Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

STRESS-CORROSION CRACKING: A PERSPECTIVE REVIEW OF THE PROBLEM

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

This is a progress report; work is continuing.

5. AUTHOR(S) (First name, middle initial, last name)

B. F. Brown

6. REPORT DATE June 16, 1970	7a. TOTAL NO. OF PAGES 26	7b. NO. OF REFS 28
8a. CONTRACT OR GRANT NO. 63M04-08 b. PROJECT NO. c. ARPA Order 878 d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 7130 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency Department of Defense Washington, D.C.

13. ABSTRACT

The introduction includes definitions of a number of terms relating to crack propagation caused by the conjoint action of stress and corrosion and related phenomena. This is followed by a brief historical review during the course of which it becomes evident that stress-corrosion cracking, far from being restricted to a few alloys, is a general phenomenon observed in most families of alloys if the composition, heat treatment, and environment are favorable. The role of fracture mechanics in conducting and interpreting stress-corrosion cracking tests is discussed, and the several classes of mechansims which have been postulated to account for stress-corrosion cracking are enumerated. The most serious deficiency in stress-corrosion technology is the inability to predict those combinations of alloys and environments which will give rise to stress-corrosion cracking.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Stress-corrosion cracking						
High strength steels						
Titanium alloys						
Aluminum alloys						
Electrochemistry						
Fracture mechanics						

CONTENTS

Abstract ii
Status ii
Authorization ii

INTRODUCTION..... 1

HISTORICAL BACKGROUND..... 2

CHARACTERISTICS..... 5

ROLE OF FRACTURE MECHANICS..... 9

MECHANISMS..... 15

ACKNOWLEDGMENT..... 18

REFERENCES..... 19

ABSTRACT

The introduction includes definitions of a number of terms relating to crack propagation caused by the conjoint action of stress and corrosion and related phenomena. This is followed by a brief historical review during the course of which it becomes evident that stress-corrosion cracking, far from being restricted to a few alloys, is a general phenomenon observed in most families of alloys if the composition, heat treatment, and environment are favorable. The role of fracture mechanics in conducting and interpreting stress-corrosion cracking tests is discussed, and the several classes of mechanisms which have been postulated to account for stress-corrosion cracking are enumerated. The most serious deficiency in stress-corrosion technology is the inability to predict those combinations of alloys and environments which will give rise to stress-corrosion cracking.

STATUS

This is a progress report; work is continuing.

AUTHORIZATION

NRL Problem 63M04-08A
ARPA Order 878

Stress-Corrosion Cracking

A Perspective Review of the Problem

INTRODUCTION

Stress-corrosion cracking (SCC) is a cracking process caused by the conjoint action of stress and a corrodent. Since this definition is based upon macrophenomenology, knowledge of the responsible mechanism is not a prerequisite for applying the term to a given alloy-corrodent system. At one period there was a widespread tendency to restrict the term "stress-corrosion cracking" to an anodic dissolution crack propagation process, and the term "environmental cracking" was introduced as a sort of semantic limbo to consign corrosion-related cracking processes in systems for which the mechanism had not been determined. The misleading terms "delayed failure" and "delayed fracture" have also been used to indicate not the delayed event (fast mechanical fracture) but the slow crack growth that precedes the fast fracture. (In this paper, "fast" fracture means "brittle fracture", which propagates at about one third the speed of sound in the metal; "slow" growth indicates a cracking process which propagates appreciably slower than one-third the acoustic velocity.) "Static fatigue" has sometimes been used to denote slow crack growth under nonrepetitive loading. "Subcritical crack growth" was introduced by some fracture mechanicians to indicate crack growth processes that occur at stress intensities less than that which is critical (sufficient) for producing fast fracture; subcritical crack growth can include hydrogen cracking (hydrogen embrittlement), SCC, liquid metal cracking (liquid metal embrittlement), fatigue, or corrosion fatigue. Such a collective noun is often confusingly nebulous.

At one time it was widely thought that there must be a common mechanism for all the slow corrosion-produced cracking processes that generate the characteristically brittle cracks in so many different families of alloys, most of which are so ductile in purely mechanical tests. This belief has been gradually eroded, and partly because of this erosion the term SCC as defined by macrophenomenology appears well on its way to general usage rather than being restricted to a single mechanism. Particularly with the growing acceptance of SCC as a general term irrespective of mechanism, the other terms above become unnecessary.

Actually even "stress-corrosion cracking" contains an unnecessary word, for as Hoar (1) has pointed out, all cracking processes require stress. "Corrosion cracking" should thus suffice, but the longer term appears to be firmly ensconced in the literature.

HISTORICAL BACKGROUND

Brass and bronze were being produced in the second millenium B.C., and because these alloys can be cracked by ammonia present in the atmosphere (particularly around stables), cold-worked brass or bronze would very probably have been the metals in which the SCC phenomenon was first observed. Figure 1 shows multiple branching of a brittle crack characteristic of SCC in cold-worked alloys, illustrating the fact that although the present name for the phenomenon was coined only in the 20th century, the phenomenon was known long ago.

In the last half of the 19th century, however, the phenomenon became widespread because of the invention of the brass cartridge case and because of the extensive use of brass condenser tubing in steam plants for the growing electrical industry. It was during this period that the term "season cracking" came into general use because of the resemblance of stress-corrosion cracks to cracks in seasoned wood.

In 1886 Roberts-Austen (2) showed that if a hard-drawn wire of 13-carat gold (33.3% Cu and 12.5% Ag) was touched with a solution of ferric chloride, the wire would split with great rapidity (Fig.2). This observation not only documented the susceptibility of a precious-metal alloy to SCC, but it also highlighted the role of residual stresses in the cracking process.

Some liquid metals also contribute to the propagation of cracks in certain metals, a phenomenon known by the misnomer "liquid metal embrittlement". This liquid metal cracking is not normally included in the term SCC even though it fits the phenomenological definition. Both mercury and brass were in the technology of antiquity, and liquid metal cracking must therefore have been observed in ancient times. Liquid metal cracking has a more direct and more modern connection with conventional SCC, for by the end of the 19th century an acidified 1% solution of mercurous nitrate was in widespread use to test whether residual stresses in cold-formed brass articles had been adequately relieved by annealing. If the stresses had not been relieved, mercury from the mercurous nitrate would rapidly crack the brass.

During the period 1900-1920, SCC was found to occur in ferritic steels (in boilers and in evaporators in the caustic chemical industry); in martensitic steels (quenched in water); and in aluminum alloys (by atmospheric moisture).

Fig. 1 - Head of a Parthian lady, showing fracture (arrow) with the brittle appearance and multiple branching characteristic of stress-corrosion cracking. Hammered silver, 1st century B.C.-1st century A.D. (By kind permission of The Freer Gallery of Art, Washington, D.C.)

Fig. 2 - Roberts-Austen's demonstration of stress-corrosion cracking in a gold alloy wire touched with a drop of ferric chloride (Ref. 2).

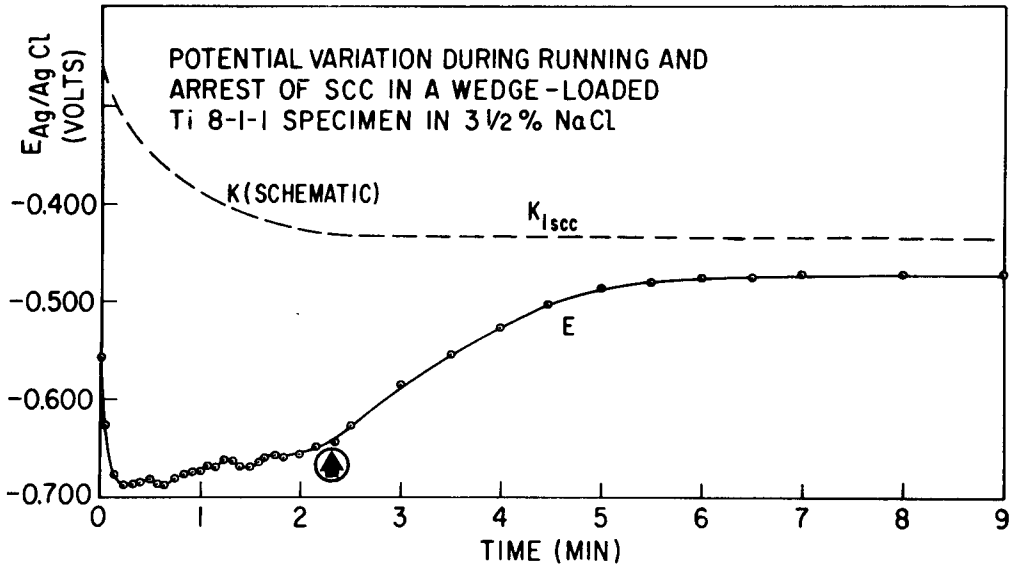

Fig. 3 - Rapid fall and slow rise of potential as stress-corrosion crack runs and then apparently arrests (arrow) as stress intensity K falls to K_{Iscc}. Potential thereafter rises to value of unstressed specimen and remains there.

During the 1930's SCC was observed in austenitic stainless steels in the petrochemical and paper industries, and in magnesium alloys in atmospheric moisture. During the 1950's the use of high strength steels particularly for rocket motor chambers (which were pressure tested using tap water) brought the problem of SCC in martensitic and precipitation-hardening steels to the fore. During the 1950's and 1960's titanium alloys were found to be susceptible to SCC in fuming nitric acid, hot salt, sea water, and a number of organic compounds.

Thus the phenomenon of SCC, once thought confined to a few alloy systems, appears to be a very general one which can confidently be expected to occur in most if not all alloy systems, given the proper combination of alloy composition and environment. Unlike alloys, the pure metals are not susceptible to SCC (with perhaps one or more rare exceptions); this susceptibility of alloys but not of pure metals is as discomfiting to the theoreticians as to the structural engineer, who can seldom use the weak, unalloyed metals.

CHARACTERISTICS

At least as early as 1886 (2), tensile stress, which may be residual from cold work or may be applied externally, was known to play a causative role in SCC. The necessary role of tensile stress may then be listed as the first characteristic of SCC. In the case of brass, the most troublesome alloy with respect to SCC at that time, the stresses of concern were those left by cold forming, and Heyn (3) showed that these stresses could approach the yield strength of the brass. Annealing to reduce the residual stress was one of the first measures taken to control SCC. In addition to residual stress from cold work and externally applied stress, it is possible to generate stresses sufficient for SCC by corrosion products forming inside cracks and by thermal gradients and transformations occurring during quenching.

A second characteristic of SCC is that the alloy is usually almost inert to the environment which causes cracking. Prof. Porter pointed this out long ago based on experience with evaporating sodium nitrate and sodium chloride in steel pans: "The action upon the steel is totally different in the case of the different solutions. You may go to a waste heap and pick out the pieces of steel that have come from a sodium chloride pan and those that come from a sodium nitrate pan. Those that have come from the sodium chloride pan are all rusty, the steel rusted through, while those from the sodium nitrate pan are not rusted at all, but they are cracked."(4)

A third characteristic of SCC is that only certain combinations of alloy and environment produce SCC, though this specificity is less strict than is sometimes stated. The ammonium ion is apparently necessary for SCC of brass in aqueous solutions, except that as noted above mercury salts can cause liquid metal cracking of brass. Somewhat parallel to chemical specificity in the environment, a temperature threshold may also be specific, as in austenitic stainless steels especially. These alloys crack readily in chloride solutions at about 150°C, but cracking is rare in chloride solutions at 100°C, and even rarer at room temperature. (Hoar has pointed out that the rarity of SCC in stainless steel cooking vessels, though perhaps due partly to the low temperature, may be attributed in part to the reducing character of the foodstuffs being cooked.(5))

A fourth characteristic of SCC is that the necessary corrodent species need not be present in large quantities or concentrations. Cinnabar pigment in lacquer was found responsible for cracking of brass cartridge cases having only a thin coat of lacquer, and only a few ppm of chloride in high temperature water causes SCC in austenitic stainless steels.

A fifth characteristic of SCC is the brittle appearance of the cracks which have little or no shear lip or other macroscopic evidence of plastic deformation, even though the metal may perform in a highly ductile manner in a mechanical fracture test.

A sixth characteristic is that metallographically the stress-corrosion fracture mode is usually different from the purely mechanical plane-strain fracture (brittle fracture) mode of the same metal, as noted in the following table:

Table I-Fracture Modes

Alloy family	Mechanical fracture	SCC fracture
Brasses (in ammonia)	Dimple rupture (microvoid coalescence)	Intergranular
High Strength steels	Dimple rupture (except may be intergranular in medium carbon steels)	Intergranular
Ferritic steels	Dimple rupture	Intergranular
Austenitic stainless steels	Dimple rupture	Transgranular
Titanium	Dimple rupture	Transgranular
Aluminum (7000 series)	Dimple rupture (but may be intergranular)	Intergranular

A seventh characteristic of SCC is that unlike corrosion fatigue, there appears to be a threshold below which SCC does not occur. To make a positive statement of the existence of a threshold one would have to prove a negative. That is, one would have to prove that below a certain stress level a crack will not grow regardless of how long one waits. There is one system in which indirect electrochemical evidence points to a true threshold stress intensity for SCC: If a notched but unstressed titanium alloy specimen is placed in salt water, the potential measured with a suitable reference electrode is found to indicate a passive condition. If a wedge of the same alloy is forced into the notch to stress the specimen, a stress-corrosion crack starts running, and the potential is observed to be quite active. As the crack runs away from the wedge, the stress intensity decreases, and the crack appears to stop. Again we have the problem of proving a negative. But the electrochemical potential invites a strong inference on this point, for after the crack has stopped as judged by the eye, the potential climbs to the same passive potential value as the unstressed specimen, and remains there. From this one can conclude that for titanium alloys in salt water there is indeed a threshold stress intensity for SCC (Fig. 3).

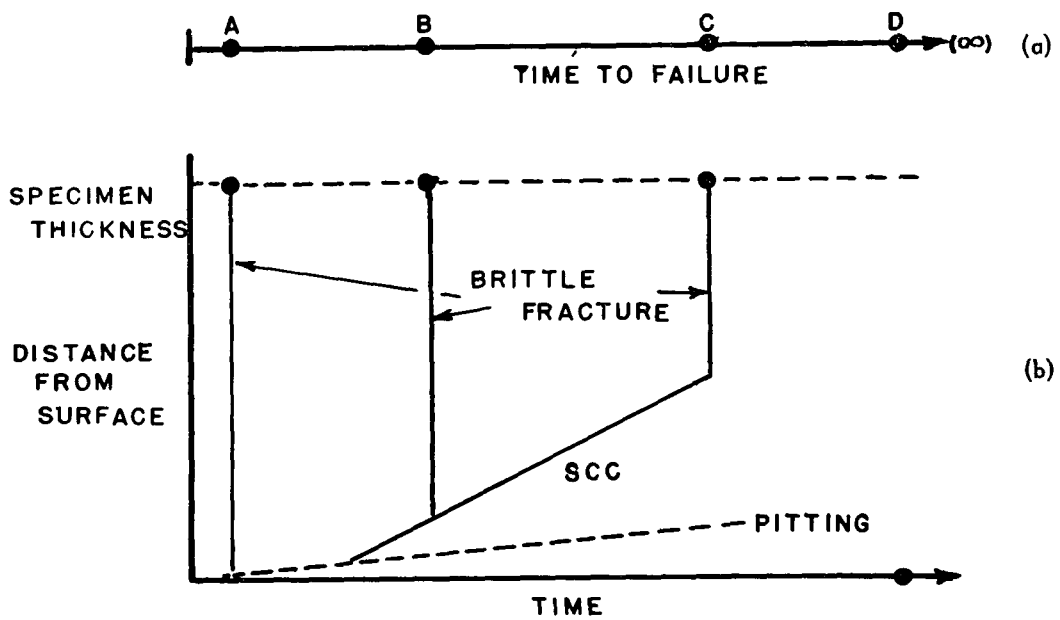

Fig. 4(a) - Time to failure for four alloys (schematic) and (b) behavior of smooth specimens of four alloys in a stress-corrosion test (schematic)

ROLE OF FRACTURE MECHANICS

Anderson appears to have been the first to publish the idea that fracture mechanics could be useful in the stress-corrosion problem (6). The role of fracture mechanics in both the conduct and the interpretation of SCC tests, particularly of high strength structural alloys, is so incompletely understood by so many investigators that this special section is devoted to placing the fracture mechanics of SCC in perspective within this wider overview of the stress-corrosion problem.

The complexities of SCC are such that for a long time to come we cannot safely predict the SCC characteristics of new combinations of alloys and environments, and we must therefore resort to experimental characterization. The use of fracture mechanics in conducting such characterization tests, particularly on high strength alloys, offers four advantages, which are as follows:

> First, the use of fracture mechanics enables one to get the right answer - and this is intended to mean that it will prevent one from getting a false indication of "susceptible" instead of the correct "immune" answer, or vice versa - not merely helping one to arrange the correct ranking of neighboring degrees of susceptibility. Second, using a fracture mechanics specimen offers economies in test time. Third, fracture mechanics analysis offers an interpretation of data from laboratory specimens readily related to the performance of larger components or structures. And fourth, the fact that a stressed crack is involved in any fracture mechanics test ensures conservative characterization because the characterization is done under worst-flaw conditions. These advantages are discussed in some detail below.

The first advantage, getting the right answer, can be understood from a consideration of the schematic total-time-to-fracture data of Fig. 4a taken on specimens initially smooth, that is, not on fracture mechanics-type specimens. One might conclude from this figure, which shows total time to fracture for four alloys, that the relative ranking of merit would be (in descending order) D, C, B, and A. If however we look at the complete record of events, shown schematically in Fig. 4b, we see that for A, B, and C there is a pitting stage having varying kinetics among the several alloys. Alloy A is so brittle that after a corrosion pit has formed, the remainder of the specimen parts in fast (purely

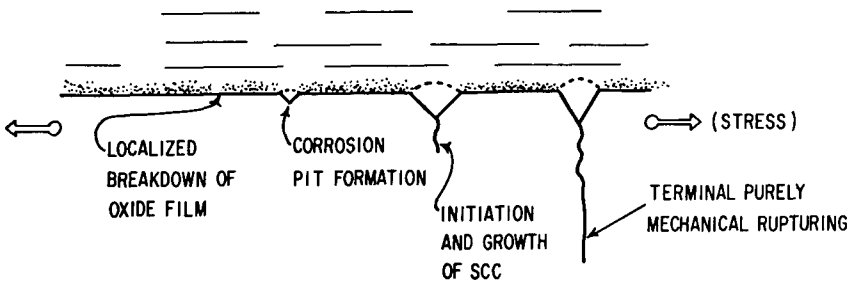

Fig. 5 - Sequence of events (left to right) in a stress-corrosion test on an initially smooth specimen. For low alloy steels in seawater, the rate of growth of stress-corrosion cracking is faster than it is for pitting by a factor of about 10^6, and fast fracture propagates about 10^{10} times faster than stress-corrosion cracking.

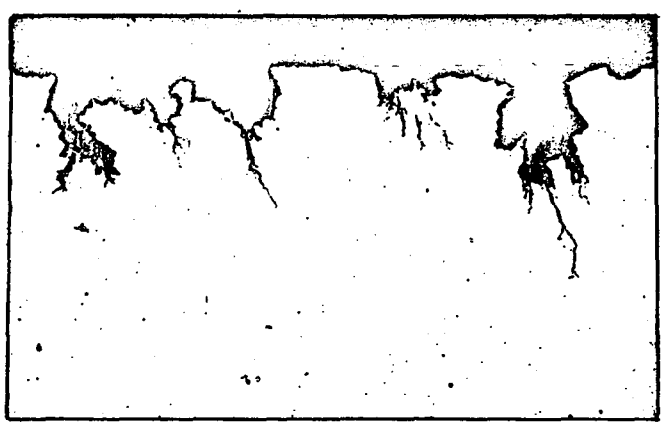

Fig. 6 - Stress-corrosion cracks in 18 Ni (250 grade) maraging steel emanating from corrosion pits after extended exposure to marine environment. (Courtesy of the U.S. Steel Corporation)

mechanical) fracture; the die steel designated H-11 heat treated to a yield strength of 240 ksi would be an example of a material which exhibits such behavior under suitable conditions of stress and thickness. Alloy D does not show any pitting at all, which is why its total time to failure is shown in Fig. 4a as "infinity." The titanium alloy containing nominally 8%Al, 1%Mo, and 1%V would behave like alloy D if tested as a smooth specimen in salt water. It is well known, however, that this alloy is so highly susceptible to SCC that it is in fact used extensively for SCC demonstration and research. Materials B and C exhibit the same pitting and SCC rates, but they have different fracture toughness characteristics, therefore they exhibit quite different total-time-to-failure values, as shown in Fig. 4b. Thus fracture toughness variations not properly taken into consideration can produce gross errors in interpreting SCC characteristics from time-to-failure data.

The second advantage is economies in test time: Generally in an erstwhile smooth metal surface, SCC is preceded by the local breakdown of any protective coating and the growth of a corrosion pit (Fig. 5). It was once thought that the essential role of corrosion pitting in nucleating stress-corrosion cracks was simply to concentrate the stresses. Such concentration of stress does indeed promote SCC, of course, but the formation of a corrosion pit proceeds because of the hydrolytic acidification (7) of a localized region which is partially screened from the bulk environment by a porous corrosion-product cap which impedes mixing of the corrodent within the localized corrosion cell and the bulk environment. A preexisting crack performs the same two functions as the corrosion pit: It itensifies the stresses locally, and by its geometry the corrodent deep within the crack does not exchange appreciably with the bulk environment. A preexisting fatigue crack has the added advantage that the stress field associated with it can be readily quantified by available fracture mechanics analysis. (Imagine trying to quantify the stress field at the bottom of the irregular corrosion pits of Fig. 6!)

The third advantage of using fracture mechanics, which may be described as affording predictability with respect to the stress factor, will become evident after the description of the treatment of data given a little further on in this section.

The fourth advantage, characterization in the presence of the worst-possible flaw (the precrack), is an advantage which may not be entirely appreciated by the

designer who can see only perfection on the drawing board or in his mind's eye; yet the history of aerospace technology (and other technologies) is replete with lessons showing the unwisdom of assuming perfection: That is why the impact test bar long ago was provided with a notch! Even if the structure is fabricated free from defects (such as quench cracks or arc strikes), a flaw may develop in service in the form of a fatigue crack, for example. Hence although one may achieve essentially perfection of fabrication, and although the satisfactory service life of a structure may require this perfection, the experience is that it is prudent to characterize candidate structural materials under more unfavorable conditions, as in the presence of a crack.

Any specimen and test method which has been devised for measuring fracture toughness using fracture mechanics methods is applicable to the stress-corrosion problem (8-11). Initially, the most popular specimens were sheet tensile specimens containing either a crack all the way through the thickness of the specimen or, later, a tensile specimen containing a surface crack. When the bend bar was developed as a fracture toughness specimen (12), it was immediately adopted for SCC because of the ease of stressing large specimens by dead-weight loading in a simple apparatus (13).

The fracture mechanics descriptor which has been most useful in SCC studies is the stress intensity parameter designated K, which has the units of stress multiplied by the square root of length, commonly expressed as ksi$\sqrt{\text{in}}$. Details of specimen design and methods for reducing data may be found in four recent reviews (8-11). There appears to be a threshold stress intensity for a given material below which SCC is not observed. This has come to be designated K_{Iscc}. The Roman numeral I indicates that the fracture is being generated in a manner like the opening of a book, rather than by sliding, for example, and the SCC designates the responsible cracking process.

In fracture mechanics terms, the subscript I refers to plane strain conditions which produce square fractures, the only ones seen in SCC; there does not appear to be an SCC analog to slant fractures, sometimes called shear fractures.

One can load several specimens at different initial K levels, note the highest K level at which no SCC is observed in an arbitrarily defined time, and designate the results K_{Iscc} for that particular alloy-corrodent combination. As with fracture toughness, this K descriptor often varies markedly with alloy composition, heat treatment, and orientation with

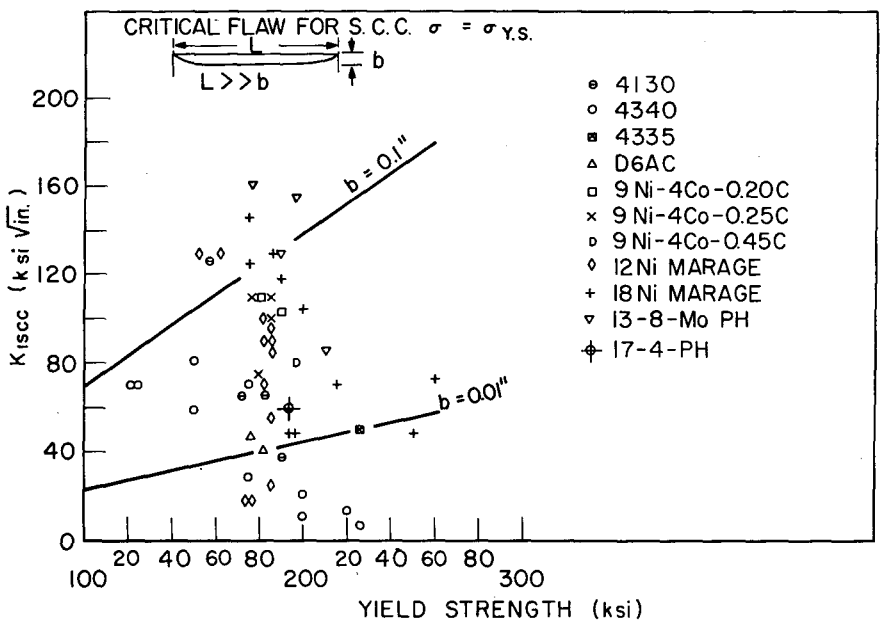

Fig. 7 - K_{Iscc} for some commercial steels in salt water, shown as a function of yield strength. Equation (2) is plotted for two values of crack size. (Data of Sandoz and Newbegin, NRL)

respect to a wrought texture. Crack-arrest methods using a single specimen appear to give similar results in the multiple specimen tests.

K_{Iscc} values determined in other geometries are readily treated for a surface crack in a structural member under tension by use of Irwin's equation

$$K^2_{Iscc} = \frac{1.2\pi\sigma^2 a}{\varphi^2 - 0.212(\frac{\sigma}{\sigma_Y})^2} \qquad \text{Eq (1)}$$

Where σ is the remote stress, σ_Y is the tensile yield strength, and a is the depth of a surface crack at right angles to the stress field. φ^2 is a shape factor whose values depend upon the depth a and the half length b of the surface crack as follows:

a/b	φ^2
0 (very long, thin flaw)	1.00
0.25	1.14
0.5	1.46
0.75	1.89
1.0 (semicircular)	2.46

If one assumes a long, thin flaw and the existence of yield point stresses, then from Eq (1) stress corrosion would be expected to propagate if the flaw depth exceeded a critical value

$$a_{cr} = 0.2\ (K_{Iscc}/\sigma_Y)^2. \qquad \text{Eq (2)}$$

The value of a_{cr} may thus be regarded as a figure of merit which incorporates both the SCC resistance K_{Iscc} and the contribution which yield strength stress levels can make by virtue of residual or fit-up stresses.

Figure 7, shows K_{Iscc} values for a number of commercial steels in salt water, plotted as a function of yield strength. Equation (2) is shown plotted for two assumed values of a. The logic of such plots is that one can assume some value of a which he considers detectable in a given design (and therefore removable), he can then plot Equation (2) for that value of a, and then select from those alloys having K_{Iscc} values above the plotted line.

Thus one can measure K_{Iscc} using any one of many different specimens, and through Eq (1) transform the result to the most common serious form of flaw in practice, namely a defect extending inward from the surface. Hence the third advantage of using fracture mechanics, noted earlier.

* * *

The application of fracture mechanics today is still largely restricted to conditions in which general yielding is absent, and thus it cannot now be used to treat the mechanical fracturing of tough, low strength alloys which yield throughout the specimen long before fracture initiates. But SCC, if it occurs in these same alloys, occurs at such low stresses that linear elastic fracture mechanics can be used to treat SCC in these same alloys.

MECHANISMS

The brittle nature of stress-corrosion cracks led to confusion with other causes of brittleness, such as the ageing embrittlement of bessemer steels. Andrew, however, writing of the SCC of mild steels in caustic solutions concluded that "It is the occlusion of, and diffusion into, the interior of this hydrogen which brings about crystalline growth and brittleness in the metal, the hydrogen being first adsorbed by the amorphous plate which exists between the crystals, thereby forcing the crystals apart...The brittleness is due rather to the molecular arrangement brought about by occlusion or evolution of hydrogen than to the mere presence of hydrogen in solution." (14). The amorphous layer theory postulated by Rosenhain to cement the grains of metal together dominated physical metallurgy in Britain for a full 15 years, and since the SCC of both brass and mild steels is largely intergranular, it is not surprising that this "cement" (long since discredited) figured prominently in many explanations which were adduced for SCC during this period.

The cracking of high strength steels in water was noted in the early 1900's, but often as a delayed phenomenon long after removal from the water environment. It is not surprising therefore that the causative role of a product of aqueous corrosion (hydrogen) was not appreciated in this form of cracking.

As noted earlier, for a long time there was a search for a fundamental process or property common to all combinations

of metals and corrodents which give rise to SCC, for the macroscopic appearance of the resulting cracks had so much in common from system to system. There is a growing doubt that a single detailed mechanism will ever by found to account for all manifestations of the phenomenon, though perhaps something like "activation by plastic straining at the advancing crack tip" covers most of the proposed detailed mechanisms. Just what is activated by straining is one of the variables left in the phrase just cited. Moore early expressed doubts about a general mechanism in these words: "I agree with Dr. Rosenhain that a general explanation of season cracking and intercrystalline cracking in all metallic materials is desirable, but is it not possible that such a universal explanation is not to be found?" (15). The proliferation of mechanisms proposed for the various systems makes Moore's attitude seem a very modern one.

The detailed mechanisms which have been proposed for various metal-corrodent systems can be grouped into the following categories:

(1) Mechano-electrochemical. Dix proposed that there were paths intrinsically susceptible to anodic electrochemical dissolution, and the role of the stress was considered to be to open the cracks enough to prevent stifling the reaction by corrosion products (16). This early model does not agree well with subsequent experience. Whatever the role of mechanical stress may be, that role is not the effect of elastic stresses on the reversible electrode potential, which changes only about 10^{-3} mv from zero stress to the yield strength stress levels. A passive surface on stainless steel in boiling 42%$MgCl_2$ may be as much as 500 mv more electropositive than the bare alloy, and one can imagine bare steel being exposed by the yielding at a crack root under stress and the cracking of the oxide coating. If the bare metal is dissolved electrolytically, one can estimate the magnitude of the current required to account for the observed crack growth rates. The current density is estimated to be about one ampere per square centimeter, which would be expected to stifle the reaction by polarizing the anodic area. Hoar and West have shown, however, that under conditions of continuous yielding the polarization may be very small, due perhaps to the increase in number of active sites by egress of dislocations (17). Evans had postulated that one of the contributions of stress to the total cracking process was the purely mechanical rupturing of ligaments of metal which resisted the mechano-chemical cracking, and this has subsequently been borne out by

fractographic studies of titanium. In these studies, the areas of SCC are cleavage surfaces, and purely mechanical rupturing produces only dimple rupture, affording a clear distinction between mechano-electrochemical and purely mechanical rupturing. Fractographic studies showed that at stress intensities just above K_{Iscc}, the fracture is almost entirely cleavage; as the stress intensity is raised, isolated areas of dimples appear, surrounded by cleavage. The proportion of dimples increases with increasing K, until at the critical stress intensity for fast fracture (K_{Ic}), the surface becomes entirely dimple rupture. Thus the overall cracking process is a dual one in which a mechano-chemical fracturing process is interspersed with islands of purely mechanical fracturing.

(2) Film Rupture. In the film rupture model, a brittle corrosion-product film is envisioned to form which, when it becomes sufficiently thick, fractures to expose bare metal; the bare metal reacts to re-form the brittle film, and the cycle repeats. Such models have been based largely upon striation markings observed with the electron microscope. Evidence of this sort is possibly explained by other models, such as for example the rupture of a thick film well behind the advancing crack front but still in a location where there is a significant bending moment on the crack surface.

(3) Embrittlement. Keating postulated a "periodic electrochemical-mechanical" cycle in which the electrochemical corrosion process was pictured as embrittling the metal directly behind the corroding metal surface by an unspecified species (18). The embrittled layer would ultimately fracture mechanically, exposing fresh metal surface. A modified version of this model is not an unreasonable one for high strength steels in aqueous environments. It is known from measurements of local pH (pH near the crack tip) and potential that the thermodynamic conditions for hydrogen discharge are met if a stress-corrosion crack is propagating in high strength steels. It is also known that these steels exhibit slow crack growth under stress if they contain hydrogen from any source. Thus it is not unreasonable to postulate that in these steels SCC occurs by corrosion-generated hydrogen cracking.

(4) Adsorption. The adsorption model pictures the reduction of the energy required to form a new surface by reducing the surface energy through the adsorption of specific species (19).

The interested reader may wish to read further details of these proposed models in Refs. 20-25. It is quite clear that any complete model must be in harmony with the observation that susceptible alloys exhibit planar arrays of dislocations (26), whereas immune alloys have tangled dislocation substructures. The model will also have to be in harmony with the fact that the corrodent near the crack tip may be grossly different from the bulk environment outside the crack (27).

Achieving predictability with respect to those combinations of alloy and environment which will cause SCC remains the major challenge facing the SCC theorist. Predictability is synonymous with theory. What investigator today, with thirty years' accumulation of papers, reports, symposia proceedings, and monographs, can suppress a smile after reading the words of Hoyt and Scheil, written in 1939: "What causes stress-corrosion cracking? The answer to this question is not fully understood, and hundreds of tests that we have made do not bring forth a simple explanation of the phenomena." (28).

The sophisticated approach which is necessary to advance our knowledge and control of SCC requires attention to all the three facets of the phenomenon, namely the nature of the metal (structure and imperfection substructure), the nature of the pertinent environment (composition of the corrodent near the growing crack tip, and the electrochemical potential of the crack surface in that region), and the state of stress in the crack-tip region. Much progress has been made in all three of these facets of the problem during the past decade, and the outlook is good for synergistic action involving these three facets in the years immediately ahead; this action should bode well for future advances in theory and technology of controlling stress-corrosion cracking.

Acknowledgment

This research was supported by the Advanced Research Projects Agency of the Department of Defense, ARPA Order 878 (ARPA Coupling Program on Stress-Corrosion Cracking).

REFERENCES

1. T. P. Hoar, Remarks at The Washington Corrosion Dialogue (1966).

2. W. Chandler Roberts-Austen, On Certain Properties Common to Fluids and Solid Metals, Proceedings Royal Inst. Gr. Britain, II (1886) 395.

3. E. Heyn, Internal Strains in Cold-Wrought Metals, and Some Troubles Caused Thereby, J. Inst. Metals, 12(1914)3.

4. Alfred W. Porter, Discussion to Paper by Cecil H. Desch, Chemical Influences in the Failure of Metals Under Stress, Trans. Faraday Soc., 17 (1921) 15.

5. T. P. Hoar, Remarks at Seminar, NRL, Wash. DC (1969).

6. W. E. Anderson, Discussion in The Physical Metallurgy of Stress Corrosion Fracture, Interscience, New York and London (1959) 147.

7. T. P. Hoar, The Corrosion of Tin in Nearly Neutral Solutions, Trans. Faraday Soc., 33 (1937) 1152.

8. E. T. Wessel, W. G. Clark, and W. K. Wilson, Engineering Methods for the Design and Selection of Materials Against Fracture, Final Technical Report on U.S. Army Contract No. DA-30-069-AMC-602(T)(1966).

9. William F. Brown, Jr., and John E. Srawley, ASTM Spec. Technical Publication 410, Plane-Strain Crack-Toughness Testing of High Strength Metallic Materials (1966).

10. B. F. Brown, The Application of Fracture Mechanics to Stress-Corrosion Cracking, Met. Reviews, 13 (1968) 171.

11. B. F. Brown, Application of Fracture Mechanics and Fracture Technology to Stress-Corrosion Cracking, ASM Lecture Series on Fracture Control (1969).

12. J. A. Kies et al., Fracture Testing of Weldments, ASTM Special Technical Publication 381, Fracture Toughness Testing and its Applications (1965) 328.

13. B. F. Brown, A New Stress-Corrosion Cracking Test for High Strength Alloys, Matls Res. & Stds, 6 (1966) 129.

14. J. H. Andrew, The Embrittlement of Iron by Caustic Soda, Trans. Faraday Soc., 9 (1913) 316.

15. Harald Moore, Discussion to Paper by Cecil H. Desch, Chemical Influences in the Failure of Metals Under Stress, Trans. Faraday Soc., 17 (1921) 15.

16. E. H. Dix, Acceleration of the Rate of Corrosion by High Constant Stress, Trans. AIME, 137 (1940) 11.

17. T. P. Hoar and J. M. West, Mechano-Chemical Anodic Dissolution of Austenitic Stainless Steel in Hot Chloride Solution, Proc. Royal Soc., 268 (1962) 304.

18. F. H. Keating, Chemical Manifestations of Internal Stress, Symposium on Internal Stresses in Metals and Alloys, Inst. of Metals, London (1948) 311.

19. E. G. Coleman et al., On a Surface Energy Mechanism for Stress Corrosion Cracking, Acta Met. 9 (1961) 491.

20. R. W. Staehle et al., Proceedings of Conference on Fundamental Aspects of Stress Corrosion Cracking, Natl Assoc. Corrosion Engineers, Houston (1969).

21. Hugh L. Logan, The Stress Corrosion of Metals, John Wiley, New York (1966).

22. R. N. Parkins, Stress Corrosion Cracking, Met. Reviews, 9 (1964) 201.

23. Thor N. Rhodin (ed.), The Physical Metallurgy of Stress Corrosion Fracture, Interscience, New York and London (1959).

24. William D. Robertson (ed.), Stress Corrosion Cracking and Embrittlement, John Wiley, New York (1956).

25. E. N. Pugh et al., Current Understanding of Stress-Corrosion Phenomena, Proc. International Conference on Interfaces, Melbourne (to be published) (Recent comprehensive review).

26. P. R. Swann and J. Nutting, Stacking Faults and the Failure of Alloys in Corrosive Media, J. Inst. Metals, 88 (1960) 478.

27. B. F. Brown, C. T. Fujii, and E. P. Dahlberg, Methods for Studying the Solution Chemistry within Stress Corrosion Cracks, J. Electrochem. Soc., 116:2 (1969)218.

28. S. L. Hoyt and M. A. Scheil, Stress Corrosion Cracking in Austenitic Stainless Steels, Trans. ASM, 27 (1939) 191.

☆U.S. GOVERNMENT PRINTING OFFICE: 1970-397-177/199