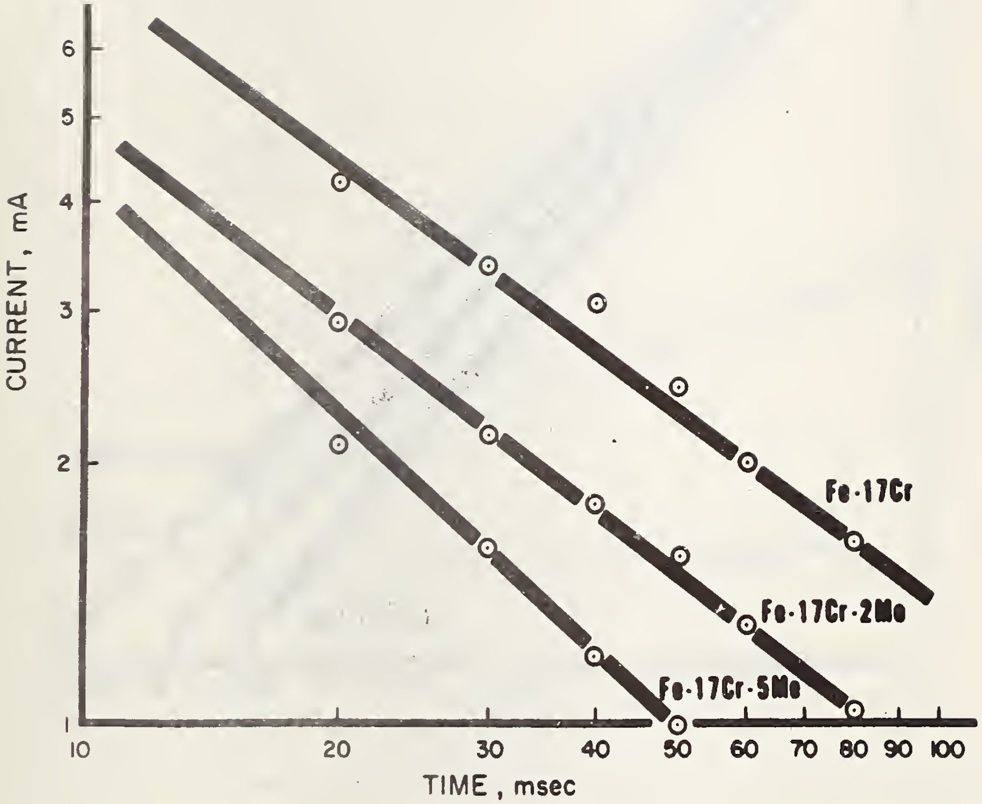

Fig. 4. $\log_{10} i$ versus $\log_{10} t$ during repassivation for Fe-17 Cr (-049 mV SHE), Fe-17 Cr-2 Mo (-062 mV SHE) and Fe-17 Cr-5 Mo (+020 mV SHE) in 1.0N NaCl solution.

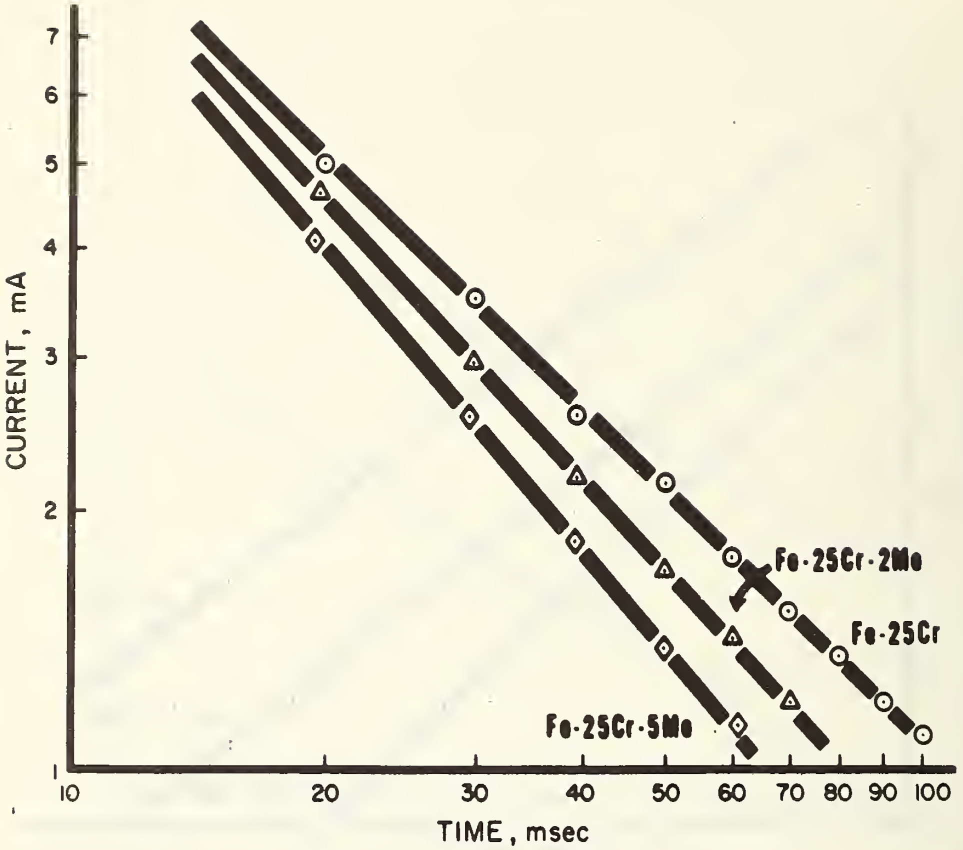

Fig. 5. $\log_{10}$ i versus $\log_{10}$ t during repassivation for Fe-25 Cr (-044 mV SHE), Fe-25 Cr-2 Mo (+142 mV SHE), and Fe-25 Cr-5 Mo (+042 mv SHE) in 1.0N NaCl solution.

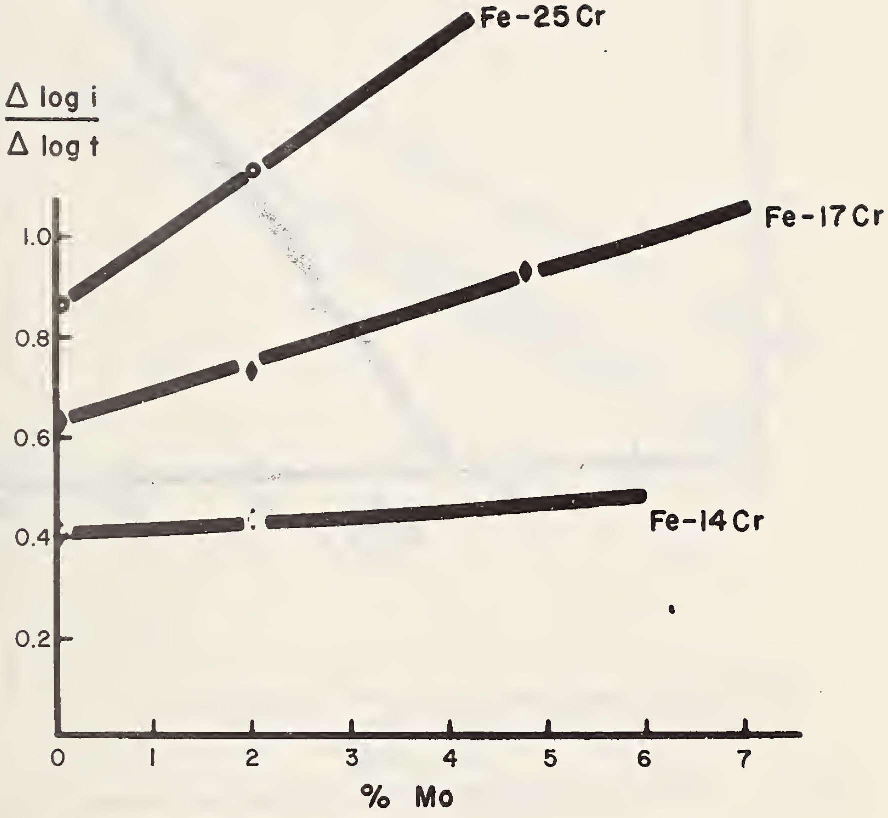

Fig. 6. Plot of k, $\frac{\Delta \log_{10} i}{\Delta \log_{10} t}$, versus weight per cent Molybdenum for Fe-14 Cr, Fe-17 Cr, and Fe-25 Cr ferritic stainless steels.

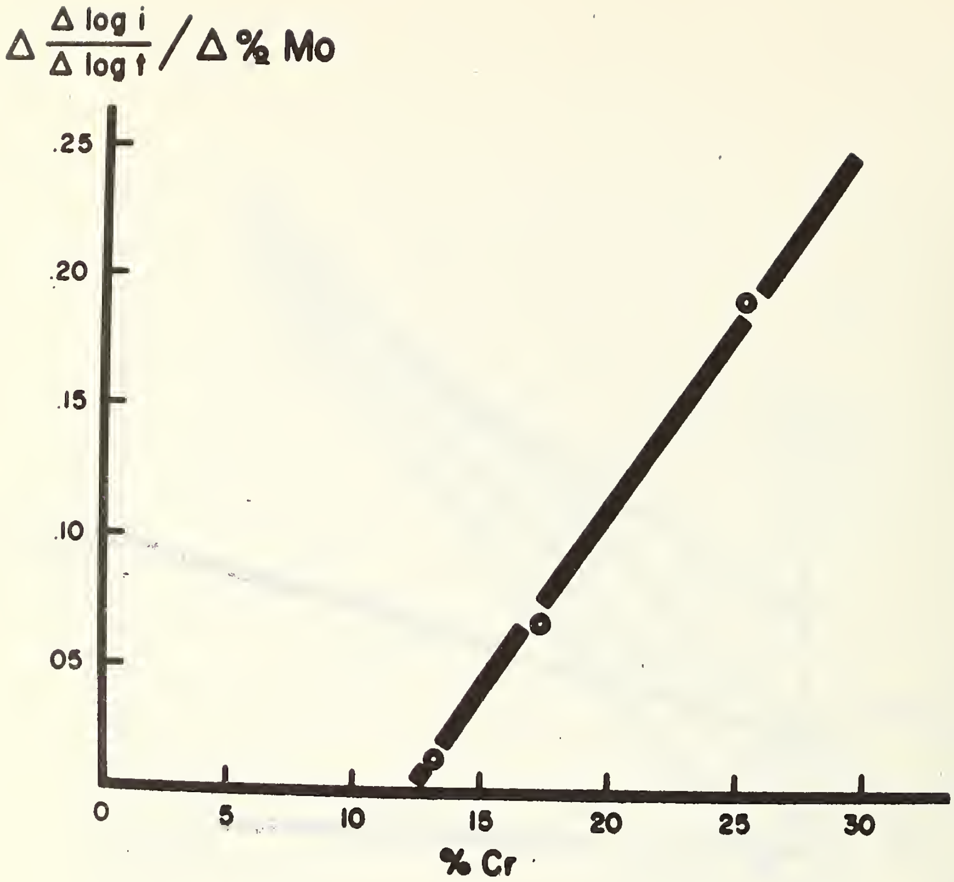

Fig. 7. Plot of $\Delta k/\Delta\%$ Mo versus chromium concentration.

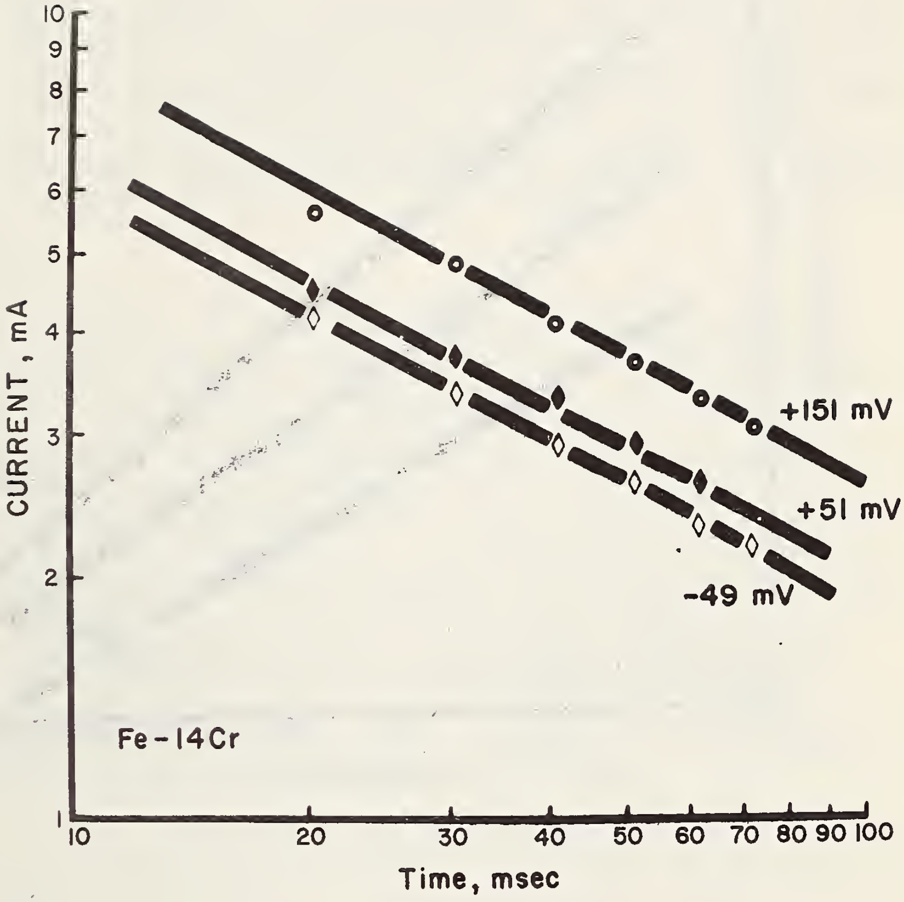

Fig. 8. Effect of increased applied potential on the current decay kinetics of Fe-14 Cr. Potentials are versus SHE.

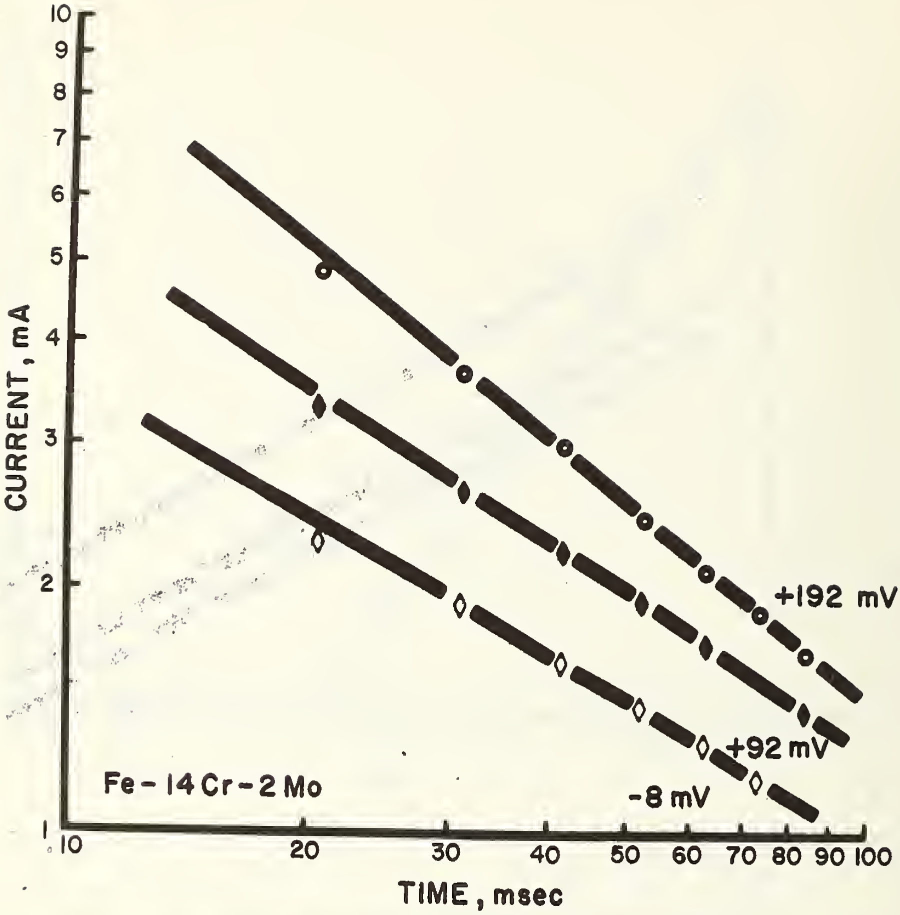

Fig. 9. Effect of increased applied potential on the current decay kinetics of Fe-14 Cr-2 Mo. Potentials are versus SHE.

Thus, one can increase the rate of repassivation of an Fe-Cr alloy either by adding more molybdenum or, for a fixed amount of molybdenum, by raising the potential.

A relationship between repassivation kinetics and stress corrosion cracking susceptibility was examined by comparing a ferritic stainless steel of composition Fe-28 Cr-4 Mo to the same alloy with a 2% nickel addition. The addition of the nickel makes the alloy more susceptible to stress corrosion (9). Current decay transients were measured in 1.0 N NaCl and are shown in Fig. 10. The less susceptible material repassivates about 20% faster then the susceptible nickel containing alloy.

Depassivation

Previous studies (7) have shown that the relative phase retardation, Δ, is a parameter that is sensitive to the processes leading to film breakdown and crevice corrosion. The changes in Δ with time are plotted for the two Fe-14 Cr alloys in Fig. 11. The rate of decrease in Δ was lowered by addition of molybdenum. Current increased steadily during the course of the experiment at about the same rate for both materials and is most likely due to oxygen depletion within the crevice. Although the three stages of change in Δ (decrease, increase, decrease) previously found for 304 stainless steel (7) were also observed here, it is the influence of alloying on the first stage that is probably the more important, since depassivation is initiated during this period by what are generally thought to be increases in concentration of soluble corrosion products within the crevice (1). Therefore, later stages in the crevice corrosion process are not included here.

The breakdown process took longer to initiate in the Fe-17 Cr series, but the results were similar to the Fe-14 Cr alloys (Fig. 12). Δ was not found to decrease to a measurable extent in the Fe-25 Cr series of alloys.

Bates (10) recently showed that application of cathodic protection for short intervals of time would inhibit the crevice corrosion process. To see if the optical changes leading to breakdown were also arrested, cathodic protection was applied and the results shown in Fig. 13. Upon switching the applied potential some 240 mV in the cathodic direction after the breakdown process had begun, it was possible to arrest both Δ and ψ values, but the system did not return to its original state.

DISCUSSION

Before examining the significance of the results described, it is necessary to discuss the possible interplay of depassivation and repassivation in localized corrosion. The concepts developed will then be applied to an examination into the effects of adding chromium and molybdenum to ferritic stainless steels.

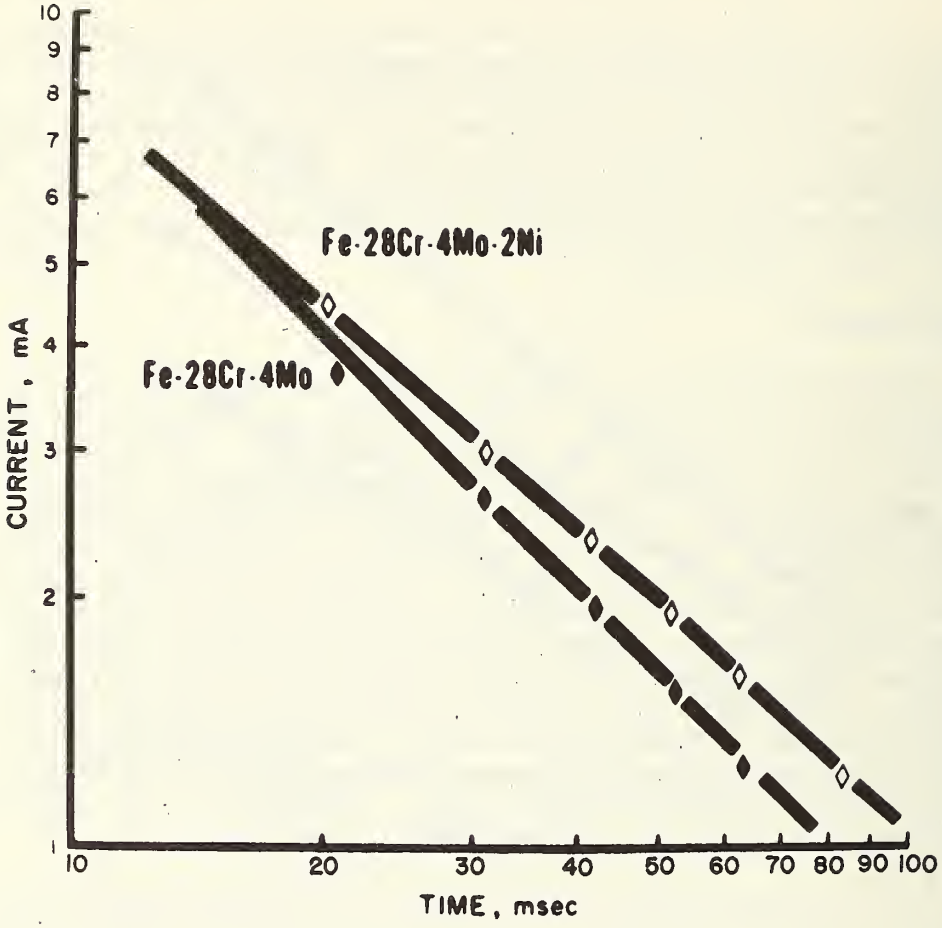

Fig. 10. $\log_{10} i$ versus $\log_{10} t$ during repassivation for Fe-25 Cr-4 Mo (-003 mV SHE) and Fe-28 Cr-4 Mo-2 Ni (+094 mV SHE).

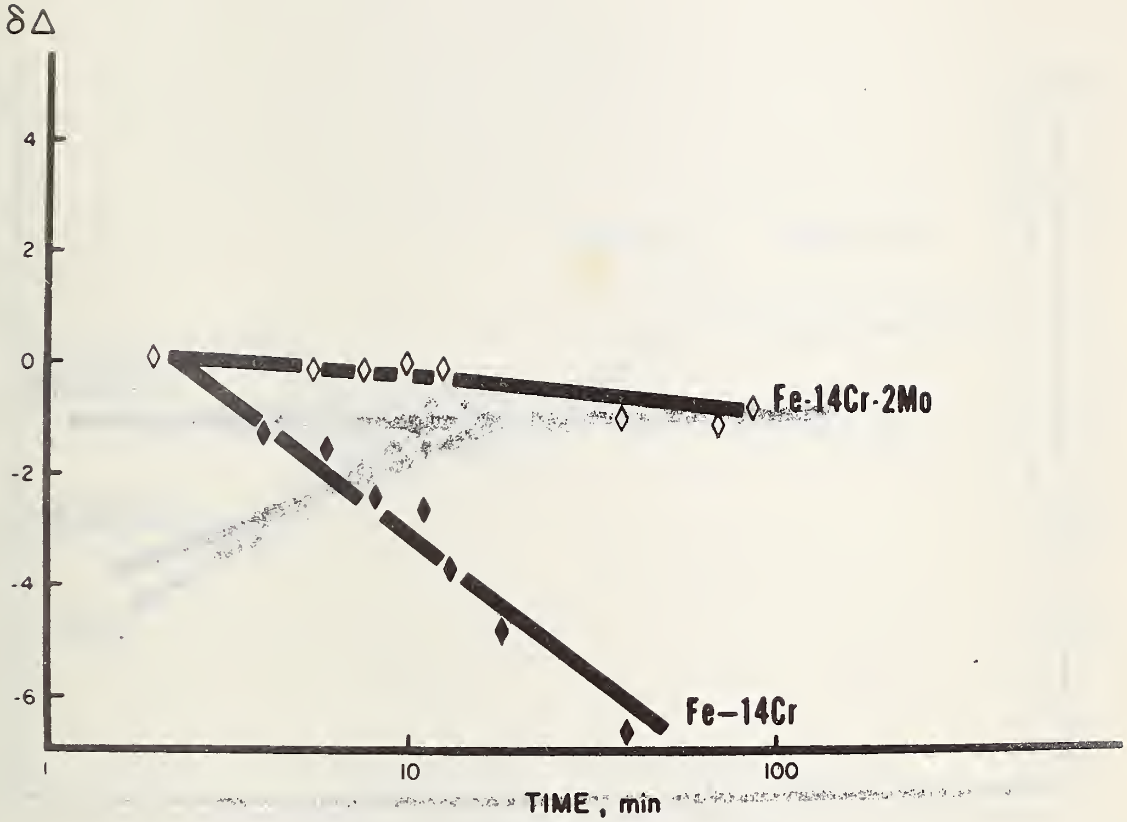

Fig. 11. Change in relative phase retardation, Δ, with $\log_{10}$ t for Fe-14 Cr (-049 mV SHE) and Fe-14 Cr-2 Mo, (-008 mV SHE) at within a crevice.

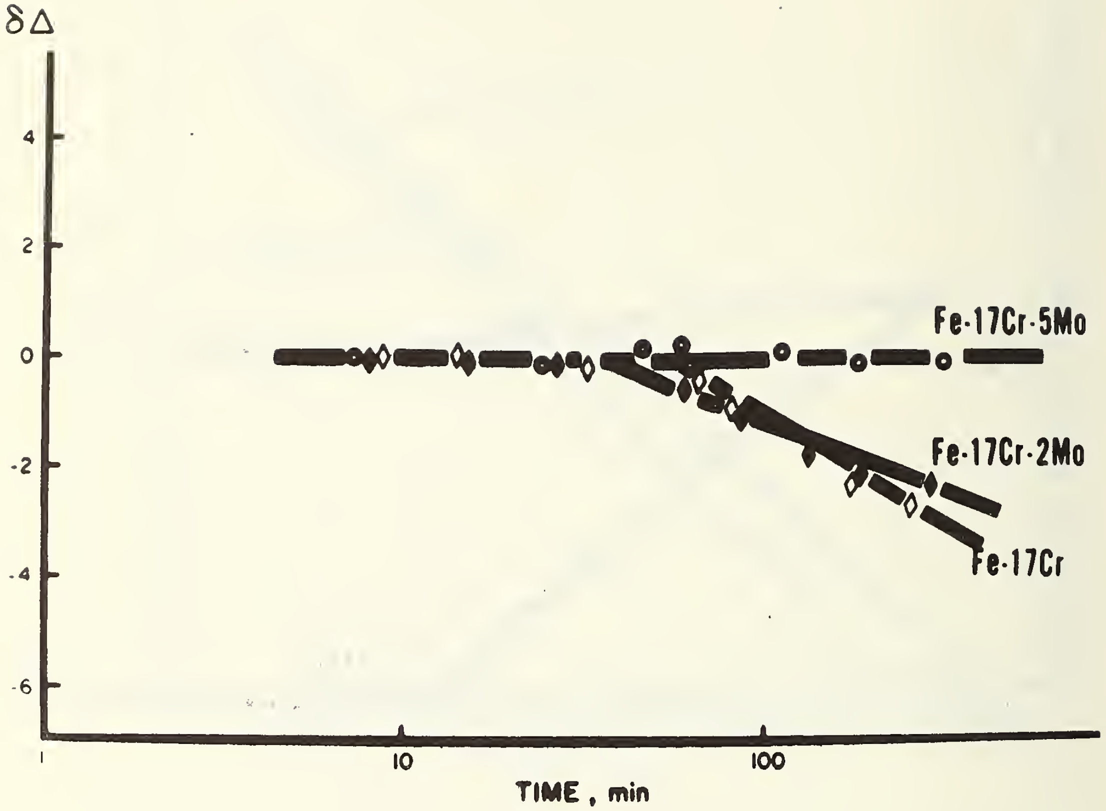

Fig. 12. Change in relative phase retardation, Δ, versus $\log_{10} t$ for Fe-17 Cr (-049 mV SHE), Fe-17 Cr-2 Mo (-062 mV SHE), and Fe-17 Cr-5 Mo (+020 mV SHE) in 1.0N NaCl solution within a crevice.

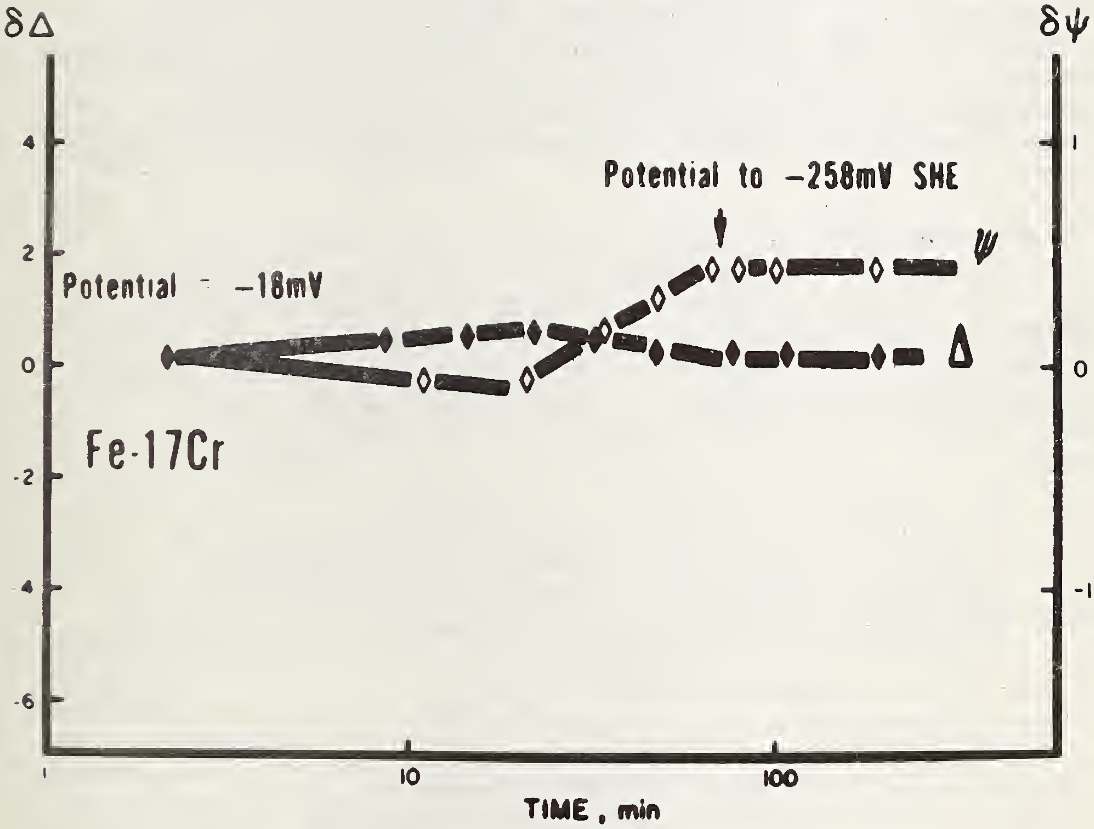

Fig. 13. Effect of application of cathodic protection on ellipsometer parameters Δ and ψ. At approximately 100 minutes, after Δ and ψ had begun to change due to onset of crevice attack, potential shift to -258 mV SHE.

Depassivation and Repassivation

If all localized corrosion is regarded as resulting from some disruption of a protective film, then those events which control access of unprotected metal to the environment will determine susceptibility to a given mode of corrosion attack, as well as affect its rate. This generalized film disruption process will be loosely defined as "depassivation". This process can result from the application of external stress that could lead to stress corrosion or it can result from breakdown of the film by some sort of interaction with the environment which could lead to crevice or pitting corrosion. Subsequent events through which the system can be returned to its former state are classified under "repassivation". The premise of this discussion will be that it is the balance between depassivation and repassivation that will be responsible for controlling the performance of a material exposed to a particular environment.

It would be useful to know the nature of the steady state conditions which exist at the metal solution interface. Okamoto has suggested that a metal capable of suffering localized corrosion experiences a dynamic process of continued breakdown and repair (17). One possibility that is consistent with all our experimental results is that the depassivation events in this dynamic balance occur mechanically through rupture of the surface film due to internal straining.

Sato has recently suggested that high fields could lead to mechanical rupture of thin films by electrostriction pressures exceeding the compressive fracture strengths of the film (18). The so-called film pressure this generates is given by:

$$p - p_0 = \frac{\varepsilon(\varepsilon - 1)E^2}{8\pi} - \frac{\alpha}{L} \qquad [2]$$

where p = film pressure
p_0 = atmospheric pressure
ε = film dielectric constant
E = electric field
α = surface tension
L = film thickness

It is possible that those ions considered to be "aggressive" in promoting corrosion attack increase film pressure by decreasing the surface tension term in equation [2] through adsorption. Yet, this should occur with all anions, not just a select few. Zero charge potentials for many anions, aggressive and non-aggressive alike, are similar on mercury (23). Since zero charge potentials would also be expected to be similar on most oxides, any increase in film electrostriction pressure due to a decrease in surface tension because of adsorption would be a general effect and could not explain a specificity of those ions which are known to cause pitting. Increase in film dielectric constant through a kind of anion doping would also lead to increased film pressure and would be somewhat specific in that ion size might be important. However, chloride ion, an aggressive species, has about the same polarizability as oxide ions and only slight changes in dielectric strength on the order of a few percent might occur, particularly at low concentrations of chloride to be expected in these films (13). On the other hand, increased film conductivity at certain active sites where grain boundaries, inclusions, or other defects exist cause decrease in local field strength and place the film at these sites under tension with respect to the electrostrictive compression forces (increased as a result of ion adsorption) exerted elsewhere. Chloride ion, or any of those species considered aggressive, could effect localized film rupture after penetration to the metal surface by promoting formation there of pockets of non-protective low density material similar to that produced as a corrosion product during active pit growth. As the pockets expand upon continuing oxidation at the metal/oxide interface, further stress is placed on the film directly atop the pockets, eventually resulting in fracture of the film. In iron, for instance, this low density material was identified as γ-FeOOH (24). This particular process of depassivation, which we shall refer to as the spontaneous film rupture mechanism, provides a finite number of access sites for solution to contact unprotected metal. By suggesting that alteration of film growth in the presence of sufficient concentration of some detrimental species at the metal/film interface could increase localized internal film stresses to a point where the tensile strength of the film could be exceeded, we have modified the basic Sato mechanism in such a way as to reasonably account for ion selectivity in promotion of localized corrosion.

Susceptibility to localized corrosion will be determined by the repassivation kinetics of the particular metal in the specific environment which it contacts. Sustained metal dissolution, whether resulting from slow film growth rates or from exceptionally high anodic overvoltages, will lead to alterations in the environment chemistry which are invariably detrimental to effective repassivation. Thus, it becomes increasingly difficult to promote repair at the local breakdown sites, and pitting corrosion can result.

If one accepts the hypothesis of dynamic breakdown and repair, then all forms of localized corrosion can be considered as extremes of one process. In stress corrosion cracking, applied tensile stress not only increases the rate of breakdown events, but can increase the rate of dislocation movement and subsequent area of bare metal production through slip step emergence. Rate of film repair in that environment then determines rate of crack propagation. Similarly, crevice corrosion results from the fact that mass transport limitations over a rather extensive metal surface area result in deleterious solution chemistry for repassivation. The process can rather quickly lead to sufficient solution acidity to attack the remaining bulk surface film and cause depassivation on a large scale with subsequent general attack beneath the crevice.

The fact that susceptibility to localized corrosion is related to some critical limiting potential cannot be explained by a dynamic breakdown and repair process unless those detrimental ions which are involved in the repair process are either 1) specifically adsorbed above this potential, thereby inhibiting film growth or 2) contribute to the formation of non-protective films above critical potential values.

Repassivation studies of iron in chloride solution by Ambrose and Kruger (11) showed that film growth was normal below a critical potential, but that films grown in the presence of chloride ion above this potential were not protective.

The examination of our results on the effect of alloying on localized corrosion susceptibility of ferritic stainless steels will be based on the following mechanism:

1) Aggressive ions (e.g., chloride) adsorb on and penetrate into surface films at specific weak sites. Such sites occur at points of higher film conductivity (around grain boundaries, inclusions, or other physical film defects) where the electric field is less, and the film will be under tensile stresses. When normal film growth is altered by the presence of chloride at the interface, growth of the resulting low density oxidation product will eventually cause rupture of the overlaying protective film.

2) The extent to which localized corrosion can proceed will depend upon the repassivation kinetics of the surface produced from film rupture in the environment to which this bare metal will be exposed.

3) Sufficient deterioration of the environment due to metal dissolution (increased soluble corrosion products and lowered pH) will at least affect film growth kinetics and in the extreme, inhibit it. Pitting attack would result.

4) Application of external tensile stress will accomplish two things: a) increase the number of breakdown sites on the metal surface and b) increase the rate of slip step emergence leading to a production of a number of sites with a relatively large surface area of bare metal. Repassivation kinetics will determine susceptibility to stress corrosion cracking, provided rate of bare metal production is of the appropriate value.

5) Creation of a crevice will provide a mass transport-limited solution volume where soluble corrosion products and charge balancing detrimental anion concentrations lead to a rapid increase in film breakdown events and finally to a general dissolution of the film within the crevice.

Effect of alloying on susceptibility to localized corrosion

Chromium additions

As Fig. 7 shows, an increase in chromium content in an alloy increases the rate of repassivation. Since chromium is known to complex chloride (14) according to the reaction,

$$Cr(H_2O)_6^{+3} + Cl^- = Cr(H_2O)_5\ Cl^{+2} + H_2O, \qquad [3]$$

it is conceivable that dissolution of chromium during depassivation ties up chloride ions. The chloride ions are thereby prevented from interferring with the rapid repassivation of the metal surface.

What effect does Cr have on the depassivation process? Some insight into this question can be gained from spectroscopic ellipsometric studies by McBee and Kruger (15,16). They showed that, when working at a few specific wavelengths of light, additions of chloride ion to the solution affected the optical parameters of surface films on pure iron, and that such alterations which lead to breakdown can be reversed by the chloride ion being removed from the environment. When the chloride was removed, the optical parameters returned to their previous values (Fig. 14). Such results suggest that chloride ion is poorly bound in the film and mobile enough to either move in or out depending on bulk solution conditions.

When the same experiments were carried out using iron-chromium alloys instead of pure iron, a significant difference in behavior was noted (16). First, much higher chloride concentrations were necessary to cause breakdown of the films on the Fe-Cr alloys than were used for the pure iron. Secondly, optical charges which occur in the film on the Fe-Cr alloys during the period prior to breakdown were not reversed when chloride ion was removed from the solution as they were in the case of pure iron (Fig. 15). McBee and Kruger attributed this difference to ability of the chloride ion to move via vacancies in the crystalline films on pure iron, whereas chloride ion had less mobility in the non-crystalline films on the Fe-Cr alloys due to the greater possibility for covalent bonding in the amorphous film. Once this film on the Fe-Cr alloy had been contaminated with chloride ion, not only would it remain contaminated even when the solution is changed, but if chloride containing solution was reintroduced, McBee and Kruger found that breakdown occurred instantly.

The Cr additions thus operate in two ways to inhibit localized corrosion. First, they retard alteration of the film's properties that would lead to depassivation. As pointed out in the preceding

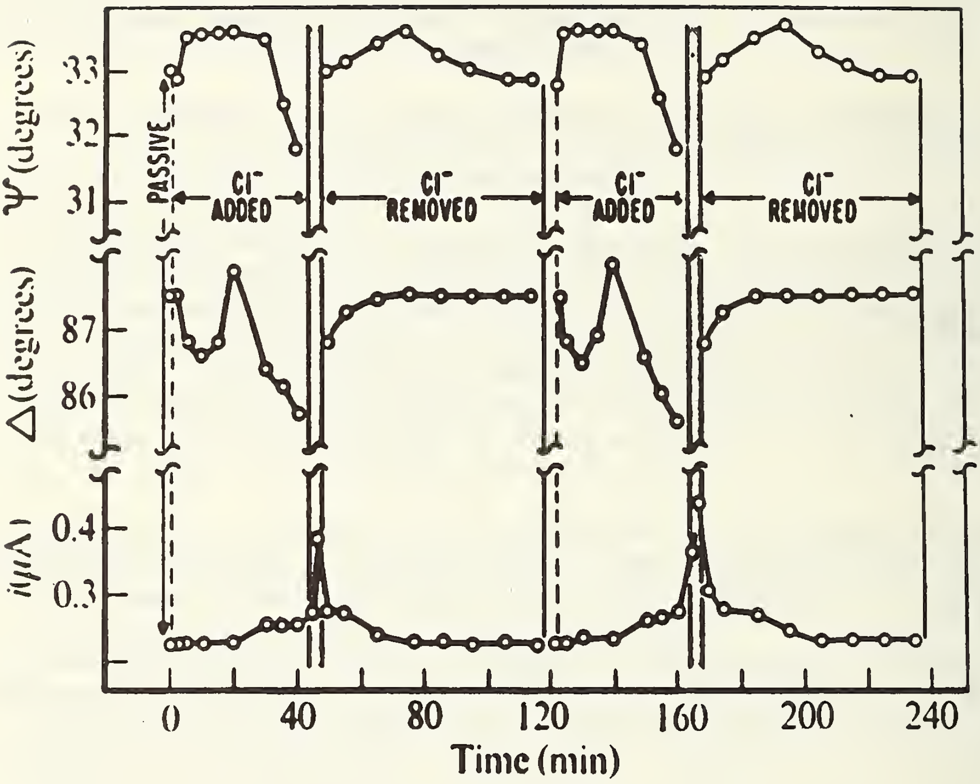

Fig. 14. Spectro-ellipsometric measurements of changes in Δ and ψ for iron after introduction of chloride (t=0), and removal of chloride from the solution. Δ, ψ, and current are seen to return to normal passive values once chloride ion is removed. 410 mn wavelength light was used. From (15).

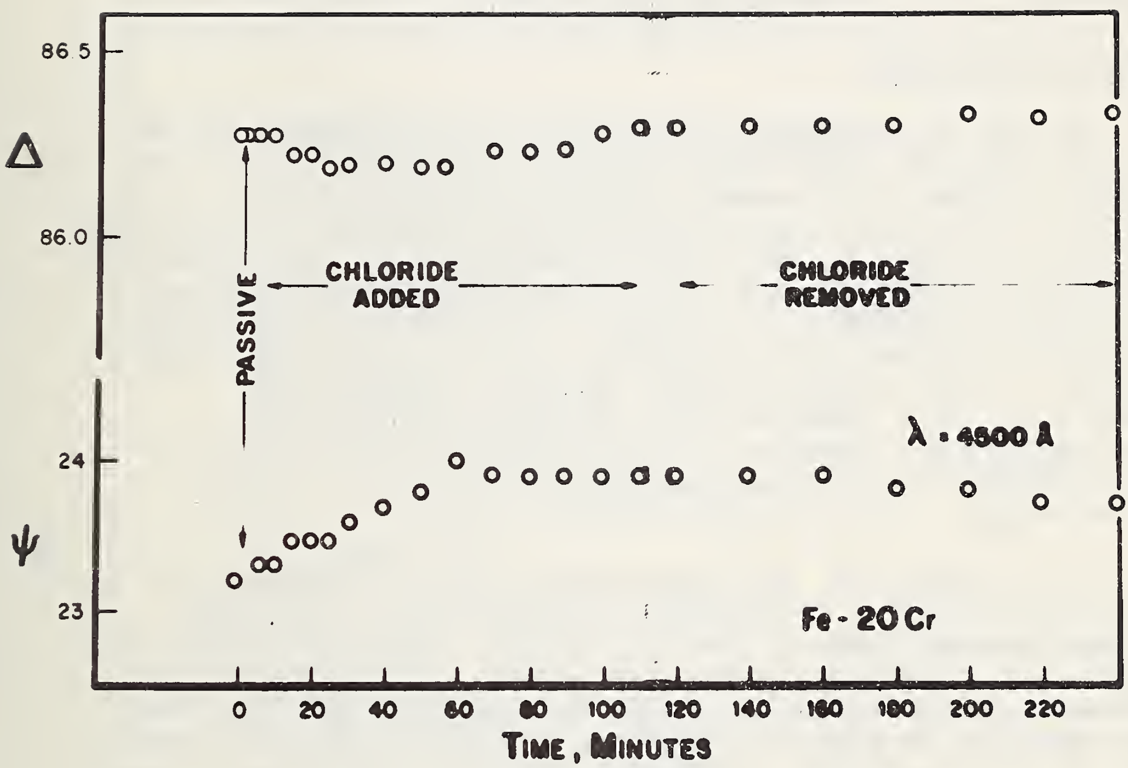

Fig. 15. Spectro-ellipsometric measurements of changes in Δ and ψ for Fe-20 Cr after introduction of chloride (t=0), and removal of chloride from solution. Δ and ψ do not return to passive values once chloride ions are removed. 450 nm wavelength light was used. From (16).

section, the most reasonable way in which the incorporation of chloride in the film affects depassivation is by changing the mechanical properties of the film so that spontaneous film rupture occurs. The second way the Cr affects localized corrosion, as shown by the results depicted in Fig. 7, is in the promotion of rapid repassivation. It is only when a large supply of chloride ion is present to retard repassivation and promote depassivation that breakdown occurs. Chromium thus has a beneficial affect on repassivation and in preventing depassivation.

Effect of Molybdenum

The role of molybdenum in increasing corrosion resistance of ferritic stainless steels is an enigmatic one because there is some evidence that Mo is not present in the passive film (4). To emphasize this point further, spectroscopic ellipsometric experiments on Fe-Cr-Mo alloys (20) show that molybdenum affects neither the retention of chloride in the film nor does it alter the magnitude of changes in ellipsometric parameters Δ and ψ. Fig. 16 shows that essentially the same change in optical properties occur when Mo is present in an Fe-Cr alloy as those found when molybdenum is absent (Fig. 15).[1] These results, therefore, indicate that molybdenum, unlike chromium, does not enhance the resistance of a passive film to undergo the breakdown that eventually leads to depassivation.

On the other hand, the repassivation process is accelerated by alloying additions of molybdenum, particularly in the higher chromium containing steels (see Figs. 2,3,4). Since molybdenum is probably not present in the film, its effect on repassivation must depend upon its existence as a dissolved species in solution. The experiments on the effect of potential on repassivation rate clearly point to this possibility. As Fig. 8 shows when molybdenum is absent, an increase in potential does not affect k, the rate of current decay, a parameter related to the rate of repassivation. The current increases with potential in this case and thus more alloy is dissolved at the higher potentials. Even when molybdenum is present in the alloy, the initial maximum current is increased with an increase in potential and results in an increase in the concentration of dissolved species (Fig. 9). Only in this case the presence of dissolved molybdenum species affects the values of k, which increase as the higher potentials provide increased molybdenum concentrations in solution. We do not know what role the dissolved molybdenum plays in repassivation. It is known to go into solution electrochemically in the +6 oxidation state (21,22) and to form molybdates or polymolybdates. These are known to be corrosion inhibitors (19), but how they enhance the rate of repassivation is unclear.

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[1] Spectroscopic ellipsometer measurements were the same for both Fe-20 Cr and Fe-17 Cr alloys.

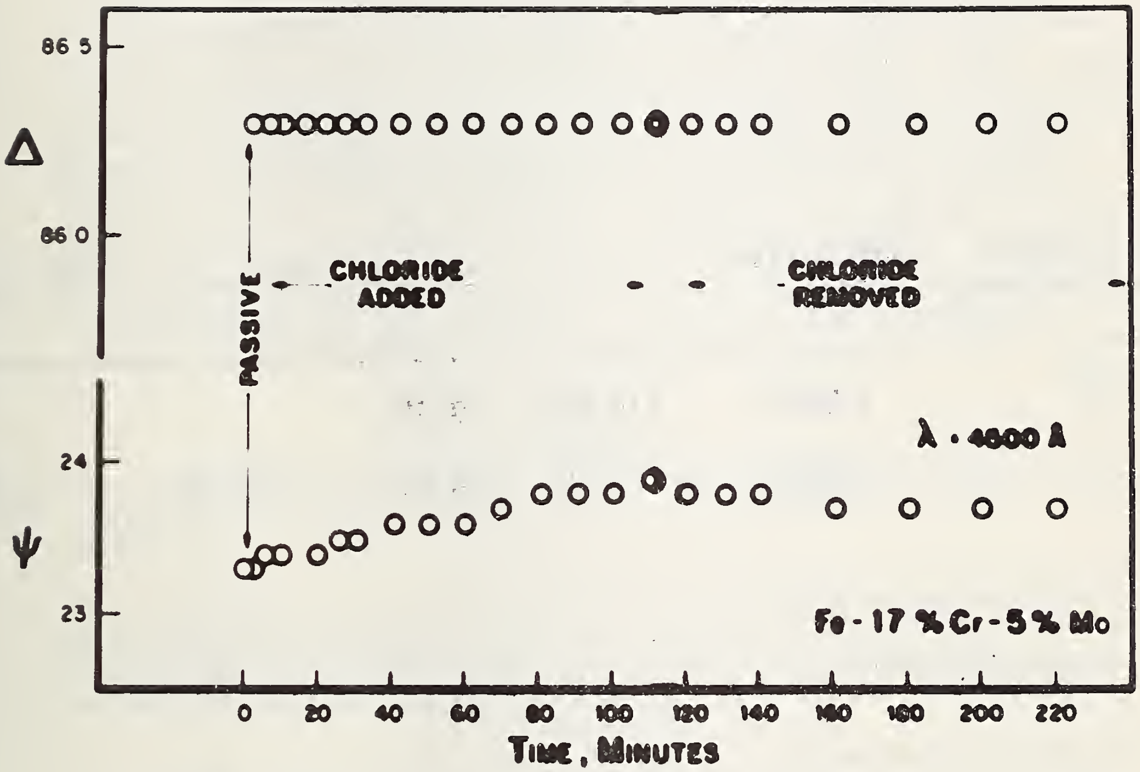

Fig. 16. Spectro-ellipsometric measurements of changes in Δ and ψ for Fe-17 Cr-5 Mo after introduction of chloride (t=0), and removal of chloride ions from solution. 450 nm wavelength light was used. From (20).

Table II.

NaCl Solution Concentration	Refractive Index	Δ	ψ	$\delta\Delta_{1.0\rightarrow2.5}$	$\delta\psi_{1.0\rightarrow2.5}$
1.0N	1.3432	113.86	29.38	-	-
2.5	1.3567	111.70	29.41	-2.16°	+.03°

Whatever the origin of effect of molybdenum on repassivation kinetics, the different rates of repassivation for alloys of different molybdenum contents lead to different concentration levels of soluble corrosion products in the crevice environment, and the Δ changes measured during the inital phases of attack were probably due to increases in refractive index of the solution. The change in Δ is in the direction consistent with an increase in concentration (Table II). Molybdenum, since it increases repassivation rate, would decrease rate of change in refractive index. The point in time at which refractive index, n, begins to range from its initial value will obviously depend on chromium concentration in the alloy, since this variable determines depassivation time. Indeed, our results show that Δ (and solution refractive index) begins to change at approximately the same time for fixed chromium concentration, regardless of molybdenum concentration, but the rate of change is proportional to molybdenum content for both Fe-14 Cr and Fe-17 Cr (Figs. 11 and 12). Thus, the elapsed time when changes in Δ occur is a measure of the depassivation kinetics and rate of change of Δ is a measure of the repassivation kinetics, the balance between the two determining the nature and severity of the corrosion attack on a metal surface.

CONCLUSIONS

1) An increase in the amount of molybdenum in Fe-Cr alloys increases the rate of repassivation of bare surfaces in 1.0 N NaCl solutions.

2) Molybdenum has no effect on the time to observe the beginning of the processes leading to crevice corrosion, but the rate at which these processes proceed is affected by the molybdenum content, the more molybdenum the lower the rate.

3) If the onset of localized corrosion is assumed to be controlled by a dynamic balance between depassivation and repassivation, the molybdenum in ferritic stainless steels only affects repassivation and not depassivation, while chromium affects both processes.

4) An addition of 2% Ni for an Fe-28 Cr-5 Mo alloy gives a 20% reduction in its rate of repassivation in 1.0 N NaCl solution.

ACKNOWLEDGEMENTS

We are grateful to A. P. Bond and M. A. Streicher for providing us with samples of alloys used in this study and to the Office of Naval Research which supported this work under contract NAONR 18-89 NRO 36-082.

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To be submitted for publication in Corrosion

Comparison of Repassivation Measurements to Constant Strain-Rate Tests in the Stress Corrosion Cracking of 304 Stainless Steel

by

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ABSTRACT

Constant strain rate studies were performed using AISI 304 stainless steel exposed to acidified 1.0N NaCl solution (pH=3.0). In this particular environment, repassivation kinetics measurements using the tribo-ellipsometric technique had shown that the metal dissolution rates were rather large due to reduced film repair kinetics, indicating the possibility of susceptibility to stress corrosion cracking (SCC). Reduced time to failure and maximum sustained load at one strain rate suggest a relationship between SCC, repassivation kinetics, and rate of pure metal production.

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Recent interest in the use of repassivation kinetics measurements to predict susceptibility of a material to stress corrosion cracking in a particular environment has provided a large amount of experimental data with which it is possible to estimate an extent of electrochemical reaction which occurs after the production of bare metal (1,2). This laboratory has been involved in the measurement of repassivation kinetics using the technique of tribo-ellipsometry (3,4). This technique is used to make optical and electrochemical observations of repassivation of bare metal produced by abrasion. It gives no information, however, about the rate of bare metal production resulting from the film rupture that occurs when a metal is stressed. Information obtained from use of tribo-ellipsometry about the repassivation ratio of metal dissolution to film growth ($R\overset{*}{p}$)[1] is, of course, essential in determining the extent of reaction during one such incident and thus giving a measure of susceptibility to SCC, but unless the rate of bare metal production provides a more or less constant and localized area of exposed metal, cracks cannot propagate. The use of slow strain tensile machines which essentially measure the effect of the rate of bare metal production on SCC susceptibility has been described by Parkins (5) and already successfully used by a number of workers (6,7). In this study, kinetics of repassivation are compared to results obtained using the constant strain-rate test. The rationale behind the use of the constant strain-rate test is that if a particular material possesses a susceptibility to stress corrosion cracking in a given environment, then there should exist an optimum rate of bare metal production for propagation of cracks to occur during straining. This would be determined by the repassivation kinetics of that system. At strain rates much

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[1] ($R\overset{*}{p}$) is the ratio of the total charge involved in repassivation to that involved in protective film regrowth.

slower than this value, the bare metal produced will repassivate without crack advance. Faster strain rates will reduce specimen cross section in a ductile manner before SCC can contribute.

Studies described here are in part based on repassivation kinetics measurements on AISI 304 stainless steel in 1.0 N NaCl solution (8). One result of those studies was that the repassivation ratio, R_p, was significantly higher in an acidified 1.0 N NaCl (pH=3) at a potential of +90 mV SHE (corrosion potential measured for 304 stainless steel in this environment) than in neutral or basic solutions. This system was therefore selected as a starting point for the determination of the relationships between repassivation kinetics, rate of bare metal production, and stress corrosion cracking susceptibility.

EXPERIMENTAL

Apparatus

Experiments in this study were performed on the slow strain tensile machine[2] shown in Fig. 1 capable of producing strain rates of 10^{-5} to 10^{-7} sec^{-1}. Load was measured potentiometrically with a load cell.

The electrochemical cell used in this study was fabricated from teflon and utilized teflon Swagelok fittings to maintain liquid tight seals (Fig. 2). The lubrication properties of teflon prevent transmission of a portion of the applied load to the cell itself during straining. The volume of the cell was about 50 cm^3. The auxiliary electrode was housed in a separate cell to prevent build up of counter electrode reaction products.

Material

Specimens were machined from 17.78 cm lengths of 6.35 mm diameter cold drawn annealed AISI type 304 stainless steel rod stock and had reduced cross sections with 2.54 cm radius shoulders which gave a 2.54 cm long guage length 3.175 mm in diameter. Before placement in the electrochemical cell, specimens were degreased with spectro-grade methanol, rinsed in distilled water and dried in a jet of compressed air.

Experiments were conducted in 1.0 N NaCl solution acidified to pH 3 with 1.0 N HCl. Solutions were prepared using reagent grade chemicals and distilled water (7.0×10^{-7} ohm^{-1} cm^{-1}). Where load or time to failure data are reported, values are normalized with respect to air. All experiments were performed in duplicate and recalibrations

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[2] I am grateful to R. N. Parkins and B. E. Wilde for their contribution to the design of this instrument.

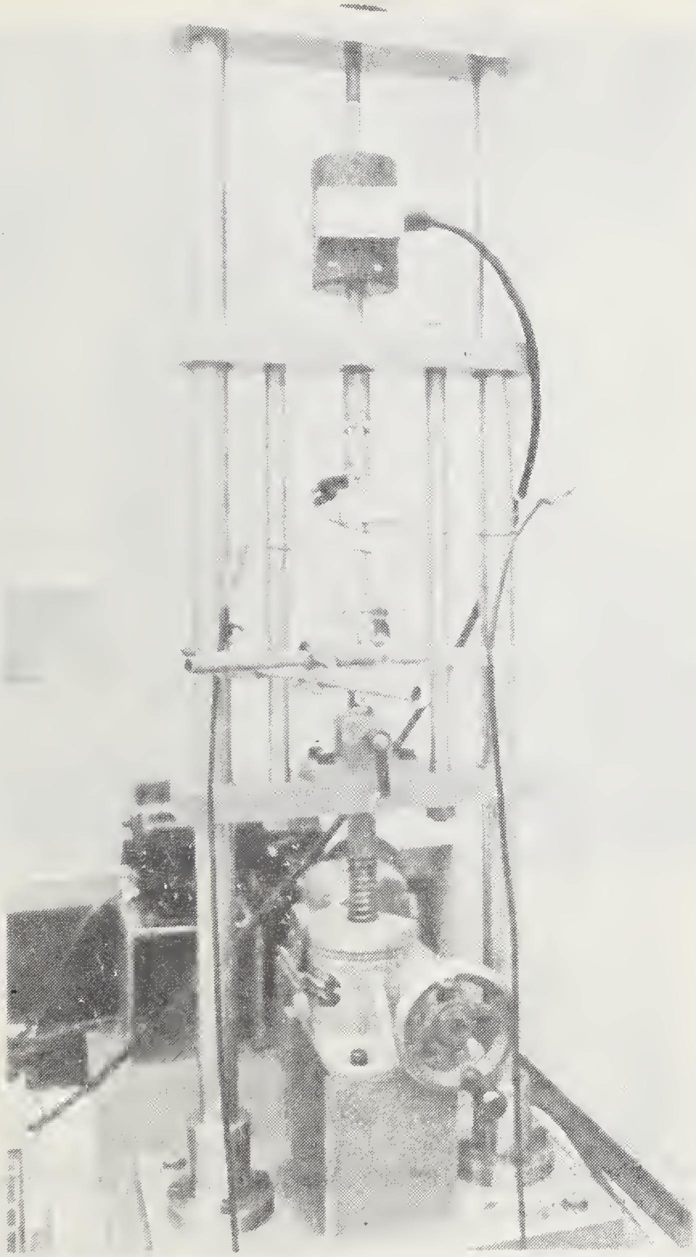

Fig. 1. Photograph of the constant strain rate machine used in these studies.

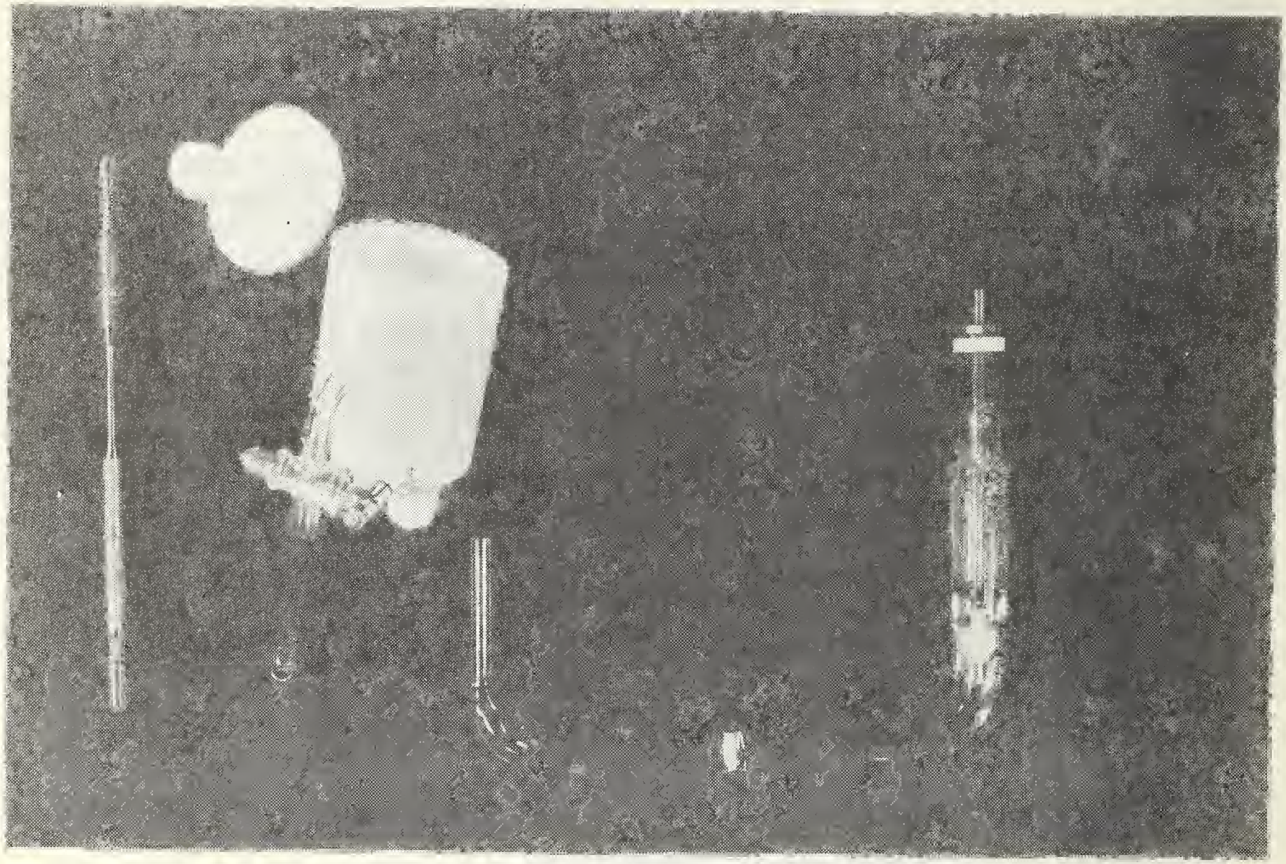

Fig. 2. Photograph of the teflon electrochemical cell (unassembled) used in these studies.

(tensile tests in air at a given strain rate) were repeated when time to failure or sustained loads varied by more than 1% from the air fracture value.

RESULTS AND DISCUSSION

Changes in specimen potential with time were measured during straining at 2.2 x 10^{-6} sec^{-1} for 304 stainless steel in air saturated 1.0 N NaCl solution (pH 3.0) and results are shown in Fig. 3. The initial potential increase is probably due to depletion of oxygen within the sealed cell. The final potential jump occurred at specimen fracture.

Stress corrosion susceptibility tests were then run in the acidified NaCl solution at several different strain rates using specimens polarized to +90 mV SHE. This environment was chosen because previous work (8) showed that the repassivation kinetics observed appeared to be favorable for SCC susceptibility. It can be seen from Fig. 4 that the repassivation ratio (R_p) determined by tribo-ellipsometry was of sufficient magnitude (at pH 3, +90 mV SHE) to indicate these conditions as the more likely of those studied for observing susceptibility to SCC.

Maximum load and time to failure data, normalized with respect to air, are given in Fig. 5 and in Table I. A scanning electron microscope was used to examine the fracture surfaces of both air fracture and <u>in situ</u> fractures at the maximum strain rate obtained with the equipment presently available. From Table I, it can be seen that the reduction in maximum load and time to failure indicate possibility of SCC attack. The fracture surface of this specimen was examined with a scanning electron microscope. The central portion of the fracture surface shown in Fig. 6 is of the dimpled nature characteristic of ductile tensile failure. However, one area of the surface (see arrow, Fig. 6) showed a markedly different topography (Fig. 7) which, under higher magnification, shows some evidence of the cleavage characteristic of stress corrosion cracking in austenitic stainless steels (Fig. 8). The fracture surface is pock-marked with two distinctly different types of holes —one similar to that produced during ductile fracture, and the other, crystallographic in appearance, probably the initial stages in formation of pits on the newly generated metal surfaces (Fig. 9).

Slow strain experiments were performed at the same potential and strain rate on 304 stainless steel specimens exposed to neutral 1.0 N $NaNO_3$, an environment in which the repassivation ratio was significantly lower. No change in maximum applied load or time to failure with respect to air was detected.

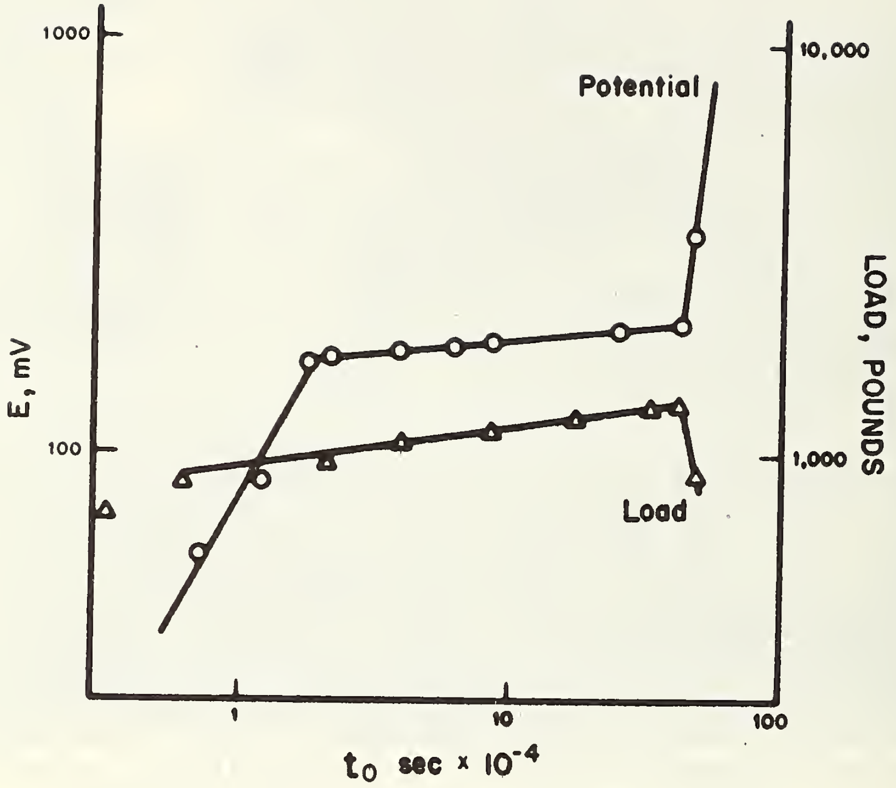

Fig. 3. Changes in potential (mV SCE) and sustained load versus time during constant strain rate experiment [2.2×10^{-6} sec^{-1}] for 304 stainless steel in acidified 1.0N NaCl solution (pH = 3.0).

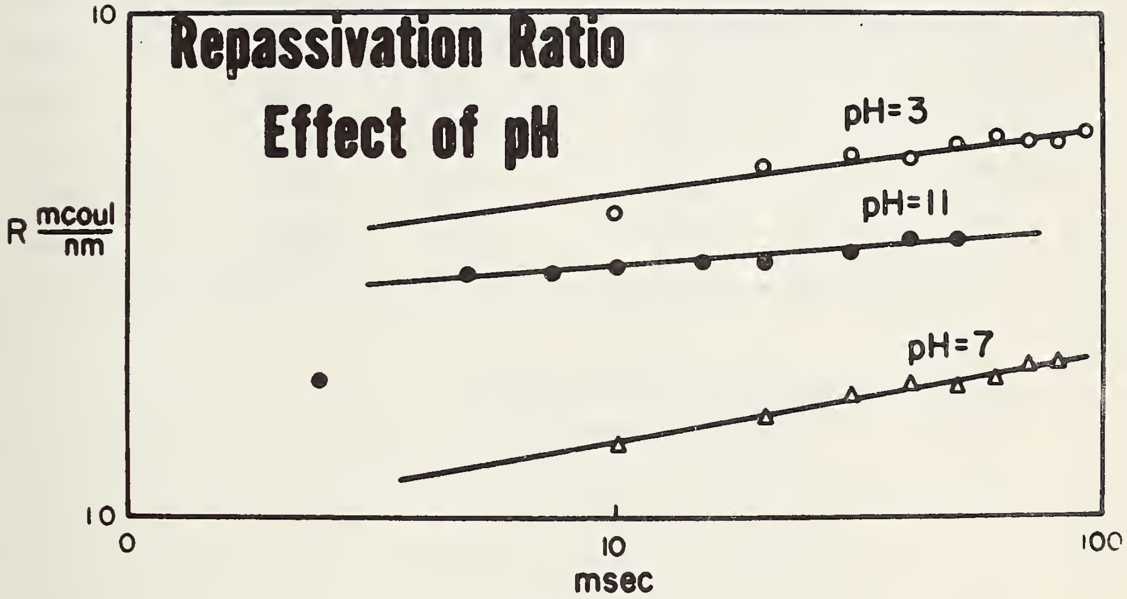

Fig. 4. [From (8)]. Changes in Repassivation Ratio, Rp ($\log_{10}$ Rp vs $\log_{10}$ ms) for 304 stainless steel in air saturated 1.0N NaCl (pH 3, 7, and 11) at +090 mV (SHE) following removal of surface film by abrasion at -1000 mV (SHE).

Table I.

strain rate, sec^{-1}	time to failure, hrs.		max. sustained load, kg.	
	1.0N NaCl (pH=3)	air	1.0N NaCl (pH=3)	air
2.1×10^{-7}	870	875	2950	2955
2.1×10^{-6}	75.1	75.0	3000	3000
6.2×10^{-6}	35.0	34.5	2960	3080
8.1×10^{-6}	24.5	24.5	2900	2900
8.3×10^{-6}	21.0	22.2	2900	3260

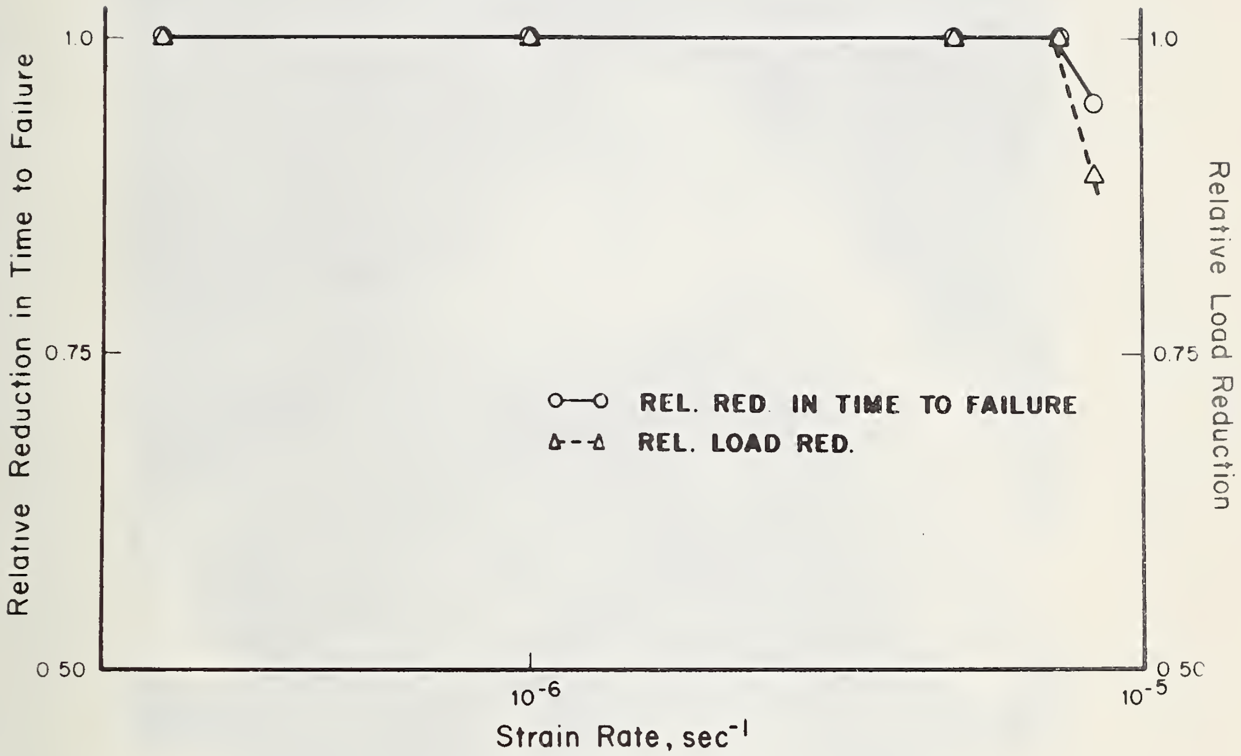

Fig. 5. Changes in time to failure and maximum sustained load (both normalized with respect to air) versus strain rate for 304 stainless steel in acidified 1.0N NaCl solution (pH = 3.0).

Fig. 6. Scanning electron micrograph (x20) of the fracture surface of a 304 stainless steel specimen fractured at a constant strain rate of 8.3×10^{-6} sec^{-1} in acidified 1.0N NaCl solution (pH = 3.0).

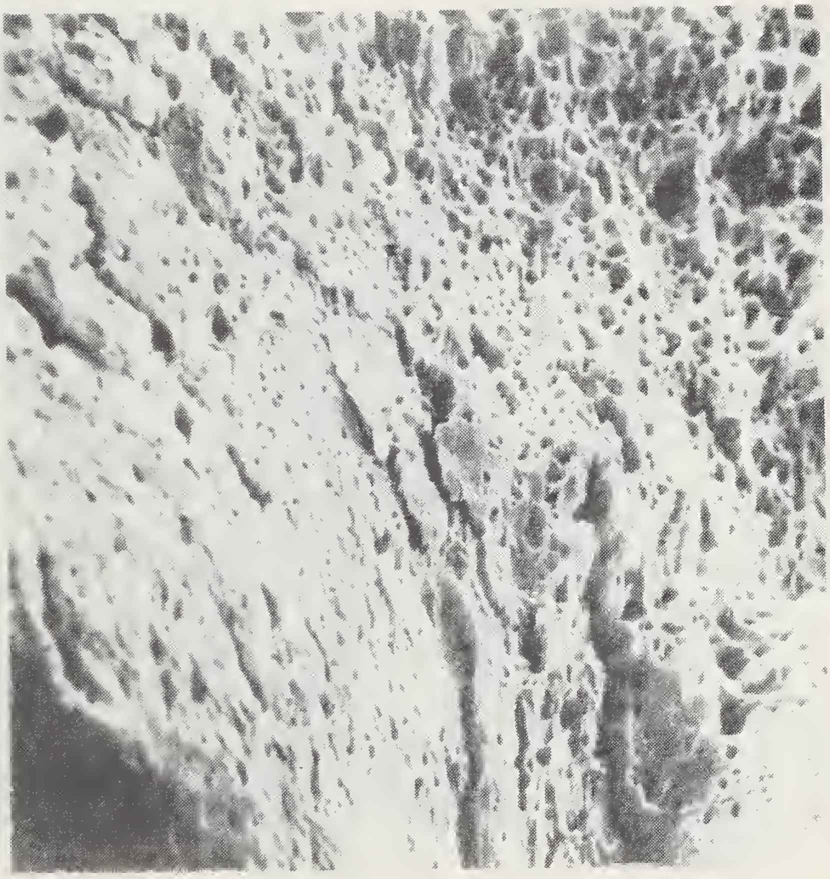

Fig. 7. Scanning electron micrograph (x500) of the area of the fracture surface indicated by arrow in Fig. 6. Specimen is 304 stainless steel fractured at a constant strain rate of 8.3×10^{-6} sec^{-1} in acidified 1.0N NaCl solution (pH = 3.0).

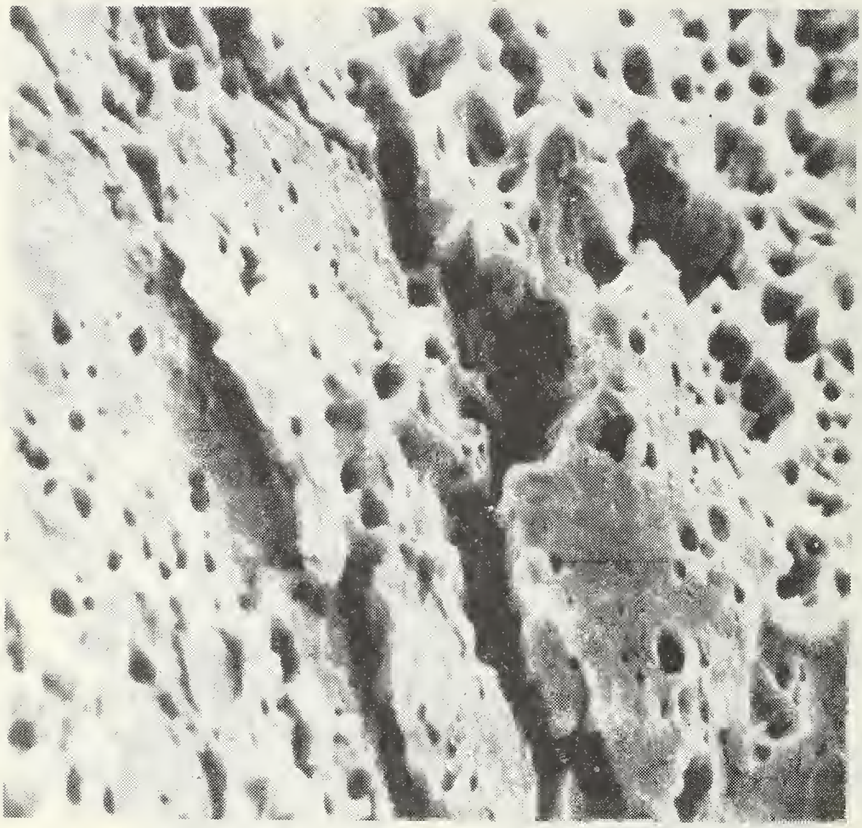

Fig. 8. Scanning electron micrograph (x2000) showing areas resembling cleavage on fracture surface of 304 stainless steel fractured at a constant strain rate of 8.6×10^{-6} sec^{-1} in acidified 1.0N NaCl solution (pH = 3.0).

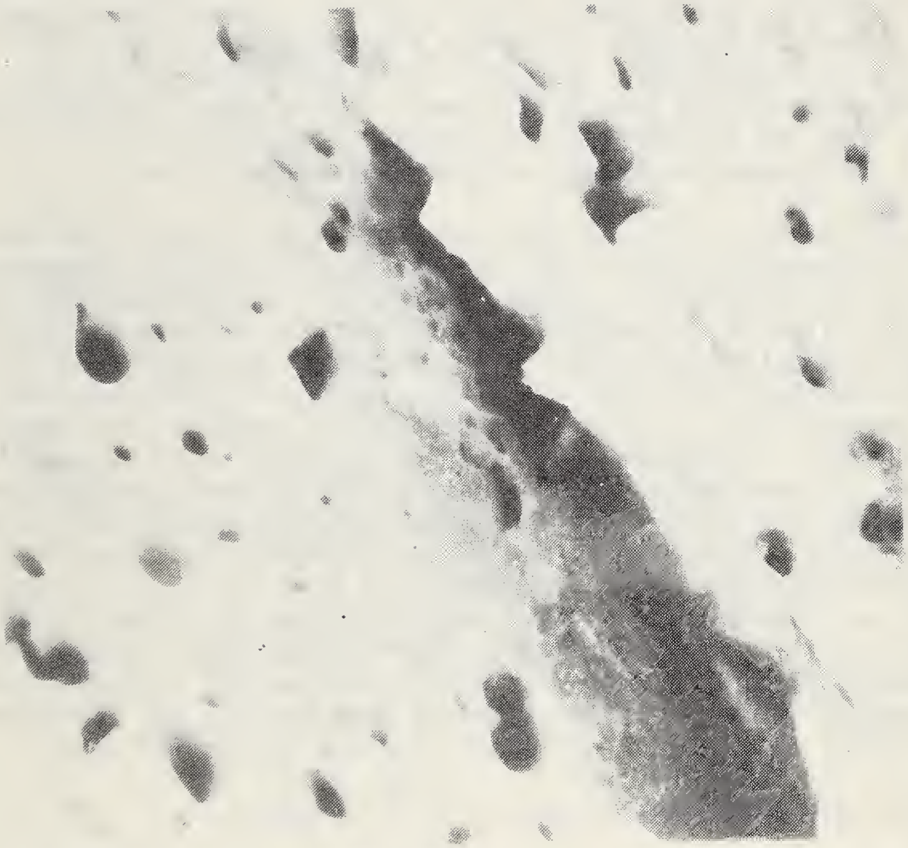

Fig. 9. Scanning electron micrograph (x5000) showing the types of pits produced on the fracture surface of 304 stainless steel fractured at a constant strain rate of 8.6×10^{-6} sec^{-1} in acidified 1.0N NaCl solution (pH = 3.0).

These results indicate that the effect of potentiostatic exposure of 304 stainless steel in acidified sodium chloride solution on time to failure and maximum sustained load during slow straining must arise from a metal removal component occurring in conjunction with ductile tensile failure during the time span of the experiment. Anodic current density measurements made during the duration of exposure lead to a calculation of an average depth of metal penetration of 5 x 10^{-6} cm which cannot account for the measured decrease in maximum sustained load. Of course, it is conceivable that localized attack in the form of pitting could reduce the effective cross sectional specimen area to such an extent as to reduce the sustained load. While examples of pitting were observed in the SEM micrographs, the crystallographic pit density was low. The evidence of some cleavage in the same SEM micrographs lends better support to the conclusion that a SCC process is operative under these conditions.

Although definitive conclusions must await further experimentation, it is interesting to note that on the basis of relative repassivation kinetics of 304 stainless steel in neutral and acidified sodium chloride solution, a greater susceptibility to SCC seemed likely in the acid solution because this environment produced lower film growth kinetics. Although the still limited evidence reported here does not confirm a marked tendency for cracking in acidified chloride environments at any finite propagation velocity under service, it does suggest replacement of conventional susceptible/non susceptible criteria which, while valid for predicting failures that occur in short time spans, are not suitable for measuring susceptibility when crack propagation is very slow. For practical situations where failures take years to occur such slow crack growth rates are still important. Here, especially for ductile alloys where fracture mechanics techniques present problems, the combination of repassivation kinetics measurements and constant strain-rate tests may be a valuable failure predictive aid.

Many questions remain, however. For example:

1) What is the effect of using higher strain rates than are presently possible with this apparatus? According to Parkins (5) it is to be expected that relative time to failure and sustained load values will reach a minimum before returning to unity at sufficiently rapid strain rates where material fails ductilely before SCC can be expected to occur.

2) What is the effect of potential on strain experiment parameters? One should find a point at which failure by general anodic dissolution or pitting will take over.

3) From Fig. 3 [Ref. (8)] it can be seen that the repassivation ratio in a pH 11 solution, although less than for the pH 3, is somewhat greater than for neutral solutions. What should be the effect of exposure to this environment on the tensile properties during slow strain?

The work is presently being directed along these lines.

ACKNOWLEDGEMENT

I gratefully acknowledge the support of the Office of Naval Research who sponsored this work under Contract No. NAONR 18-69, NR 036-082.

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To be published in the Proceedings of the
20th Meeting of the Materials Failure Prevention Group

Failure by Stress Corrosion Cracking - Current Approaches Toward Failure Prediction

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ABSTRACT

Stress corrosion cracking (SCC) produces failures in a material when it is subjected to the combined effects of mechanical stress and reaction with an environment. All proposed mechanisms of SCC seek to explain how the combination of a given level of stress, a particular material, and a given environment can lead to the initiation and propagation of cracks. The three major categories of mechanisms that are generally proposed are (1) active path dissolution, (2) stress-sorption, and (3) embrittlement.

In recent years attempts to determine the mechanisms have been enhanced by new concepts and techniques that flow from the three major scientific disciplines that underlie the complex problem of SCC - chemistry, metallurgy, and mechanics. From chemistry have come two main currents: (a) increased awareness of the importance of characterizing the altered environment inside a growing crack, and (b) a recognition of the importance of the regrowth rate of a protective film on a bare surface exposed when that film is broken by stress. The main emphasis in the metallurgy of SCC has been on the crucial role played by structure in general, and particularly at the tip of a crack. Aiding this objective has been the use of the high voltage electron microscope which can directly look at the interaction of the environment with structural defects, e.g., dislocations. Finally, the major thrust in the mechanics of SCC has been the application of the concepts and techniques of fracture mechanics.

The impact of these new concepts and measurement techniques on predicting and preventing SCC failure will be discussed.

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Far too often the failure of a metal part involves an alloy that was chosen because of its good corrosion resistance to the environment in which it is designed to operate. Moreover, it failed at stress levels well below its normal fracture stress. More than likely, this and similar such unexpected failures were due to stress corrosion cracking (SCC). The insidious nature of this mode of failure results from the situation just described where, in the absence of the possibility for SCC, one would expect both good fracture and corrosion resistance. Fig. 1 from a paper by Staehle (1) illustrates how SCC markedly reduces the load carrying cross section of a part over that to be expected from environmental attack (corrosion) alone or from purely mechanical failure. Thus, it is from this synergistic interaction of corrosion and stress that SCC arises, and the definition of the phenomenon reflects this fact. For example, the ASTM Committee on the Corrosion of Metals defines it as "a cracking process requiring the simultaneous action of a corrodent and sustained tensile stress. This excludes corrosion-reduced sections which fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion which can disintegrate an alloy without either applied or residual stress." This definition embraces many of the other terms that focus on particular mechanisms such as "hydrogen embrittlement," "caustic embrittlement," "season cracking," etc.* This diversity of terms has tended to produce confusion. Many workers, for example Staehle (1) and Brown (2), have proposed that the term "stress corrosion cracking" be used as a generic term to avoid entangling and confusing the macro phenomenon with any special mechanism that may govern a particular situation. This proposal is being increasingly adopted in the modern literature.

Because of the diversity of mechanisms affecting SCC, and because it takes place in what are thought to be innocuous environments, this mode of failure was not generally considered too important as late as 1940.

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*It does not include "corrosion fatigue" which involves a cyclic stress rather than a sustained static stress.

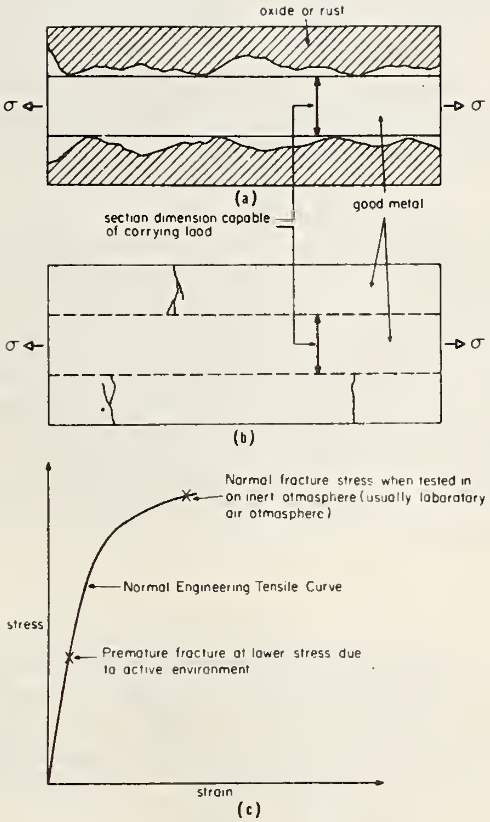


Fig. 1. A comparison in the reductions in load-carrying cross section as a result of (a) general corrosion and (b) stress corrosion. The effect of stress corrosion on the tensile curve is shown in (c). From Staehle (1).

In a discussion accompanying a 1940 paper by Hodge and Miller (3) which clearly highlighted the problems of SCC, Brooks pointed out that "... the industrial implications of this phenomenon do not loom large. Failures are rare and will become more so as understanding spreads...." Not only were his predictions not realized, but the systems where SCC is recognized as the cause of a failure have increased markedly throughout this century. It was first recognized at the end of the 19th century when brass cartridge cases (containing residual stress) failed because of exposure to the ammonia present in stables. Table I documents the marked increase in the recognition of SCC as a source of failure, going from the days of transportation by horse-drawn vehicles to the space vehicles of today. The number of systems where previously failures were not expected continues to grow, especially as greater demands are made on materials.

Because of the increased identification of SCC as a major cause of failures, there has resulted a significant increase in research directed towards understanding the phenomenon and developing mechanisms to explain it. Two recent proceedings of major meetings (5,6) and a forthcoming one (7) give excellent accounts of the current state of thinking on the origins of SCC. This paper will briefly outline the major mechanisms that are currently believed to explain SCC and then show how these mechanisms have pointed the way to the development of new experimental approaches which, besides enhancing our understanding of SCC, have, more importantly, provided us with opportunities for the development of new capacities for failure prediction and prevention.

Mechanisms

In order to consider the important mechanisms that have been proposed to explain the origins of SCC, we must first list the characteristics, most of which must be present to produce this mode of failure. This is necessary because a valid mechanism must explain the necessity for these characteristics to be present if SCC is to occur. Brown (4) has listed the following features generally common to SCC:

1) The existence of a tensile stress either applied or present as a residual stress.

2) The alloy usually shows good resistance to corrosive attack by the environment causing cracking. This is why alloys chosen because of their corrosion resistance to an environment may be subject to SCC.

3) SCC for a given alloy usually occurs more readily in a rather specific environment. Moreover, the key damaging species in that environment need not be present in large concentrations. Recent studies (9,10) have indicated that the dependence of SCC on environmental specificity is not as pronounced as originally thought in early SCC studies.

4) The microscopic appearance of stress corrosion cracks is that of a brittle fracture in spite of the fact that the metal itself may still be quite ductile in a mechanical test. The cracks frequently exhibit multiple branching, but this does not always occur.

Table I

HISTORY OF STRESS CORROSION PROBLEMS

[Adapted from Brown (4)]

WHEN	WHAT
Late 19th Century	Brass in ammonia
End 19th Century	Boiler steels in caustics
Early 20th Century	Mild steels in nitrates
Early 20th Century	Aluminum alloys in moist atmospheres
1930's	Stainless steels in chlorides
1930's	Magnesium alloys in moist atmospheres
1950's	Martensitic steels in aerospace environ.
1950-60's	Titanium - Hot salts, N_2O_4, methanol

5) In order for SCC to occur a threshold stress or stress intensity must be exceeded.

To Brown's list must be added another characteristic becoming increasingly recognized (9,11). There exists a critical potential. Any metal in an environment where its potential lies below this critical potential is thought by some to be immune from SCC. This is a more recently proposed characteristic that has been strongly advocated by Uhlig (11).

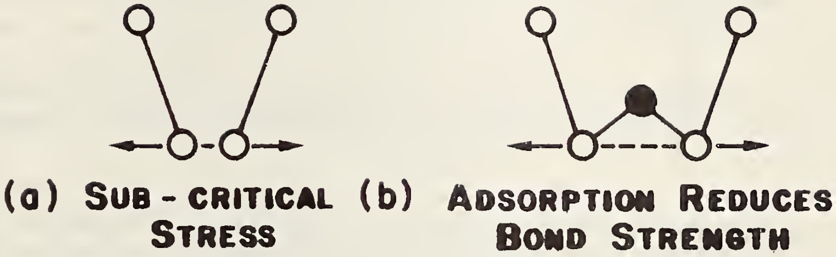
At one time it was believed that SCC could not occur for pure metals, but some recent work (13,14) has found SCC for high purity copper. As with all the other characteristics, one can usually find exceptions.

Using these characteristics of SCC as a basis, a number of mechanisms have been developed. At one time some believed that there existed a universal mechanism that applied to all systems where SCC was found. It is now widely held that SCC can be due to a number of different mechanisms, and that there are alloy-environment systems where one or more of the mechanisms outlined here may apply. Of the many proposed, three major mechanisms are currently the ones most actively used. Moreover, the others proposed can be considered as variations or sub-sets of the three major ones. All of the mechanisms involve the complex interactions of the three disciplines that control SCC, chemistry, (electrochemistry), metallurgy, and mechanics. None of the mechanisms will be discussed in great detail, and a critical evaluation of their pros and cons is outside the scope of this paper. Instead these mechanisms will be briefly described, their strong and weak points detailed, their failure prevention implications indicated, and, in the next section of this paper, the techniques that they point to as possible tools for failure prediction will be discussed.

Stress-Sorption Mechanism - This mechanism, most actively advocated by Uhlig (14,15), proposes that a specific species adsorbs and interacts with strained bonds at the crack tip causing a reduction in bond strength, or, thermodynamically stated, a reduction in the surface energy, γ, which leads to a lowering in the stress required to produce brittle fracture. The relationship between the theoretical stress to produce brittle fracture, σ_f, and γ is given by the well known expression

$$\sigma_f = \left(\frac{E\gamma}{d}\right)^{1/2}, \qquad [1]$$

where E is the elastic modulus and d is the atomic spacing. The adsorption of a damaging species at a crack tip lowers σ_f and therefore the threshold stress for SCC is the minimum value to which γ is lowered by adsorption. Fig. 2 outlines the mechanism schematically. Uhlig proposes that an important factor arguing for this mechanism is the existence of a critical potential below which SCC does not occur. He explains that the effect of potential can be attributed to the strong dependence of adsorption on potential. He bases this on many studies by electrochemists who have found



(a) SUB-CRITICAL STRESS

(b) ADSORPTION REDUCES BOND STRENGTH

Fig. 2. Stress sorption mechanism for SCC.

(a) chemisorption of ion at tip of crack.

(b) weakening of interatomic bond at the tip of the crack so that applied tensile stress leads to the breaking of this bond.

that the adsorption of an anion (usually the damaging species for SCC) takes place at potentials above the point of zero charge for a given surface in a given environment. (This strong dependence of failure or potential explains why SCC can be prevented by cathodic protection in some systems). Environment plays a role in the stress-sorption mechanism because of the specificity of adsorption of a particular species on a surface, and because environment brings the potential to a value where adsorption can or cannot take place. Moreover, if one can introduce into the environment an extraneous species that displaces the damaging bond-weakening adsorbed species, cracking becomes more difficult. Uhlig (14) gives examples where such extraneous species inhibit SCC. The stress-sorption mechanism is more widely accepted in the case of liquid metal embrittlement or stress cracking of plastics. In the former case, for example, Preece (15) points out that the theory is successful in explaining the observations of a brittle to ductile transition with increase in temperature (desorption), an "instantaneous" failure mode, the increase in severity of embrittlement with increase in strain rate and flow strength, and, possibly, specificity.

For SCC in aqueous environments, however, a number of problems with the stress sorption mechanism have been pointed out (9,10). Among them are the following:

1) In the cracking of ductile alloys, the ductility present is sufficient to produce extensive plastic deformation at a crack tip. The blunting that this produces eliminates the infinite sharpness required for this mechanism to work.

2) The large amount of metal dissolution observed in many straining electrode experiments (to be discussed later) poses the question of what happens when the metal dissolves out from under the adsorbed film.

3) Crack growth rates are considerably slower than one would expect from this model.

4) Studies (17) have shown that thin protective films exist on metals in SCC environments, and that these films reform rapidly, on the order of milliseconds in some cases. The weakening of metal bonds require that rapid direct access to the base metal surface is necessary, but the existence of these films would prevent or strongly influence this adsorption process.

The measures suggested by the stress-sorption mechanism to promote SCC failure avoidance are as follows:

1) Lower the potential of a metal to be protected below the critical potential for SCC either by coupling another more active metal to it or by cathodic protection using an applied current.

2) Introduce inhibiting anions in the environment.

To properly apply these measures requires techniques that enable both the determination of the critical potential for SCC and the potential of the metal in an environment. The latter requirement is not as easily met since the environment that counts is that environment existing in flaws or cracks. In addition to a realistic characterization of the environment, there exists an equal need for realistic characterization of the stress system acting on a crack tip, since the model requires adsorption at strained bonds or dislocations. Thus, techniques that yield both the geometry of stress application and expected dislocation configuration would be valuable for failure prediction using the guidelines provided by this mechanism. Finally, ways to measure the rate of adsorption of the relevant species as a function of stress geometry and potential would be invaluable if this mechanism has merit.

Film Rupture-Metal Dissolution Mechanism - This mechanism was originally suggested by Logan (18) and Champion (19). It has also been refined and extended by a number of workers (10,17,20-24). The mechanism proposes that the protective film normally present on a metal surface (if it were not present the metal would fail by corrosion alone) is ruptured by continued plastic deformation at a crack tip where the exposed metal becomes a very small and restricted anodic region where metal dissolution takes place. The rest of the metal surface, especially the walls of the crack acts as a cathode. Susceptibility depends on the rate at which the metal exposed by film rupture is repassivated vis a vis the rate of metal dissolution. Fig. 3 gives a schematic representation of this mechanism. A clear picture of this process has been provided by Vermilyea (24) in a recent paper where he lists the following five steps in the process that leads to crack extension:

1) The film is ruptured at time zero.

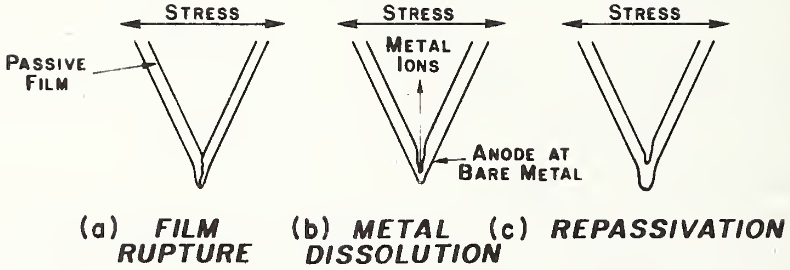
2) Crack growth by dissolution occurs for a distance of L during the time of repassivation t_L.

3) The dissolution process removes the material at the old crack tip and thereby creates a strain transient just ahead of the newly created crack tip as shown in Fig. 4.

4) At a time t_L a critical strain builds up to a value sufficient to cause rupture of the newly reformed film at the base of the new crack.

5) The process repeats itself, the crack propagation rate, $\frac{dL}{dt}$, given by Vermilyea as

$$\frac{dL}{dt} = \frac{L}{t_c} \qquad [2]$$



(a) FILM RUPTURE (b) METAL DISSOLUTION (c) REPASSIVATION

Fig. 3. Film rupture-metal dissolution mechanism for SCC.

(a) Rupture of the protective film at tip of a crack by the application of a tensile stress.

(b) Dissolution of the metal exposed when film is ruptured. Tip of crack is an anode and film covered walls of the crack is a cathode.

(c) Repassivation of the exposed metal at the tip of the crack.

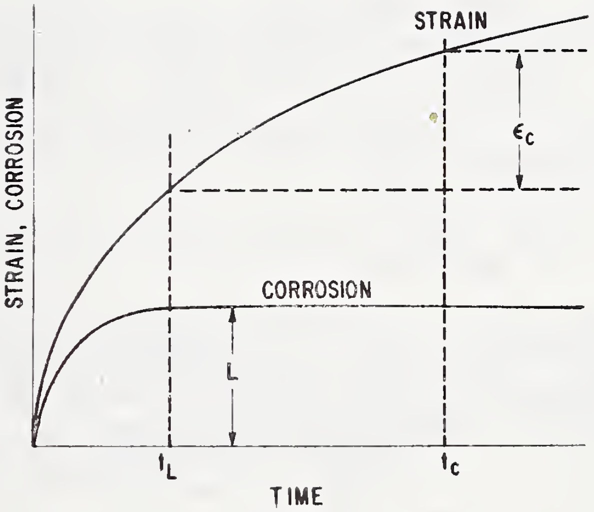


Fig. 4. Time dependence of events occurring after film rupture. Repassivation time is t_L. The time to produce the critical strain, ε_c, necessary to cause film rupture is t_c. From Vermilyea (24).

A sub-set or variation of the active path dissolution mechanism just described is the brittle-film mechanism (25,26). It differs from the dissolution mechanism in that crack advance is mainly by the production of a penetrating brittle film which undergoes fracture when tensile stress is applied. The crack produced enters the ductile metal below this brittle film and a new layer is formed on the bare metal so produced. The process continues by a repetition of the film fracture-reformation cycle.

One can conceive of at least three factors that affect the general mechanism.

1) The rate of production of bare sites, which is dependent on the magnitude of the stresses applied, the metallurgy of the material, and the geometry of the stressed system (the value of t_c is important here).

2) The rate at which the bare sites produced by the applied stress are repassivated (t_L is important here).

3) The resistance of the protective film (its ductility) to rupture [see (24)], (again t_c is important).

The nature of the species in the environment has an effect on t_p, or probably more importantly, the rate of repassivation (17). This is so because small impurities can affect the composition of the newly reforming film and rates of growth are sensitive to the presence of impurities (27). Also, environment can affect t_c through its influence on film ductility (28). Potential affects both film growth kinetics and metal dissolution rate so that the balance of these two competing factors is important, the latter affecting L, the distance of crack advance. The concept of a critical potential for SCC is as valid for the film rupture-metal dissolution model as it is for the stress-sorption mechanism.

There are a number of facts that create problems in accepting the film rupture-metal dissolution model for all cases of SCC. Among the most important are the following:

1) The quasi-cleavage character of some SCC transgranular fracture surfaces indicate brittle failure rather than dissolution.

2) Crack propagation occurs at a surface which is itself rapidly dissolving at a high rate (29).

3) There is a possible discrepancy between crack growth rate and the currents observed in straining electrode experiments which purport to measure the current involved in dissolution at crack tips (22).

The measures suggested by the active path dissolution model to promote SCC failure avoidance will include one suggested for the stress sorption model, i.e., control of potential to a value below the critical potential for SCC. Another measure is the control of repassivation kinetics by environment or alloy modification. In order to apply the latter measure for SCC avoidance, techniques for measuring repassivation kinetics as a function of potential and environment are required. However, in order to make such measurements one must, as suggested earlier for stress-sorption, be able to characterize the environment and potential existing in cracks. Finally, and most difficult, one must have a technique for determining t_c, the time required to build up a rupturing stress in a film as a function of the metallurgy of the alloy whose failure we wish to prevent. This requires the measurement of the ductility of the protective film on an alloy and the geometry of the stress system acting on a crack.

Hydrogen-Embrittlement Mechanism - This is considered by some to be a different phenomenon from SCC, but since cathodic reactions (which produce hydrogen under the proper conditions) are as much a part of corrosion as anodic ones (producing films and/or metal dissolution), it is difficult to exclude it in a discussion of SCC. In this mechanism fracture results from the production of a brittle region at the crack tip because of the introduction of hydrogen into the alloy via cathodic reactions (see Fig. 5). The production of this brittle region has been attributed to a number of causes among which decohesion (30), new phase formation (31-33), and pinning of dislocations (34) can be mentioned. The environment can affect the process by influencing the rate of production of hydrogen ions and by enhancing or inhibiting the entry of hydrogen into the metal by the interposition of adsorbed or reaction layer films. In aqueous systems the potential at the crack tip determines whether the production of hydrogen at the surface is thermodynamically feasible. The composition of the environment influences what potential is necessary to produce hydrogen, its rate of production, and by means of the presence of inhibiting or enhancing species, whether it can readily enter the metal lattice. In gaseous systems, hydrogen pressure plays the same role as potential in aqueous environments. Inhibiting species, e.g., oxygen, can also be added to gases (35).

It has been suggested by some workers, for example, Troiano and coworkers (36), that almost all aqueous SCC is hydrogen embrittlement. They found that austenitic stainless steels, which have been assumed to be non-susceptible to hydrogen embrittlement, could be made less ductile by hydrogen charging, and that one could observe the permeation of hydrogen at positive currents (where one should only expect metal dissolution). Other workers (31-33,37-39) have found the formation of a phase or phases capable of undergoing hydrogen embrittlement.

All of these findings do point to greater universality of application for the hydrogen embrittlement mechanism. However, as always, there are counter arguments that rule against such universality. Recent work by Wilde and Kim (40) showed that for an austenitic stainless steel while rate of hydrogen permeation was higher at negative potentials, time to failure was also higher at these hydrogen producing potentials. This finding also agrees with results that show that cathodic protection (which should promote the production of hydrogen) does retard SCC for a number of alloys (16). Indeed, to confuse the picture further, it has been found by Bernstein and Pickering (41) that anodic dissolution can occur in the cracks of cathodically polarized ferrous alloys.

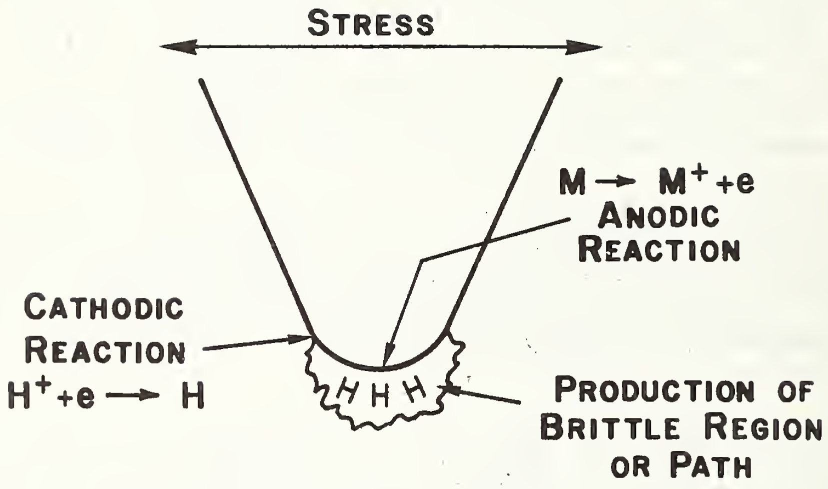


Fig. 5. Hydrogen embrittlement mechanism for SCC. Cathodic reduction of H+ at the tip of a crack produces hydrogen which enters the vicinity of the tip and embrittles the metal immediately ahead of an advancing crack.

This difficulty in determining whether hydrogen embrittlement is an operative mechanism is most important in developing measures for failure prevention. For example, unless one knows the operative mechanism, a change of the potential to what is believed to be a protective value may actually accelerate failure. Obviously techniques that determine what are the real potential and environment at the tip of the crack are crucial. Likewise, electron micrography of fracture surfaces which help in determining the mode of failure and can thereby suggest the proper prevention measures are also of utmost importance.

Techniques Suggested by Mechanisms

In the preceeding section the discussion of the major mechanisms of SCC pointed to the types of information that are needed in order to develop our ability to predict SCC susceptibility and to institute suitable measures for prevention. In this section the techniques developed in recent years, in many instances under the influence and stimulation of the concepts of these mechanisms, will be discussed. The techniques brought into being in this manner have their roots in the three broad disciplines that control the phenomenon of SCC: chemistry, metallurgy, and mechanics.

Techniques Dealing with the Chemistry of SCC - Two areas have been attacked with increasing interest in recent years. As pointed out in the previous section they are both important in all three major mechanisms although not always well recognized. They are the techniques directed towards determining the environment in cracks and the kinetics of repassivation.

a) The environment in cracks - While it has been recognized for a number of years that the environment trapped in the interior of restricted regions on a metal (cracks, pits, and crevices) has a different composition than the bulk environment surrounding the metal, it has been only in recent years that such knowledge was considered important, and serious attempts made to measure the composition of the occluded environment in a crack. Brown and co-workers (42-44), using the insights provided by the large body of work of Pourbaix [see the review in (45)] that systematized the role of pH and potential in all corrosion processes, set about to measure these parameters in SCC cracks. Their original approach was to immobilize the corrodent within SCC cracks by freezing it in liquid nitrogen, breaking open the crack mechanically, and then analyzing the thawed out solution removed from the crack. A later development is illustrated in Fig. 6 where microelectrodes determine the pH and potential in the crack's environment. Other developments in this fast moving field have been the use of a capillary to sample the crack solution (46) and the combination of a capillary technique with thin layer chromatography (47).

The value of these crack chemistry techniques becomes evident when Fig. 7 is inspected. It shows for a large number of steels of different compositions in environments of either high or low pH that the potential and pH inside the crack falls in a region of the pH-potential diagram (Pourbaix diagram) where one expects both corrosion and,

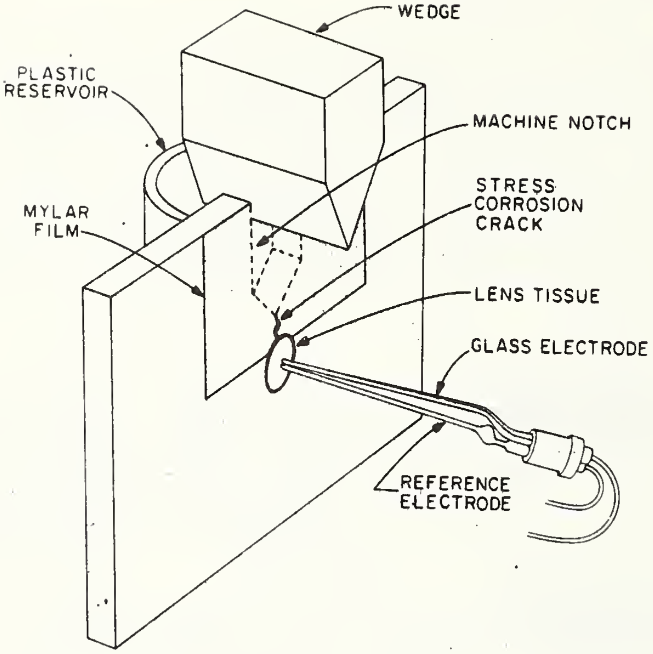


Fig. 6. Experimental arrangement for determining the acidity (pH) and potential at a crack tip. The glass and reference electrodes measure the pH electrochemically by sampling the solution that wets the lens tissue after the solution travels the length of the crack. From Smith, Peterson, and Brown (44).

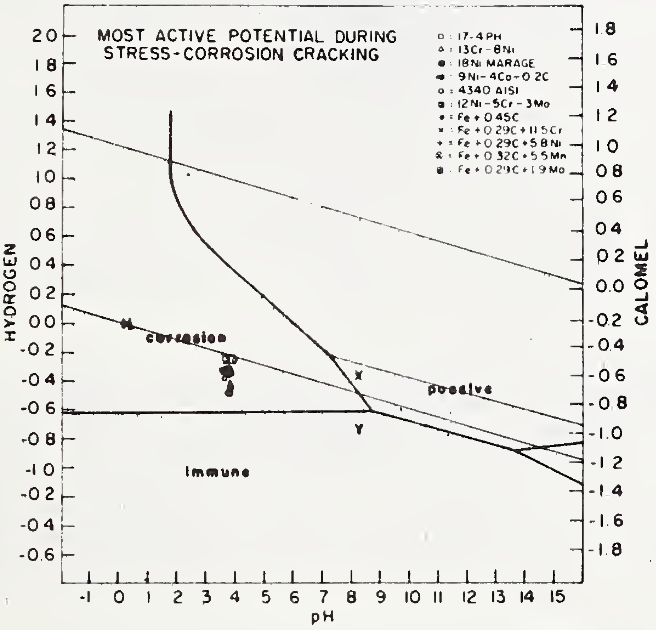


Fig. 7. Potential-pH diagram showing the potential-pH values in the crack tip environments for a number of high strength steels. From Brown in Ref. (6), p. 197.

because the points on Fig. 7 are below the line marked H, the presence of hydrogen. Thus, any failure prevention measures using bulk composition or potentials could be based on non-realistic conditions and lead to an improper choice. A good discussion of the electrochemical ramifications of knowing the proper environments in a crack is given by Pourbaix (45). In addition to knowing the nature of the solution in a crack and the potential at the crack tip, it is of great importance to know another aspect of the events occurring at the crack tip, e.g., how much hydrogen is entering the metal lattice? As the discussion on the hydrogen embrittlement mechanism stresses, this knowledge is of crucial importance. A tool for obtaining this information has been developed based on the work of Devanathan and Stachurski (48). By using a thin membrane of the metal studied it is possible to measure the amount of hydrogen that is evolved on one side of the membrane when it passes through the metal by oxidizing it electrochemically in a chamber on the other side of the membrane. The anodic current density at steady state involved in the oxidation of the permeated hydrogen is a measure of the amount of hydrogen entering the lattice on the hydrogen evolution side of the membrane. A discussion of the technique, its difficulties, and validity has been given recently by Bockris (49). Fig. 8 from a paper by Kim and Wilde (40) illustrates the importance of this technique. It shows that the rate of hydrogen penetration cannot always be related to SCC susceptibility.

b) Repassivation Kinetics - In all the mechanisms proposed for SCC, access of the environment must be provided to the metal surface. This surface, if it is suitable for withstanding ordinary corrosion, usually has a protective film. Therefore, as discussed earlier, the breaking of this film and the rate at which it regrows (repassivation kinetics) are of great importance in determining the time during which the environment can interact with the bare metal surface in any one of the different ways the various mechanisms propose.

Scully (20,50) was one of the earliest workers to emphasize the importance of repassivation kinetics, and it has become an important element especially in the film rupture metal-dissolution mechanism because coupled with the concept of slip step dissolution it explains why restricted lateral dissolution occurs; the slower the repassivation, the more of the metal slip step that has emerged and ruptured the film can be dissolved before new film forms. If too little dissolves, no SCC occurs; if too much dissolves, the dissolved areas are not restricted enough, and the crack is too blunt to propagate. Only when the environment and alloy provide a system where the repassivation kinetics produce a highly restricted region for dissolution is SCC found. In addition to Scully, Staehle (10) has given a detailed discussion of the significance of repassivation kinetics.

These considerations have resulted in a number of techniques aimed at determining the repassivation kinetics (51-56). These techniques produce a bare surface either by straining an alloy wire or by scratching or abrading a surface. In most of these techniques, the specimens are either strained or scratched while maintaining their potentials at a fixed value and measuring the current transient that takes place during

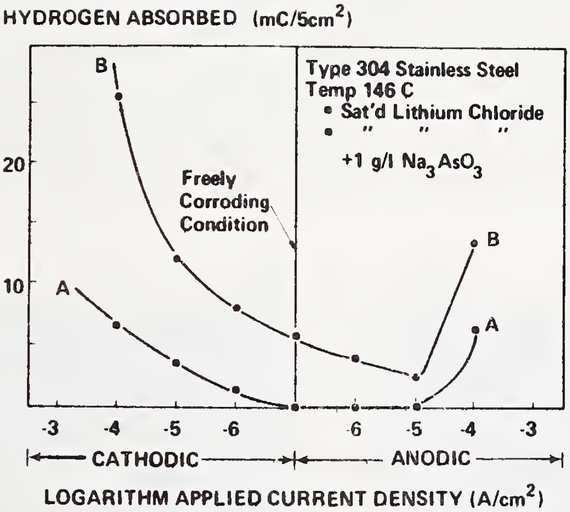


Fig. 8. The amount of hydrogen absorbed in 304 stainless steel as a function of applied current. Na_3AsO_3 (curve B) enables greater amounts of hydrogen to enter the metal. In spite of the fact that more hydrogen enters the metal in the cathodic region no SCC failures were observed for currents greater than a cathodic current of around 10^{-7} A/cm^2. From Wilde and Kim (40).

the dissolution-repassivation event that occurs subsequent to exposure of bare metal. The rate of current decay is related to the rate of repassivation (Fig. 9). In these mainly electrochemical techniques, one cannot separate out the current involved in dissolution from that involved in passive film formation. A technique recently developed by Ambrose and Kruger (56), however, does attempt to measure separately the film regrowth transient by optical means (ellipsometry) and to compare it to the overall dissolution-repassivation current. With this technique, called tribo-ellipsometry one removes the protective film on a metal in an environment by means of a polishing wheel and then records both the film growth kinetics and the current as shown in Fig. 10. In Fig. 10 we can see that the rate of film growth on a titanium alloy is considerably slower in the susceptible chloride environment than it is in the non-susceptible nitrate solution. With tribo-ellipsometry one can determine the ration of the total current to that involved in repassivation only. This ratio R_p* when the exposed surface area is known is given by the expression

$$R_p* = 1 + \frac{Q_d}{Q_r} \qquad [3]$$

where Q_d = charge involved in dissolution and Q_r = charge involved in repassivation.

R_p* is a measure of the effectiveness of the repassivation process. Work on the cracking of low carbon steel (17) has shown that SCC does not occur when the effectiveness of repassivation is neither too high nor too low. Thus, for low carbon steel at the time required to form a complete film R_p* is 2.8 in 1 N $NaNO_2$ (25°C) where it is nonsusceptible; R_p* is 26 in 4 N $NaNO_3$ (90°C) where it does undergo SCC, and R_p* is >75 in 1 N NaCl (25°C) where it undergoes widespread pitting attack but not SCC. Thus, a delicate balance between repassivation and dissolution must be maintained to lead to SCC. The determination of this balance is dependent on the environment, the alloy, and finally the metallurgy and mechanics of the system that control the rate at which bare metal sites (generally slip steps) are produced as well as their density and size.

This section, devoted to chemistry, has described techniques for evaluating the role of the environmental side of the equation; the next two sections are concerned with the other side of the equation.

Techniques Dealing with the Metallurgy of SCC - In recent years two experimental approaches have become increasingly important in providing insights into the role of metallurgy in SCC. They are constant strain rate tests and a variety of applications of electron microscopy.

a) Constant Strain Rate Tests - This test, which produces experimental data as depicted in Fig. 11, can be applied both to mechanistic studies as well as used for a routine testing. The technique has been applied to studies of mild steels (59), Ti alloys (60), and Mg alloys (23). The mechanistic importance of the technique is that it ties the metallurgically

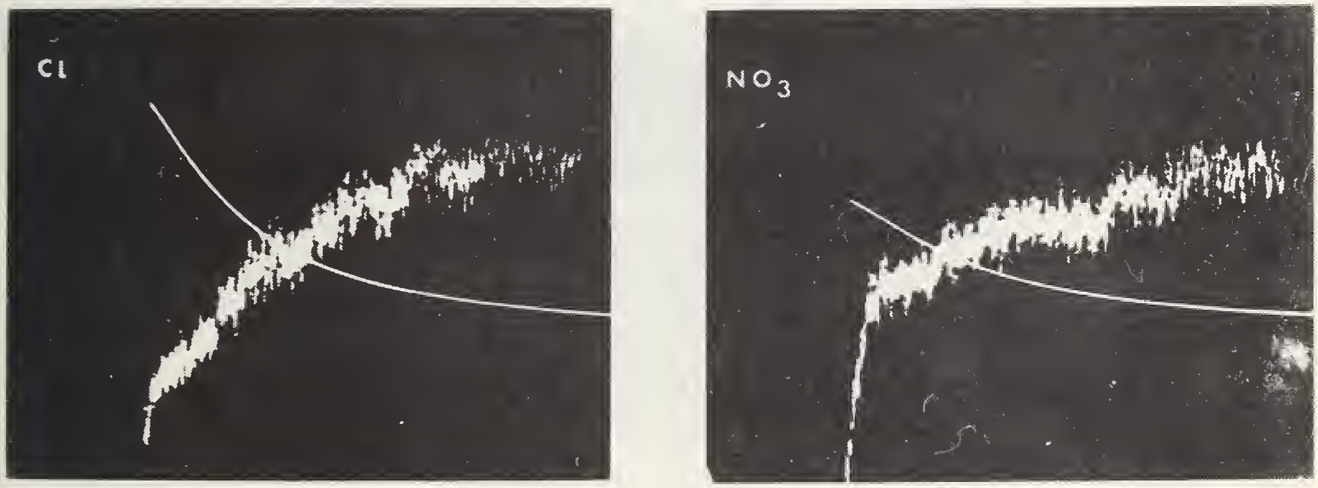


Fig. 10. A comparison of oscilloscope repassivation transients for Ti-8 Al-1 Mo-1 V alloy in 1N NaCl and 1N NaNO$_3$ solutions at +706 mV (SHE) (Ellipsometric film growth - jagged trace; current - solid line trace). From Ambrose and Kruger (57).

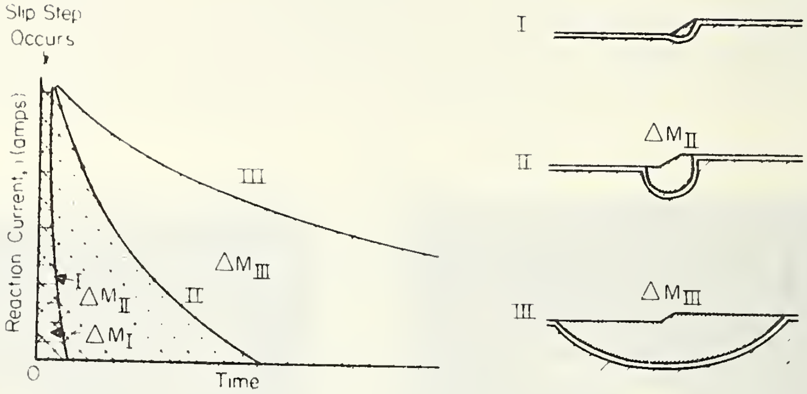


Fig. 9. A schematic representation showing the different current transients expected from straining electrode experiments and relating these transients to the amount of material dissolved after the rupture of a protective film by an emergent slip step. I, rapid repassivation with little metal dissolution. II, intermediate repassivation rate producing restricted dissolution and favoring SCC. III, slow repassivation producing extensive metal dissolution. From Staehle (10).

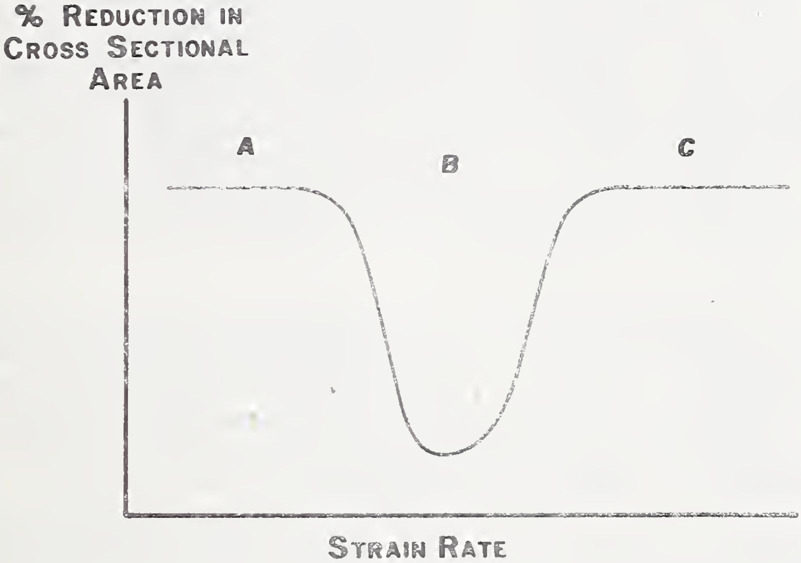


Fig. 11. A schematic representation of the results obtained in constant strain-rate tests. Region A - repassivation is rapid enough and strain rate slow enough to prevent damaging interaction with the environment. Region B - strain rate high enough so that repassivation does not prevent environmental access. Region C - strain rate is so rapid that ductile pulling apart takes place.

controlled rate of bare metal exposure, resulting from film rupture by slip step emergence, to the chemical process of repassivation of the exposed metal. This can be seen by examining the significance of the three regions shown in Fig. 11. For Region A where stain rates are too low to lead to SCC, the rate of repassivation is high enough to prevent any significant and damaging interaction between the environment and the bare metal exposed during straining. At the opposite extreme, Region C, the strain rate is so rapid that the interaction of the exposed metal with the environment is of no consequence because the rate that the metal fails by ductile fracture exceeds the rate by which the environment can affect fracture via any of the possible SCC mechanism (dissolution, hydrogen embrittlement, or adsorption of damaging species). It is only in the intermediate range of strain rates, Region B, where the rate of production of bare metal sites has a value sufficiently high so that the rate of repassivation does not prevent environmental access. However, the strain rate is sufficiently low so that environmental interaction and not ductile pulling apart produces fracture. Under these conditions SCC takes place. If SCC is not possible for the system studied, the dip shown in Region B will not occur.

Does this test, whose development and increasing use was stimulated for mechanistic reasons and was mainly guided by the implications of film rupture and repassivation, provide a valid routine material-environmental evaluation test? Parkins (58) has pointed out that there are certain features of the constant strain rate technique that make it a useful routine laboratory test. These features are as follows:

1) It is a relatively severe test so that it will promote laboratory SCC failures where other tests on smooth specimens will not unless inordinately long testing times are used;

2) It always produces fracture by SCC or some other mechanism and therefore is a positive test;

3) The time of testing is relatively short.

These three somewhat interrelated attributes, severity, positiveness, and rapidity, are especially valuable in comparative testing where one wishes to intercompare materials and environments.

The promise that the constant strain rate approach offers for laboratory testing is somewhat tempered by the lack of good ways to quantify the results of the tests. For example, how does one relate the strain rate in Region B where SCC susceptibility is the greatest to crack growth rate? Moreover, it is not known what relation, if any, this strain rate bears to the strain rate that exists at the tip of a growing crack. Parkins (23) has made some valuable qualitative connections between this value and the threshold stress for SCC or the threshold value of the stress intensity factor (described in the next section on mechanics) but the quantitative relationships require new theoretical and experimental advances. Despite these problems, the constant-strain rate tests have provided evidence of SCC in systems where other tests have been difficult or not possible to apply (61-63).

b) Electron-Microscopy of SCC - With the advent of such powerful tools as the scanning electron microscope (SEM), and high voltage electron microscopy, have come new opportunities for the diagnosis of SCC failures as well as for the prediction of the likelihood of failure. The predictive ability provided by these tools is based more on the mechanistic insights they provide (by allowing the examination of the crack tip itself at nearly atomic resolution) than on any testing procedure employing them. For example, using mechanisms that rely on repassivation as a step in the SCC process, Scully (50) has proposed that the width of the slip steps produced when a metal is stressed plays a role in determining SCC susceptibility. He suggests that the wider the step, the more time is allowed for the migration (under a potential gradient) of a damaging ion (usually chloride) to the point on the metal surface where the slip step is emerging. Thus, a greater concentration of this ion will build up at the emergence point and thereby retard repassivation or enhance dissolution at this point. For fine slip steps, the time for the build up of concentration of damaging ions via migration along the emerging step is less and repassivation is more effective. Therefore, Scully points out that the metallurgical substructure that determines the width of the step becomes crucial. By means of transmission electron microscopy one can determine the metallurgical substructure. For example, it has been found that some alloys that suffer transgranular SCC have lattices of co-planar arrays of dislocations (Fig. 12a) which produce wide slip steps [e.g., α brasses (64)]. On the other hand, alloys where cross slip is easy (Fig. 12b) are less susceptible to SCC because deformation results from fine slip and the process described by Scully would be less likely to lead to cracking. The width of the slip steps produced is probably not critical for all combinations of environments and alloys and, indeed, has been strongly questioned (65). Nevertheless, it is mentioned to illustrate how a transmission electron microscopic study of metallurgical substructure can be used as a failure predicative tool.

Metallurgical substructure plays an important role in the formation of corrosion tunnels which have been found by some workers using electron microscopy to be associated with SCC (66,67). Scamans and Swann (68) describe a technique whereby they are able to look at U-bend specimens in a high voltage electron microscope and thereby observe the effects of stress and environmental interactions. High voltage transmission electron microscopy (500-1000 kV) allows the use of specimens approximately six times thicker than those used on conventional electron microscopes (100 kV) and thus come closer to studying phenomena in bulk material. With double tilting capabilities they could analyze the three dimensional morphology of the crack tip. By this means they could relate attack morphology of austenitic stainless steels to slip traces and found that more susceptible alloy compositions showed a greater tendency to promote the formation of corrosion tunnels. They found tunnel diameters increased

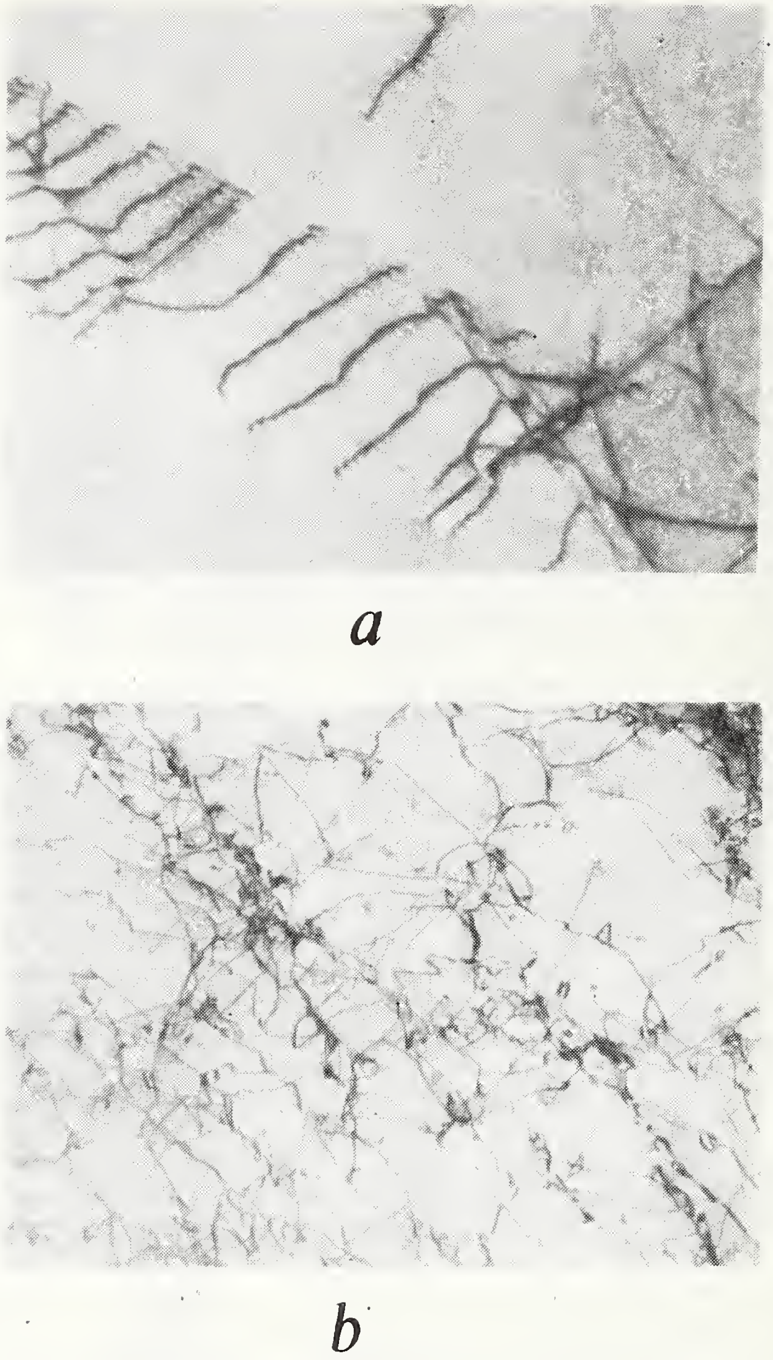


Fig. 12. Transmission electron micrographs showing;

(a) Coplanar array of dislocations leading to wide slipsteps.
(b) Tangled array of dislocations leading to fine slipsteps.
(Photographs courtesy of L. K. Ives).

with decreasing susceptibility. For the purposes of this paper, a detailed discussion of the role of attack morphology and susceptibility is not necessary. What is important is to stress that by means transmission microscopy one can determine morphological or metallurgical features (tunnel formation, dislocation array, etc.) which can serve as potential failure predictive aids when their significance has been more firmly established.

Unlike the just mentioned examples of applications of transmission microscopy, the use of SEM for the study of fractured surfaces (fractography) is more useful for diagnostic, rather than predictive, purposes. As such, it is extensively use for failure analysis which serves as a basis for suggesting measures to prevent future failures. A comprehensive discussion of the use of fractography in the study of SCC is given by Scully (69). Fig. 13 shows a fracture surface that is indicative of a failure that was brought about by the hydrogen embrittlement mechanism of SCC. The flat crystallographic damage planes are typical of the brittle mode of fracture that would result from this kind of failure. In contrast, Fig. 14 shows the dimpled fracture that results from ductile failure that could not be attributed to hydrogen embrittlement. The introduction of the SEM in recent years into many laboratories has given an enormous impetus to fractographic studies. This is so, because, as pointed out by Scully (69), the SEM has the following valuable advantages:

1) The microscope has a wide range of magnifications. This is important in SCC failure analysis because it can quantitatively determine dimple/cleavage or dimple/intergranular ratios and thereby give information about the general pattern of crack propagation. Also, by working at different magnifications it can look at the different varieties of fracture features that can result from different grain orientations.

2) The microscope has an extremely large depth of field. Because in SCC where corrosion, corrosion products, and rough surfaces are common, this feature is of great, actually essential, utility.

3) No replication is necessary so that one need not be concerned about an alteration of the fracture surface (removal of corrosion products, for example) by the replication process.

4) It can distinguish between the metallic and nonmetallic materials (corrosion products, inclusions) making up the fracture surface. This can be a source of misinterpretation when replication techniques are used.

Therefore, the advent of SEM fractography has provided a powerful tool for the failure diagnosis which is an essential step in the prevention of SCC failure.

Fig. 13. A scanning electron micrograph of the fracture surface of a high strength steel showing transgranular quasi-cleavage typical of hydrogen embrittlement. Arrows show dimpled rupture where some ductility is occurring at a few local sites. (Photograph courtesy of C. G. Interrante and G. E. Hicho).

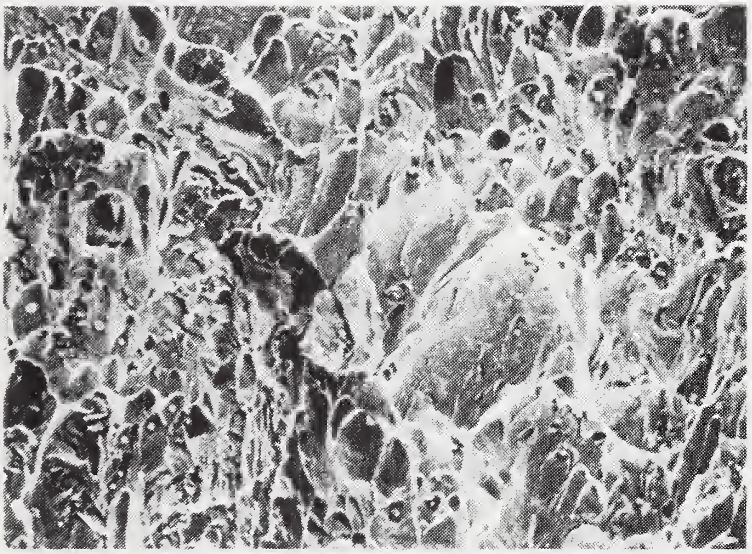


Fig. 14. A scanning electron fractograph showing typical ductile fracture of a high strength steel which indicates no hydrogen embrittlement. (Photograph courtesy of C. G. Interrante and G. E. Hicho).

Techniques Dealing with the Mechanics of SCC - Up to this point most of the new techniques described have had their origins in the different mechanisms of SCC and are aimed at providing predictive abilities. However, while some offer hope that such opportunities to predict failure will materialize, the engineer's best present hope lies either in utilizing past experience or in utilizing laboratory tests that adequately model service conditions. Presently, the tests developed using the concepts of linear elastic fracture mechanisms come closest to answering this latter need. A good review of the theory and application of these techniques to SCC is given in a book edited by Brown (70). Previously most laboratory tests for evaluating the susceptibility of an alloy to SCC in a given environment used smooth specimens subjected to a stress and measured the time required to observe a failure of the stressed specimens. One description of the kinds of specimens and experimental apparatus used can be found in the book by Logan (71). The two major criticisms of the test methods that do not use the concepts of linear elastic fracture mechanics are that the geometry of the stress field around a crack is poorly defined or unknown and that time to failure involves the time for crack initiation as well as crack propagation. Brown and Beachem (72) showed, for example, that titanium alloys, which appeared to be completely immune to SCC because they did not pit readily and thereby provide initiation sites, were highly susceptible to SCC once initiation sites were present. Therefore, since initiation may be highly variable depending on whether or not flaws exist in the specimen studied, the time to failure can be an unreliable and hence unreproducible measure of susceptibility.

The testing techniques for characterizing SCC susceptibility by the use of fracture mechanics seek to overcome these shortcomings of time-to-failure techniques by providing a pre-existing flaw or crack and by clearly defining the stress field around a crack through the use of specimens whose geometry allows the characterization of a parameter K*, the stress intensity factor. This parameter depends on the loading and configuration of the specimen, including crack size, and determines the magnitude of the local stresses. If a certain value of K is found to cause the growth of a stress corrosion crack, any combination of structure and crack geometry which duplicates this level of K will produce the same crack growth rate for the same material and environment. Thus, using K allows one to relate SCC tests carried out for one crack and body geometry to another. Brown and Srawley (73) have made calculations that allow the determination of K for a number of practical test specimens. The pre-existing flaw used to overcome the problem of crack initiation is for many specimens a fatigue crack intentionally introduced for this purpose.

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*For a crack of length 2a in an infinite plate where the crack is normal to the tensile stress field of value σ, $K = \sigma\sqrt{\pi\alpha}$.

The argument for this approach is that most structures have flaws in them so that crack initiation is not of great practical importance.

In SCC tests using specimens designed for the application of fracture mechanics concepts results similar to those shown schematically in Fig. 15 will be obtained. In these tests the rate of crack growth is measured as a function of K and, as is pictured, there can be regions (I,II,III) where the functional dependence of crack growth rate on K differs markedly. Of more importance for SCC testing is the existence of a threshold value of K, the K_{ISCC}* shown in Fig. 15, below which the crack growth rate is zero or insignificant for practical purposes. Determining K_{ISCC} is an important goal in SCC testing because one can relate it to a critical flaw depth, a_{cr}, and the yield-point stress that may exist in a structure whose SCC behavior is being determined. Brown (73) has shown that

$$a_{cr} = 0.2\left(\frac{K_{ISCC}}{\sigma_Y}\right)^2, \qquad [4]$$

where σ_Y is the yield strength. He proposes that a_{cr} be used as a figure of merit which includes both K_{ISCC} and any yield strength stress whether applied or residual. Fig. 16 shows how one can use a_{cr} and σ_Y to evaluate SCC characteristics of materials. Thus, a material whose value of K_{ISCC} in a given environment gives a value of X as shown in Fig. 16 would suffer SCC (crack propagation) if it had a flaw of 0.1 in., but not if it had a flaw of 0.01 in.

There have been a number of criticisms of the general applicability of the pre-cracked specimens to SCC testing. Parkins (58) has spelled out a number of these shortcomings. Among these are the following:

1) In order to achieve conditions of plane strain (the conditions upon which the relationship between K and specimen geometries are based) for ductile materials, test specimens of impractical size must be used;

2) There may exist problems when pre-cracked specimens are usually cracked transgranularly although the SCC process for the alloy is intergranular;

3) The significance of the initiation stage may be to produce a proper environment for cracking rather than just provide a notch to promote crack propagation;

4) The frequent observation of crack branching may modify the significance of the values of K_{ISCC} determined in fracture mechanics testing.

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*The I in the subscript of K_{ISCC} represents Region I and could be left out because SCC occurs only in Region I (4).

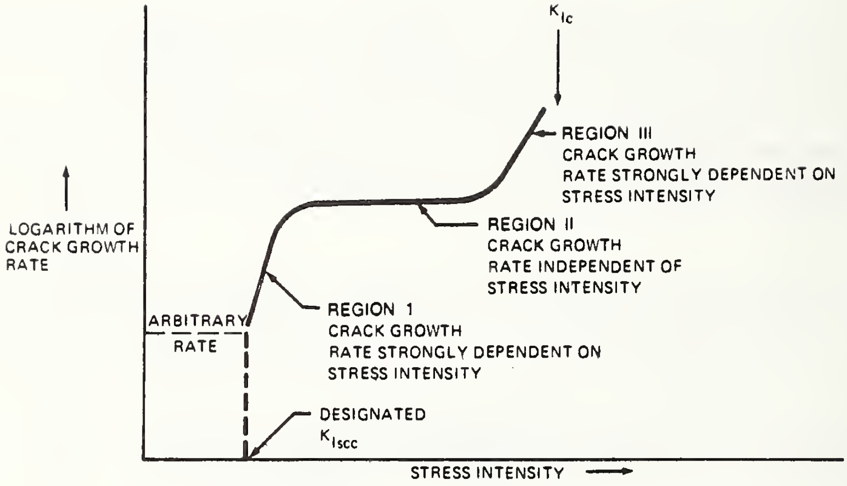

Fig. 15. Schematic diagram of the data obtained from fracture mechanics techniques applied to stress corrosion cracking. From Smith and Piper (74).

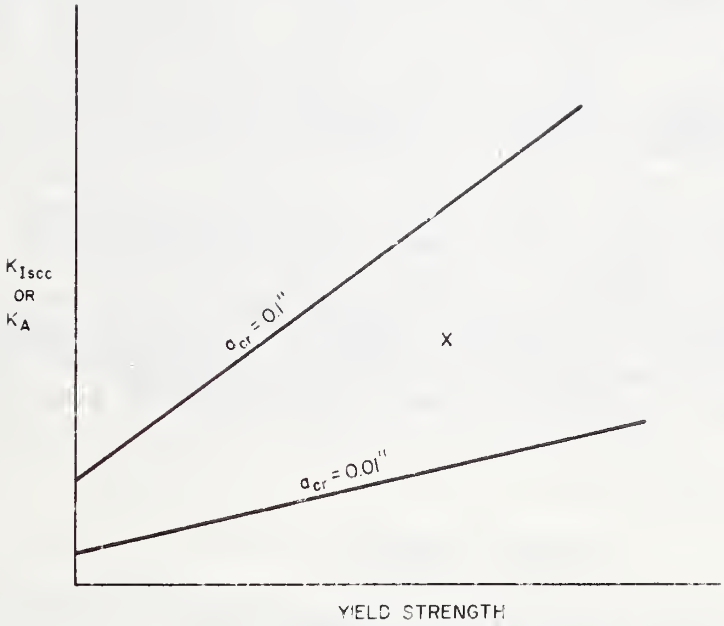

Fig. 16. A plot of Eqn. [4] using 0.1" and 0.01" values for a_{cr} assuming long surface flaws and yield strength stresses operating. A material with a K_{ISCC} value of X would not undergo SCC in the environment where measurements were made if surface flaws were no deeper than 0.01". If, however, the flaws were as deep as 0.1", SCC would occur. From Brown (73).

These shortcomings are not serious for the many cases where they do not apply and where fracture mechanics techniques have been successful, but it is obvious that one cannot rely exclusively on one testing approach. Moreover, a recent paper (23) describes ways to interrelate results obtained from pre-cracked specimens using fracture mechanics concepts and those obtained from smooth specimens used in constant strain rate tests. Thus, a combination of the two approaches may be in the offing.

New Opportunities for Failure Prediction and Diagnosis

This brief survey of new approaches towards developing failure predictive tools to cope with SCC have identified new opportunities provided by the three disciplines that govern the phenomenon of SCC. From chemistry comes the recognition of considering the changes in environment that occur in the crack and the important effect of environment on repassivation kinetics. From metallurgy comes the recognition of the importance of metallurgical substructure and the role that the rate of bare metal production via slip step emergence plays. From mechanics comes the recognition of properly characterizing the geometry of the stress field around a crack. When these tools have been refined further, both through experiment and theory, the eventual goal of being able to predict susceptibility to SCC in going from one environment to another (chemistry), from one metallurgical structure to another (metallurgy), and from one geometry to another (mechanics) will be realized. This paper has described some of the beginning steps toward such a goal.

ACKNOWLEDGEMENT

I am most grateful to the Office of Naval Research which supported this work under contract NAONR 18-89 NRO 36-082.

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NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBSIR 74-583	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

The Role of Passive Film Growth Kinetics and Properties in Stress Corrosion and Crevice Corrosion Susceptibility

5. Publication Date

6. Performing Organization Code

7. AUTHOR(S)
J. Kruger and J. R. Ambrose

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.
3120449

11. Contract/Grant No.
NAONR-18-69, NR 036-092

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*

Office of Naval Research
Dept. of the Navy
Arlington, Va. 22217

13. Type of Report & Period Covered
Interim
3/1/73-12/31/73

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A study of the effect of alloying chromium and molybdenum in ferritic stainless steels has been made using techniques to study repassivation kinetics (tribo-ellipsometry) and depassivation kinetics (a recently developed ellipsometry technique for studying optical changes occurring within a crevice). Results indicate that chromium additions affect both repassivation and depassivation processes while molybdenum appears to affect only the repassivation processes. A discussion is given of a generalized mechanism for localized corrosion which postulates that susceptibility to attack is determined by the competition between depassivation and repassivation processes.

Constant strain rate studies were performed using AISI 304 stainless steel exposed to acidified 1.0N NaCl solution (pH=3.0). In this particular environment, repassivation kinetics measurements using the tribo-ellipsometric technique had shown that the metal dissolution rates were rather large due to reduced film repair kinetics, indicating the possibility of susceptibility to stress corrosion cracking (SCC). Reduced time to failure and maximum sustained load at a one strain rate suggest a relationship between SCC, repassivation kinetics, and rate of pure metal production.

A review of current approaches to the study of stress corrosion and a discussion of how these approaches can lead to new failure prediction tools is given.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Chloride; crevice corrosion, ellipsometry failure prediction; molybdenum; repassivation kinetics; stainless steels; stress corrosion; testing techniques

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19. SECURITY CLASS (THIS REPORT)
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21. NO. OF PAGES
87

22. Price

USCOMM-DC 29042-P74


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