

**STRESS CORROSION
CRACKING OF METALS
—A *STATE OF THE ART***

STP 518



AMERICAN SOCIETY FOR TESTING AND MATERIALS

STRESS CORROSION CRACKING OF METALS— A STATE OF THE ART

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H. Lee Craig, Jr., symposium chairman

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FOREWORD

The Symposium on Stress Corrosion was presented at the American Society for Metals, Metals Conference held in Detroit, Michigan, 18 October 1971. Subcommittee 6 on Stress Corrosion Cracking and Corrosion Fatigue of the ASTM Committee G-1 on Corrosion of Metals sponsored the symposium. H. Lee Craig, Jr., Reynolds Metals, Co., presided as symposium chairman.

Related ASTM Publications

Stress Corrosion Testing, STP 425 (1967)

Metal Corrosion in the Atmosphere, STP 435 (1968)

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INTRODUCTION

This publication is a concrete example of the cooperation that exists between technical societies — in this instance, the American Society for Metals and the American Society for Testing and Materials. Subcommittee 6 of ASTM Committee G-1 on Corrosion of Metals presented a symposium on stress corrosion at the Fall 1971 meeting of the ASM in Detroit, Michigan. These papers are based on the talks given at that time. The objective was to present a timely report on the state of stress corrosion from a practical, engineering standpoint.

The excellent attendance at this symposium was mute testimony to the widespread nature of the problem of stress corrosion cracking. Project managers, designers, metallurgists, metallurgical engineers, each is concerned with this problem. Unexpected failure of metal parts has plagued the defense, chemical, petroleum, and other industries. However, analysis of each stress corrosion failure is seldom surprising — usually one or more caveats have been violated through ignorance, accident, or lack of precaution. Many of us, active in the field of stress corrosion, have come to the conclusion that the educational part of our work is the most significant, from the standpoint of prevention of failures.

Thus, experts from all phases of the metals industry, from government laboratories, research institutes and from universities gathered together to present the best, current thinking about the problems and the solutions to the use of high strength materials which may be susceptible to stress corrosion cracking.

In this volume information will be found on steels, including the new, high strength steels as well as the stainless and mild steels. Aluminum alloys are discussed with emphasis on the newer versions of high strength alloys and tempers specifically designed for stress corrosion resistance. Other engineering metals and their alloys are covered, including copper, titanium, and nickel.

These materials are discussed in relation to the newer testing methods that have evolved during the past decade. Several authors develop the concepts of linear elastic fracture mechanics as they are applied to specimen design and the interpretation of data. However, the older, time tested methods are not overlooked, as one author details the efforts of ASTM to standardize specimens and solutions used in stress corrosion testing.

This volume is presented to increase the understanding of the interested person who has a need to deal with stress corrosion cracking, either in the design of structures, the selection of materials, the specification of fabrication or maintenance procedures, or regretfully, in failure analysis. Each author was encouraged to deal with his subject using a practical, engineering approach. In

addition, I encourage anyone who has an interest or a problem dealing with stress corrosion, to become affiliated with Subcommittee 6 of Committee G-1 on Stress Corrosion Cracking and Corrosion Fatigue, and work with us in the development of standard test methods that will be used to help select materials and thereby minimize failures from stress corrosion cracking.

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A Preface to the Problem of Stress Corrosion Cracking

REFERENCE: Brown, B.F., "A Preface to the Problem of Stress Corrosion Cracking," *Stress Corrosion Cracking of Metals—A State of the Art, ASTM STP 518*, American Society for Testing and Materials, 1972, pp. 3-15.

ABSTRACT: The characteristics of stress corrosion cracking (SCC) are enumerated in the context of a historical sketch of the problem. The roles of pitting and brittle fracture in affecting the behavior of materials in tests of smooth specimens are depicted. The rationale for using fracture mechanics in evaluating crack propagation behavior is given, and a rudimentary composite of the results of smooth specimen tests and crack propagation ("fracture mechanics") specimen tests is presented. We lack predictive capability with respect to SCC from one chemical environment to another.

KEY WORDS: stress corrosion cracking, corrosion, fracture properties, fracture tests, corrosion tests, crack propagation, pitting, notch tests

Stress corrosion cracking (SCC) is one of those irritating considerations of the designer who may have to select materials of construction to meet a series of other property requirements that cannot be waived at all or can only be waived within narrow limits. The stress corrosion problem must therefore be considered in the context of the other constraints on design and maintenance, including costs. The designer who must use high strength materials will not be able to select structural alloys which are totally immune to SCC, so that he must understand the meaning of test data characterizing susceptibility to this form of failure. The alloy developer also needs to understand the significance of macroscopic characterization data since theory is inadequate to guide alloy development.

Much of this introductory paper will therefore treat macroscopic phenomena, macroscopic tests, and the interpretation of macroscopic test data. It is helpful first to summarize the characteristics of SCC, which is conveniently done in a historical review of the problem.

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Historical Sketch

SCC first became a widespread problem with the introduction of the cold drawn brass cartridge case during the last half of the 19th century. Toward the end of the century it appeared in the brass (but not in the unalloyed copper) condenser tubing in the rapidly growing electric power generation industry. During this era the problem became sufficiently important to acquire its own name, "season cracking." Also during this period Professor W. Chandler Roberts-Austen (whence "austenite") made two important contributions to the problem: he showed that a cold drawn wire of an alloy of gold, silver, and copper would undergo SCC if touched with a drop of ferric chloride solution, thus demonstrating that the phenomenon was not restricted to brass or even to base alloys. And in analyzing the stresses in the wire he placed emphasis for the first time on the necessary role of tensile stress in SCC. By the close of the 19th century the role of residual stresses in causing SCC in brass was so widely known that stress relieving heat treatments for cold formed products were developed as mitigative measures, and acidified mercurous nitrate, which will cause mercury cracking ("liquid metal embrittlement") of stressed brass, was in widespread use to verify the effectiveness of a stress relief treatment for a given brass product.

It will be appreciated that the tensile stresses which caused SCC in cartridge cases and in condenser tubes were residual stresses caused by cold forming operations and that therefore the stress fields tended to have complex geometry. As a consequence, it is not surprising that the stress corrosion cracks seen in this era tended to branch in response to the geometric complications of the stress fields, and that this branching was so common that it has remained accepted as a characteristic of SCC. We will see that there is another reason for branching of stress corrosion cracks. But under many practical circumstances where SCC is caused by service stresses, branching may be entirely absent.

It was during the late 19th century that ammonia was found to play a causative role in the SCC of brass, a finding which contributed to the development of the rule that there is a specificity of environment which will cause SCC in a given alloy. This specificity is usually cited as a prime characteristic of SCC, but the growing number of known exceptions makes the specificity rule of questionable merit. Regardless of the question of specificity, it became obvious that the responsible species need not be present either in large quantities or in high concentration in most cases, at least not in high concentration in the *bulk* environment.

By the end of the 19th century "caustic cracking" of riveted boiler steel could also be cited as an example of SCC and as another indication that the problem might occur in a number of alloy systems, given the wrong conditions. The wrong conditions in caustic cracking are a combination of local high concentration of free alkali and elevated temperature.

By this point the pattern of failures and mitigative measures had become discernible: there are three elements of the phenomenon, mechanics, metallurgy, and chemistry of the environment. A given problem can be solved only by changing one or more of these three elements, and valid research in the laboratory requires adequate attention to all three.

Early in the 20th century SCC was seen in aluminum alloys, attributable to atmospheric moisture. Also during this period SCC was observed in martensitic steel, but the problem did not become widely recognized for what it was until the era of the aerospace programs.

Also early in the 20th century the cracking of mild steel due to nitrates became of practical importance in the chemical industry. From this experience we have a clear statement of an important characteristic of SCC, namely, that often it occurs when the alloy is almost inert to the environment which does the cracking. Based on experience with evaporating sodium nitrate and sodium chloride solutions in steel pans, Professor Porter pointed out that

the action upon the steel is totally different in the case of the two solutions. You may go to a waste heap and pick out the pieces of steel that have come from a sodium nitrate pan. Those that have come from a 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 [1].

During the 1930s when stainless steels came to be used extensively in the paper, chemical, and petroleum industries, SCC was observed in this class of alloys, particularly in chloride or caustic solutions at elevated temperature. Also during the 1930s, magnesium alloys for military aircraft were found to be susceptible to SCC in moist atmospheres.

During the 1950s the aerospace programs encountered, in addition to SCC of martensitic steels indicated earlier, cracking of titanium alloys in contact with nitric acid, or in contact with salt at high temperatures.

During the 1960s, titanium alloys were also observed to be susceptible to SCC in nitrogen tetroxide, in water, and in methanol. Also, a zirconium alloy was found to be susceptible to SCC in iodine bearing environments. This experience confirmed the growing supposition that SCC is a general phenomenon to be expected in all alloy systems.

By 1960, the technique of producing high resolution replicas of fracture surfaces had been developed in basic form, and during the 1960s passed into the hands of a large number of investigators. Its application to SCC was inevitable, and fruitful as well, for it disclosed that on the fracture surfaces there were micron scale details important to the development of theory as well as helpful in critical failure analyses. This electron fractography demonstrated the gross differences in the fracture topology on the micron scale between stress corrosion cracks, which are always macroscopically brittle in appearance, and "brittle fracture" in the same material. The fact that stress corrosion cracks are always macroscopically brittle, even in alloys which are

highly ductile in purely mechanical fracture toughness tests, is another general characteristic of SCC.

By the 1960s, fracture mechanics had matured to the point of being applicable to treat the stress field around a stress corrosion crack in a useful way, particularly after the analysis for the bent beam specimen made fracture mechanics not only applicable but also practical for long term tests. In addition to the fracture mechanics analysis, much of the methodology and some of the instrumentation developed in fracture mechanics have been useful in the evolution of SCC testing concepts and procedures.

Characteristics of SCC

The characteristics of SCC may be summarized as follows:

1. Tensile stress is required. This stress may be supplied by service loads, cold work, mismatch in fit-up, heat treatment, and by the wedging action of corrosion products.
2. Only alloys are susceptible, not pure metals, though there may be a few exceptions to this rule.
3. Generally only a few chemical species in the environment are effective in causing SCC of a given alloy.
4. The species responsible for SCC in general need not be present either in large quantities or in high concentrations.
5. With some alloy/corrodent combinations, such as titanium and crystalline sodium chloride, or austenitic stainless steel and chloride solutions, temperatures substantially above room temperature may be required to activate some process essential to SCC.
6. An alloy is usually almost inert to the environment which causes SCC.
7. Stress corrosion cracks are always macroscopically brittle in appearance, even in alloys which are very tough in purely mechanical fracture tests. (Shear lips may occur in conjunction with stress corrosion cracks, but these shear lips are not part of the stress corrosion process. As a corollary, there does not appear to be a stress corrosion fracture analog to the full shear slant fracture of purely mechanical origin.)
8. Microscopically the fracture mode in SCC is usually different from the fracture mode in plane strain fractures of the same alloy.
9. There appears to be a threshold stress below which SCC does not occur, at least in some systems. This characteristic was not mentioned in the foregoing historical sketch but will be treated in a subsequent section.

Sequence of Events in SCC

In the most general case, if a smooth specimen is placed in a corrodent in which it will eventually undergo SCC, the sequence of events is as shown in the top row (Row A) of Fig. 1. First a corrosion pit forms. There is an important feature of most corrosion pits, the significance of which is not

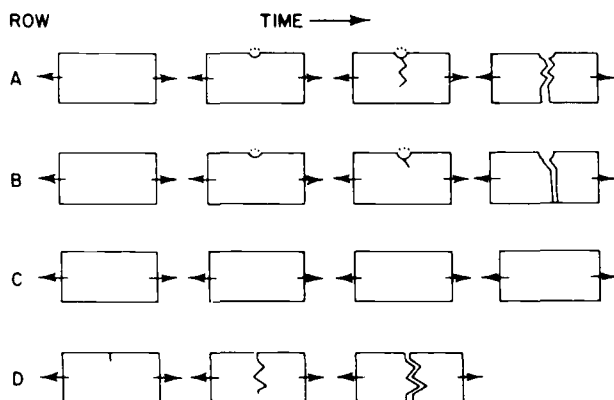


FIG. 1—Sequence of events (left to right) in alloys under stress in a corrosive environment. Materials in Rows A and B pit, and that in Row B is the brittlest. Material of Rows C and D does not pit, but specimen in Row D has a preexisting flaw.

always appreciated, namely, a porous cap of corrosion products which must be removed in order to see the pit itself. This cap impedes exchange between the corrodent within the pit and the bulk corrodent outside the pit, but it permits inward migration of anions such as chloride. This inward migration, also seen during the growth of stress corrosion cracks, represents “uphill diffusion” in terms of concentration of anions. The driving force for this “uphill diffusion” is of course the active metal surface. In general the pH within corrosion pits also differs from that outside the pit. The function of a corrosion pit in initiating SCC was once widely thought to be purely mechanical, to concentrate stresses. It now appears that the essential function of the pit when it initiates SCC is not primarily mechanical, but is rather to provide a mechanism for altering the solution chemistry locally to one favorable for SCC.

Continuing to the right in Row A of Fig. 1, representing the passage of time, we see in the third column a stress corrosion crack emanating from the corrosion pit. Assuming the stress is maintained, eventually the stress corrosion crack grows to such a length that the remaining metal ligament snaps in purely mechanical brittle fracture (fourth column). The combination of stress corrosion crack length and stress required to set off brittle fracture depends upon the fracture toughness of the alloy, and in fact that combination is a quantitative measure of the toughness. Lower strength alloys such as brass, austenitic stainless steels, and the older aluminum alloys are so tough that brittle fracture would not occur in the usual laboratory specimens. The material in Row B is more brittle than that of Row A, and after a short stress

corrosion crack grows (third column), the remaining ligament snaps. Some alloys are so brittle that the corrosion pit itself has been observed to initiate not SCC but brittle fracture, so that although there is a "delayed fracturing," there is no SCC or other slow crack growth process.

The material of Row C does not pit in the corrodent, and no SCC occurs. However, the same material containing a cracklike flaw at the surface, as in Row D, may experience rapid SCC. Titanium alloys in seawater are examples of materials which behave as depicted in Rows C and D.

It should be emphasized that neither a preexisting flaw nor a corrosion pit is necessary for initiating SCC if the environment has the correct composition for the alloy. For example, although a titanium alloy may not undergo SCC in salt water except from a preexisting crack or flaw, in methanol SCC initiates readily at a smooth surface of the same alloy. Also the precipitation hardening steel designated "13-8 Mo" will not initiate SCC in neutral salt water under given stress conditions until a corrosion pit is formed. But if the salt water is acidified with HCl, presumably to simulate the acidity within corrosion pits in that steel, SCC initiates readily at a smooth surface.

The important point of the foregoing discussion is that if one wishes to establish stress corrosion characteristics of a material, he must exclude possible confusion from either pitting or nonpitting behavior on the one hand and brittle fracture on the other.

Mechanics

The budgets available to the corrosionist working on the SCC problem have traditionally tended to encourage economy of experimentation. Accordingly simple strip specimens, stressed by bending in a simple fixture of one kind or another, were typical. Sometimes the specimens were notched, but not precracked. The characterization descriptors in such a test setup are customarily the initial stress on the specimen and the time for failure. It is thought by some that there is a limiting stress, designated σ_{TH} below which SCC does not initiate. It is difficult if not impossible to establish the existence of a σ_{TH} for it would require proving a negative. If for example one demonstrates that no SCC occurs below a specified stress level within a stated observation time, he has not thereby excluded the possibility that after a longer period SCC would occur. There does not seem to be any way around this difficulty. Nevertheless, arbitrary though it may be, a defined threshold stress would seem to be a useful thing to know.

Much progress has been made in alloy technology by the use of such tests, and also progress in the fundamentals of the process. Inevitably however, this test concept encountered difficulties when undetected effects of pitting behavior and of fracture toughness caused serious experimental artifacts, as discussed above in connection with Fig. 1. It finally became clear that to grapple successfully with the SCC problem one must study the cracking process itself, especially its kinetics. But the kinetics might reasonably be

assumed to be stress-dependent, so that any meaningful treatment of the cracking process required a method to quantify stress in the presence of a crack.

Stress intensification theory of notches cannot be applied to an essentially infinitely sharp crack because notch theory involves the reciprocal of the notch root radius; in the case of the infinitely sharp crack the reciprocal would be infinite and meaningless. "Nominal" stress has been used extensively to treat stress in a solid containing a crack by imagining removal of all the cracked material. A glance at Fig. 2 will suggest intuitively the weakness of



FIG. 2—“Nominal stress” treats a deeply cracked specimen as being equivalent to a smooth specimen equal in depth to the uncracked ligament of the cracked specimen.

this procedure. On the left in this figure a specimen is shown under stress with a crack, and on the right a smooth specimen of the same thickness as the unbroken ligament of the cracked specimen. The nominal stress rationalization would say that the stress situation at the bottom of the crack is the same as on the surface of the uncracked specimen. Not only is this rationalization intuitively bothersome, but it has actually been demonstrated to be fallacious [2]. In short, a nominal stress in a cracked solid is a fiction which can cause confusion and error.

There is available, however, another way to quantify the stress factor in an elastic body containing a crack, an analysis known as linear elastic fracture mechanics, or more commonly simply fracture mechanics. The useful metals and alloys are not purely elastic, particularly in the region around the tip of a growing crack. Thus fracture mechanics in its present form does not treat the very portion of the metal which is of most direct importance to SCC. Nevertheless, fracture mechanics can quantify the elastic stress field associated with the crack, and it is this elastic field which produces the plastic zone at the crack tip. Since it is the elastic field which produces the plastic zone, we can usefully apply elastic fracture mechanics even though it doesn't tell us anything at all directly about the material at the crack tip. Fracture mechanics thus does not of itself give us new knowledge about SCC processes, it simply provides a means of referencing stress in a body containing a crack in a manner applicable to various geometries. (It should be noted that in stating that the elastic conditions control the plastic conditions, there may be an important time dependence of this plasticity in some metals.)

The fracture mechanics descriptor of stress is useful for describing SCC kinetics involving a lengthening crack, and it is also useful in using experience gained with small specimens with one type of loading to predict the behavior of larger components or structures of a different shape and with different loading conditions. For example, SCC behavior in a small bar stressed in bending can be used, with fracture mechanics methodology, to predict the behavior of large plates in tension.

The fracture mechanics descriptor which has been most useful to date is the stress intensity factor K , which is proportional to the stress multiplied by a function of the square root of the crack length. The usual units in the United States are $\text{ksi}\sqrt{\text{in.}}$.

Studies of SCC kinetics as a function of K have shown that the crack growth rate is often approximately an exponential function of K up to a certain value of K . Beyond this K level, the rate is insensitive to K , as shown in Fig. 3 (after Ref 3). At still higher K levels there may be another

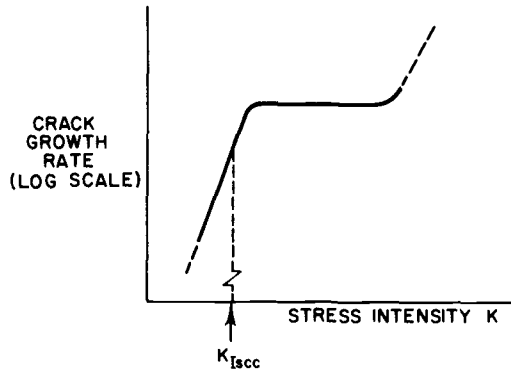


FIG. 3—Generalized representation of effect of K on SCC kinetics. There is a change in the scale of the ordinate so that the origin represents zero crack growth rate. Some systems exhibit the abrupt drop in kinetics apparently to this zero rate, at a finite value of K , denoted by $K_{I\text{SCC}}$. After Ref 4.

K -dependent regime. The features of Fig. 3 emphasize the hazard of conducting basic research studies involving cracking kinetics without knowing which regime one is working in, and without knowing whether he is crossing regime boundaries. In the K -independent regime there is a tendency for crack branching caused by mechanics alone.

Figure 3 also shows that in some systems the crack growth rate may drop abruptly to zero, as far as can be detected. The K level below which crack growth has not been observed but above which it is observed (for a specified combination of alloy and corrodent) has been termed $K_{I\text{SCC}}$. The usefulness of such a parameter, for those systems for which it exists, is that it quantifies

SCC resistance with a single number, and a number which has predictive capabilities with respect to combinations of preexisting crack depths and stress levels which would cause SCC. If one assumes that any cracklike flaw in the surface is long compared to its depth, and if he further assumes that yield point stresses exist around this flaw, then if he knows the value of K_{Isc} for this material in a given environment, he can estimate how deep the flaw must be before it will initiate SCC by the equation

$$a = 0.2 \left(\frac{K_{Isc}}{\sigma_Y} \right)^2 \quad (1)$$

where a is the critical flaw depth and σ_Y is the yield strength.

This method of characterizing SCC can be extended to provide a convenient method for displaying and comparing SCC characteristics of various alloys, as shown in Fig. 4. In this figure K_{Isc} data for the alloy Ti-6Al-4V in salt water is shown as a function of yield strength. The lines drawn represent Eq 1 for four selected values of flaw depth. The significance of these lines is as follows: if a surface flaw can be present as deep as the value of a shown for a given line, and if yield point stresses are present, one would want to use only materials having K_{Isc} values above that line.

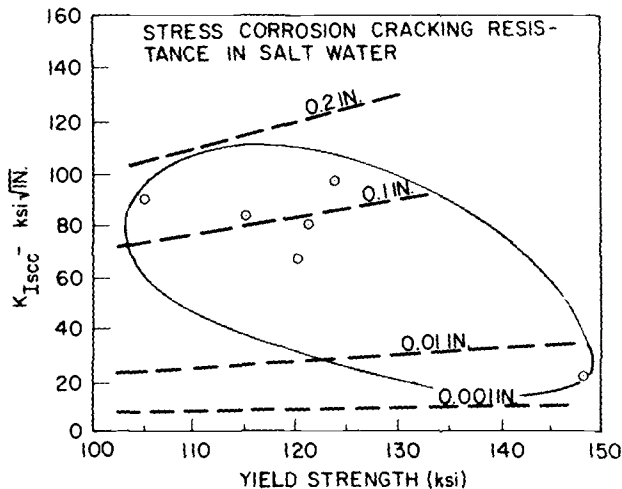


FIG. 4— K_{Isc} data for various heats of Ti-6Al-4V alloy in salt water, illustrating one method for displaying the SCC resistance of various alloys for materials selection purposes. Three alloys would experience SCC if stressed at their yield strength if there were a long surface crack 0.1 in. deep; one alloy would fail if the surface crack were only about 0.005 in. deep. Encircled area contains all other known data on K_{Isc} of Ti-6Al-4V alloy in salt water.

Those who have heard the rule that "fracture mechanics does not apply to low strength materials" should be reminded that the limitations on fracture mechanics are not fixed by strength alone but by the ratio of K to strength. If SCC occurs at sufficiently low values, then fracture mechanics is applicable even to low strength materials as long as crack branching does not occur.

No part of the SCC problem has been more troublesome than combining the methodology of crack propagation using fracture mechanics and the initiation and growth experience using initially smooth specimens. If there is a true SCC cracking threshold, it is designated K_{Isc} . If there is a threshold stress for SCC initiating from an originally smooth surface, it is designated σ_{TH} . The predictions of these two measures of SCC resistance may be combined as in Fig. 5. The curve represents the Irwin equation for a long surface crack:

$$K_{Isc}^2 = \frac{1.2 \pi \sigma^2 a}{1 - 0.2 \left(\frac{\sigma}{\sigma_Y} \right)^2} \quad (2)$$

The horizontal line indicates the σ_{TH} . In this figure one would expect SCC if the stress is above the solid line or if the combination of stress and flaw size lies to the right of the curve.

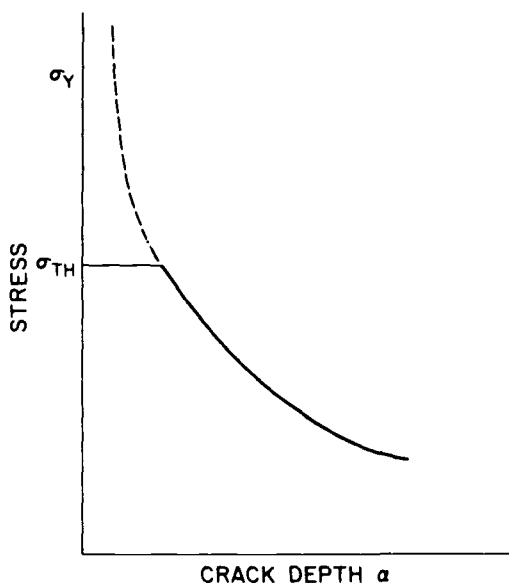


FIG. 5—Combining SCC data from smooth specimens (σ_{TH}) and crack propagation ("fracture mechanics") specimens (the curve). If the data are valid, the intersection of the horizontal line and the curve should indicate a corrosion pit that would reasonably function mechanically about the same as a crack of the indicated depth at the intersection. After Ref 4.

Unfortunately we do not have many data from which to construct a diagram such as the schematic one of Fig. 5. There has been one attempt to make such a diagram for the aluminum alloy 7075-T6510 [4]. In this instance the intersection of the horizontal line and the curve occurred at a very large value of a , as though a corrosion pit were acting like a very deep crack. One possible explanation for this behavior is that the alloy does not appear to possess a real K_{Isc} and that therefore cracking occurs at much lower K values than that for which the curve was drawn (K_{Isc} does not apply, and the number assumed for it is too large). A second possible reason for the unreasonably large equivalent value of the corrosion pit is that possibly the solution within the corrosion pit may differ in an important way from the solution near the tip of a growing crack. Conceivably an important difference in solution chemistry could make an important difference in K_{Isc} and hence in the position of the curve of Fig. 5 and the intersection point.

Local Solution Chemistry

The alterations which occur in the corroding solution within the cavity of a pit while it is growing have already been mentioned. It has been found that the corrodent within stress corrosion cracks in high strength steels, aluminum alloys, and titanium alloys is acid, as shown in Fig. 6, even though the bulk corrodent was nearly neutral (pH 6, due to dissolved carbon dioxide). This acidification may be described in terms of traditional hydrolysis reactions, such as a metal salt reacting with water. Alternatively one can describe the reactions as involving the combining of metal with oxide or hydroxyl ions, leaving an excess of hydrogen ions. These hydrogen ions are balanced by the

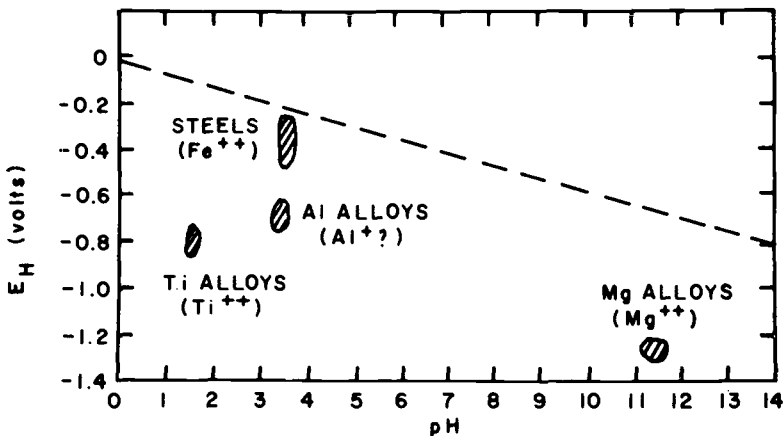


FIG. 6—Potential and pH data at the tips of growing stress corrosion cracks in four alloy families. The bulk corrodent is nearly neutral salt water. The broken line indicates the Nernst potential for the reversible hydrogen electrode.

influx of anions such as chloride. The result is an acid solution which simultaneously may promote the reduction of hydrogen and oppose the repassivation of the metal surface. In the instance of magnesium alloys, the local pH is buffered to a high value by the presence of magnesium hydroxide.

The acidic nature of the corrodent within stress corrosion cracks in the heavy metals is only one reason that effective inhibitors for SCC propagation are virtually nonexistent. It is difficult enough to solve the problem of inhibiting acid chloride solutions. This task is made even more difficult by the exceedingly small amount of corrodent within stress corrosion cracks, the amount being too small to provide a sufficient reservoir for inhibitors. For the same reason, the addition of buffers to the bulk environment makes only a modest change in stress corrosion crack propagation — the buffering capacity of even concentrated buffers is not sufficient to overcome entirely the hydrolytic acidification capacity of the clean metal surfaces of the crack.

Mechanisms

Many investigators and commentators have asked the question whether there is a single mechanism which can explain SCC in all the systems in which it has been observed. The prevailing present opinion is that such a common explanation is improbable. The mechanisms that have been advanced fall into the following categories:

1. Mechano—electrochemical. This category includes such models as the high strain rate at the tip of the growing crack causing continuous depolarization of the anodic area so that cracking by electrochemical dissolution can continue. As an added feature, another model envisions a separate role of strain in causing the rupturing of islands of material resistant to electrochemical dissolution which has previously produced all the fracture area except the resistant islands.
2. Film rupture. This model envisions the cyclic formation and rupture of films of corrosion product.
3. Embrittlement. This model envisions electrochemical corrosion causing embrittlement of the metal immediately behind the corroding surface. This model may picture either a continuous or a cyclic process.
4. Adsorption. This model envisions the reduction of energy to form a new surface by adsorption of specific species.

The interested reader may wish to study Refs 5 through 7 for more detailed discussions of mechanisms.

There is limited agreement among various investigators on the applicability of any one of the above categories of mechanisms for a given combination of metal and corrodent. Furthermore, none of the models has been useful either in alloy development or in predicting SCC in fundamentally new combinations of alloys and environments.

Fracture mechanics has given us predictive capability from one geometry to another, within limits. We are lacking predictive capabilities from one environment to another, and the outlook does not seem favorable for early substantial improvement in this element of the problem. Macroscopic test data will therefore continue to be of paramount importance until theory is much better in hand. This is in no way intended as a criticism of the work on theory past or present, merely a recognition of the status of this difficult problem.

Acknowledgments

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Stress Corrosion Cracking of a High Strength Steel

REFERENCE: Sheinker, A.A. and Wood, J.D., "Stress Corrosion Cracking of a High Strength Steel," *Stress Corrosion Cracking of Metals—A State of the Art*, ASTM STP 518, American Society for Testing and Materials, 1972, pp. 16-38.

ABSTRACT: Stress corrosion crack growth rates (da/dT) as a function of stress intensity factor (K) were determined over a wide range of electrode potentials for AISI 4340 steel (200-ksi yield strength level) in deaerated 3.5 percent sodium chloride solution buffered to pH 3.8. Particular emphasis was placed on conducting the stress corrosion tests under well defined electrochemical and mechanical conditions. At intermediate K levels, da/dT was essentially independent of K , suggesting that crack growth is limited by mass transport. Crack growth is apparently dominated by localized mechanical rupturing at high K levels where da/dT increased rapidly with increasing K . Except at a very cathodic potential, da/dT at intermediate K levels was also independent of potential, implying that the electrochemical conditions at the tip of the stress corrosion crack are not the same as those outside the crack. The tendency for the stress corrosion cracks to branch was found to be electrochemically, as well as mechanically, controlled.

KEY WORDS: stress corrosion cracking, fracture properties, mechanical properties, high strength steels, electrochemistry, hydrogen embrittlement, failure, crack propagation, crack initiation, stress analysis, plastic deformation

Definition of Stress Corrosion Cracking

Stress corrosion cracking is the failure of a metal resulting from the conjoint action of stress and chemical attack. There are two different types of mechanisms by which stress corrosion cracking is believed to occur: active path corrosion and hydrogen embrittlement. In the active path corrosion type, cracking is caused by localized corrosion at the crack tip, and proceeds along a path which is electrochemically active with respect to the surrounding metal. In the hydrogen embrittlement type of mechanism, cracking results from the entry of hydrogen into the metal, which reduces its ability to deform plastically.

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Since hydrogen embrittlement is not a corrosion process in the classical sense, cracking occurring by this mechanism is sometimes excluded from the term "stress corrosion cracking." However, since it is often not clear which of the two types of mechanisms is responsible for cracking, it is convenient and practical to use the generic term "stress corrosion cracking" to refer to cracking occurring by either type of mechanism. This usage is adopted in this paper.

In order for stress corrosion cracking to occur, the following conditions are necessary: (1) a susceptible metal, (2) a specific environment, and (3) a tensile stress. Metal susceptibility and environment specificity depend on the particular metal-environment couple. A metal may be susceptible to stress corrosion cracking in only a few specific environments, and conversely, a particular environment may induce cracking in only certain metals. The tensile stress usually must exceed a certain level, depending on the particular metal-environment couple, to produce stress corrosion cracking.

In general, the sequence of events leading to failure of a metal by stress corrosion cracking begins with localized chemical attack of the metal surface. A crack then initiates at a sharp intrusion produced by localized attack, and grows slowly. When the crack reaches a size at which the metal can no longer support the load, rapid fracture occurs. If a crack like flaw is already present in the metal surface, localized attack is unnecessary, and slow crack growth proceeds from the flaw, sometimes after a period of incubation.

The process of stress corrosion cracking involves a complex interaction of metallurgical, chemical, and mechanical factors. Since these three factors correspond to the three conditions necessary to produce stress corrosion cracking, it is evident that the role of each factor must be understood to completely understand this phenomenon. Much emphasis has been placed on the metallurgical aspect of stress corrosion cracking, but considerable progress is being made in understanding the chemical aspect by the application of the principles of electrochemistry, and in understanding the mechanical aspect by the application of the concepts of fracture mechanics.

Use of Electrochemistry to Study Stress Corrosion Cracking

It is well known that corrosion of metals is an electrochemical process, and it is also now well established that stress corrosion cracking of metals in aqueous solutions is governed, at least to some extent, by electrochemical reactions [1]. Previous studies of the effects of electrochemical variables on stress corrosion cracking have been mainly devoted to the determination of the relation between electrode potential and the time-to-failure of stressed specimens for various metal-environment systems. For steels, this so-called "electrochemical polarization method" has been used to determine whether the mechanism of stress corrosion cracking is one of active path corrosion or hydrogen embrittlement [2]. If anodic polarization decreases the failure time with respect to that at the "open-circuit" or "rest" potential, then the

mechanism is said to be of the active path type. Conversely, if cathodic polarization decreases the failure time with respect to that at the rest potential, then the mechanism is said to be one of hydrogen embrittlement.

Most of these studies, however, have been deficient in that they were not conducted under well defined electrochemical conditions, including solution pH and dissolved ion and oxygen contents. These conditions probably varied during the course of the experiments. In some, the pH of the corrosive solution was adjusted by the addition of simple acids and bases which have low buffer capacities, that is, ability of the solution to resist changes in hydrogen ion concentration [3]. This is an important consideration, as it has been observed that the pH of the solution within a stress corrosion crack is markedly different from that of the external bulk solution [4-6].

Application of Fracture Mechanics to Stress Corrosion Cracking

The traditional method of evaluating the stress corrosion susceptibility of a metal is the determination of the time required to produce failure (time-to-failure) in smooth specimens tested at different gross stress levels in the appropriate corrosive environment. However, the gross stress is not an accurate measure of the mechanical driving force for crack propagation, since it does not relate to the tip of the crack where the stress corrosion process operates. In addition, the time-to-failure of smooth specimens incorporates the time required for both crack initiation and slow crack growth so that the separate effect of the environment on each of these stages cannot be ascertained.

An accurate quantitative description of the mechanical driving force for stress corrosion crack propagation is provided by the stress intensity factor K from fracture mechanics [7-9]. K is a measure of the intensity or magnitude of the stresses near the tip of a crack in a solid body [10]. It is a function of the loading and the configuration of the body, including the crack size. The units for K are those of $(\text{force/area}) \times (\text{length})^{1/2}$, and in the English system the units are psi $\sqrt{\text{in.}}$ or ksi $\sqrt{\text{in.}}$.

The crack tip stress analysis is based on the assumption of limited plasticity, so that the use of K is valid only when plasticity at the crack tip is limited. This is true when the state of stress at the crack tip is essentially that of plane strain, which requires minimum values of crack size and section thickness [11].

In order to utilize fracture mechanics concepts in stress corrosion studies, precracked specimens, into which cracks have been deliberately introduced, must be employed. Besides enabling the use of K to characterize the crack driving force, the use of precracked specimens offers several other advantages over smooth specimens. Precracking eliminates the localized attack stage, which is highly variable and often not representative of material behavior in service. It also avoids variations in the metal surface, to which the localized attack stage is very sensitive. In addition, the use of precracked specimens facilitates measurement of the slow crack growth rate.

Much of the stress corrosion research utilizing the fracture mechanics approach has been concerned with the determination of the relation between the initially applied stress intensity factor K_i and the time-to-failure of precracked specimens for various metal-environment systems [7-9]. The time-to-failure usually increases as K_i is decreased from the level required for the onset of rapid fracture (designated K_{Ic} , the "fracture toughness") to a threshold level (designated K_{Isc}) below which stress corrosion cracking does not occur. (The fracture toughness and stress corrosion cracking threshold are designated K_{Ic} and K_{Isc} , respectively, only when the state of stress at the crack tip is essentially that of plane strain.) However, neither K_i nor the failure time are fundamental parameters. For most specimen configurations, under constant load, K increases as the crack propagates through the specimen, with the relation between K and crack length dependent upon the particular configuration. The time-to-failure depends on (1) the size and configuration of the specimen, (2) the length of the incubation period which may precede the commencement of slow crack growth, and which may be K -dependent, (3) the relation between crack growth rate (dA/dT) and K , and (4) the fracture toughness of the metal, which determines how far the crack will grow before rapid fracture occurs.

Since K is an accurate measure of the mechanical driving force for stress corrosion crack propagation, a unique relationship between dA/dT and the instantaneous K level should exist for a given metal-environment system, provided the metallurgical and environmental conditions are held constant. Relatively little is known about the relation between dA/dT and K for various metal-environmental systems. For high strength steels in distilled or salt water, linear [12-14] and logarithmic [15,16] relationships have been reported, and it has also been observed that dA/dT is independent of K over a wide range of K levels [13,17]. However, none of these reported relationships was obtained under well defined electrochemical conditions. In addition, many of these relationships may be misleading because, either they were obtained over a narrow range of K relative to the range K_{Isc} to K_{Ic} , or they are based on relatively few data points.

Stress Corrosion Cracking of High Strength Steels

The term "high strength steels" here refers to martensitic, precipitation-hardenable, and maraging steels, which have yield strengths in excess of about 150 ksi. These steels are susceptible to stress corrosion cracking in a wide variety of both aqueous and nonaqueous solutions [2]. The susceptibility of these steels generally increases with increasing yield strength.

Stress corrosion cracks in high strength steels usually initiate at the bases of sharp corrosion pits which invariably form at the sites of nonmetallic inclusions in the surface of the metal [2]. The path of crack propagation is usually intergranular, but is sometimes transgranular, with respect to the prior austenite grain boundaries.

There has been no general agreement on whether the mechanism of stress corrosion cracking in high strength steels is one of active path corrosion or hydrogen embrittlement, or possibly a combination of both types of mechanisms [2]. Use of the electrochemical polarization method has indicated that either type of mechanism may be operative, depending on the particular steel and the nature of the environment. However, in recent years, the following evidence has been produced which indicates that hydrogen embrittlement may be the major mechanism, at least in martensitic high strength steels:

1. The electrochemical conditions (solution pH and electrode potential) at the tip of a stress corrosion crack in a high strength steel are apparently favorable for hydrogen liberation regardless of the external electrochemical conditions [6].
2. Hydrogen can permeate through steel under anodic as well as cathodic polarization [18].
3. Hydrogen permeation correlates with stress corrosion susceptibility [18].
4. Martensitic structures absorb atomic hydrogen at an increasing rate with increasing tensile stress [19].
5. Atomic hydrogen diffuses to and concentrates in the region of highest tensile stress [19].

Purpose of This Investigation

The purpose of this investigation was to gain a better understanding of how the kinetics of stress corrosion cracking in high strength steels are controlled by electrochemical reactions. The objective was the determination of the effect of electrode potential on the slow crack growth rate as a function of stress intensity factor. Particular emphasis was placed on conducting the stress corrosion tests under well defined electrochemical and mechanical conditions.

Experimental Procedure

Material and Specimens

The material selected for this study was AISI 4340 steel heat treated to a yield strength of about 200 ksi. This material was obtained in the form of a 1-in. thick hot rolled plate. The chemical composition of this steel is presented in Table 1.

TABLE 1—Composition of AISI 4340 steel, weight percent.

C	Mn	P	S	Si	Ni	Cr	Mo	Al
0.39	0.65	0.005	0.008	0.35	1.69	0.88	0.21	0.03

In order to utilize the stress intensity factor K to characterize the mechanical driving force for stress corrosion crack propagation, precracked

cantilever bend specimens were employed. In this type of precracked specimen, under constant load, K increases rapidly with increasing crack length, thereby providing a large variation in K within a single specimen.

The specimen dimensions are shown in Fig. 1. The thickness (0.5 in.) was sufficient to ensure a plane strain state of stress at the crack tip at all K levels attained. The specimen depth (1.5 in.) was large enough to provide a reasonable amount of slow crack growth prior to rapid fracture.

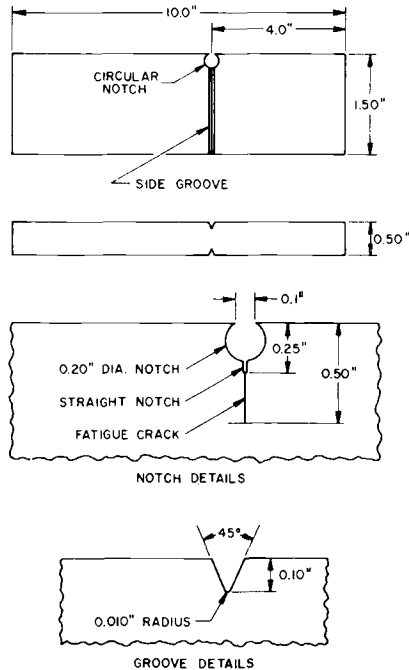


FIG. 1—Stress corrosion test specimen.

The circular notch in the upper edge of the specimen was used to provide knife edges for attaching a crack opening displacement gage. The straight notch below the circular notch was used to promote initiation of the fatigued precrack. The grooves in the sides of the specimen were employed to prevent crack branching.

The specimen blanks were cut from the 1-in. thick plate such that the applied stress direction and the crack growth direction were in the RW orientation, that is, with the specimen length (applied stress direction) parallel to the plate rolling direction and the specimen depth (crack growth direction) parallel to the width of the plate. Equal amounts of material were machined

from both sides of the blanks so that the resulting specimen thickness corresponded to the middle of the plate thickness.

The specimens were heat treated as follows:

1. Normalized at 1700 F for 1 h in an inert atmosphere.
2. Austenitized at 1550 F for 1 h in an inert atmosphere.
3. Quenched in still oil at room temperature.
4. Immersed in liquid nitrogen for 30 min.
5. Tempered at 750 F for 1 h in air, and air cooled.

The hardness of the heat treated specimens was Rockwell C 48 ± 0.5 .

Following heat treatment, the specimens were ground to final dimensions. The straight notch was cut by electrical discharge machining. The specimens were precracked by cyclic loading, with a maximum K level in the final increment of fatigue crack growth of $15 \text{ ksi}\sqrt{\text{in}}$. The precrack length was 0.5 in. including the circular and straight notches. The side grooves were machined after precracking. The specimens were stored in a dessicator until ready for stress corrosion testing.

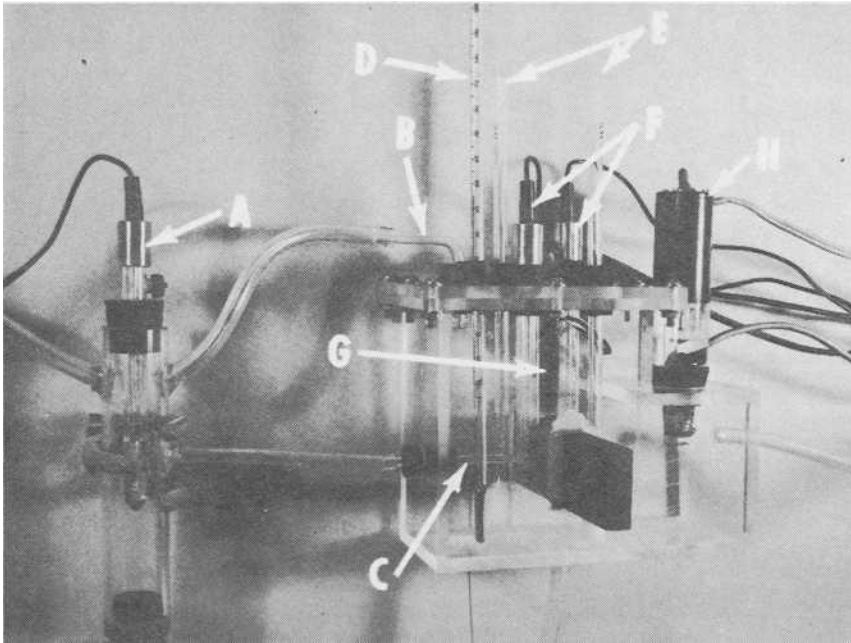
Prior to stress corrosion testing, the specimen was wiped clean with acetone followed by methanol. In order to restrict access of the corrodent to the mouth of the crack, the surface of the specimen to be exposed to the corrodent, with the exception of the circular and straight notches, was then masked with an inert polymeric coating.

Stress Corrosion Tests

A series of stress corrosion tests was conducted at electrode potentials ranging from +240 to -960 mV on the standard hydrogen electrode (SHE) scale. These tests were conducted under carefully controlled electrochemical conditions. In each test, the corrodent was deaerated and the electrode potential of the specimen was held constant. All the tests were conducted at room temperature in an air conditioned laboratory.

The corrodent employed in the stress corrosion tests was an aqueous solution of 3.5 percent (0.6M) sodium chloride buffered to a pH of 3.8 by the addition of 1.02 percent (0.05M) potassium biphthalate ($\text{KHC}_8\text{H}_4\text{O}_4$). This pH level was chosen because it has been found to be the pH at the tip of a stress corrosion crack in several high strength steels, including AISI 4340, in the absence of an applied potential, regardless of the pH of the bulk solution outside the crack [4,5]. The water used to prepare the corrosive solution was deionized water having a specific conductance no greater than $2 \times 10^{-6} \text{ (ohm} \cdot \text{cm)}^{-1}$.

The precracked section of the specimen was immersed in the corrodent using an enclosed Plexiglas chamber, as shown in Fig. 2. Holes were provided in the top and sides of this chamber for insertion of various instrument probes. The specimen was sealed to the sides of the chamber with the same polymeric material used to mask the specimen. The corrodent was fed to the



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|--------------------------|-----------------------------------|
| A—Reference electrode | E—Gas dispersion tubes |
| B—Gas vent tube | F—Platinum auxiliary electrodes |
| C—Luggin capillary probe | G—Crack opening displacement gage |
| D—Thermometer | H—Dissolved oxygen probe |

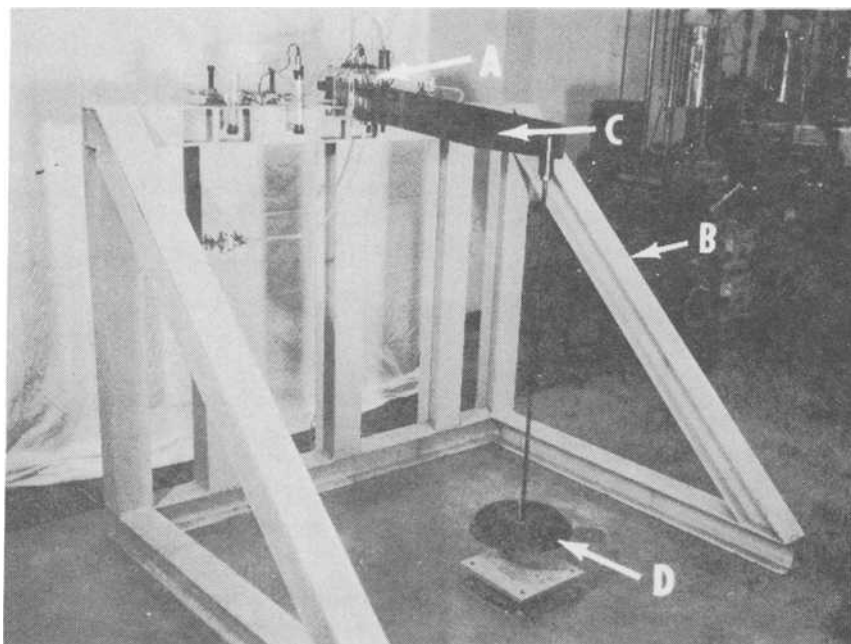
FIG. 2—Stress corrosion test setup with instrument probes.

environment chamber by gravity flow from a 5-gal supply tank, and was allowed to flow through the chamber at a rate of about 30 ml/min to prevent accumulation of corrosion products in the chamber. The corrosive flow rate through the chamber was controlled by means of inlet and outlet stopcocks. The pH of the effluent solution was measured periodically with a pH meter, and remained constant throughout each test.

The corrosive was deaerated by bubbling purified nitrogen gas through the solution in the supply tank. This gas was also bubbled through the solution in the environment chamber by means of two fritted glass gas dispersion tubes immersed in the solution on either side of the specimen, as shown in Fig. 2. This arrangement also served to agitate the solution around the specimen. The dissolved oxygen content of the corrosive in the chamber was monitored by means of a dissolved oxygen meter with a polarographic probe immersed in the solution (Fig. 2). The dissolved oxygen content in all of these tests was 0.1 ppm.

The electrode potential of the specimen was controlled by means of an electronic potentiostat with two platinum auxiliary electrodes and a saturated calomel reference electrode. The two auxiliary electrodes were immersed in the corrodent on either side of the specimen, but the reference electrode was immersed in the corrodent in a separate cell beside the chamber (Fig. 2). This cell was connected to the chamber by a Luggin capillary probe to form a salt bridge. To eliminate the voltage drop through the solution from the potential measurement, the tip of this probe was positioned about 1 mm from the side of the specimen and midway down the depth of the specimen, at the precracked section.

The specimen was loaded as a cantilever beam by clamping one end to a rigid test stand, and the other end to a lever arm, as shown in Fig. 3. Disk shaped weights were then suspended from the other end of the lever arm to obtain the desired bending moment. The load was applied after the specimen was immersed so the corrodent would be immediately drawn into the crack. Each test was conducted at a constant load with an initial K level of about 25



A—Environment chamber
B—Test stand
C—Lever arm
D—Weight

FIG. 3—Arrangement for loading test specimen.

$\text{ksi}\sqrt{\text{in.}}$, since crack growth did not commence in a reasonable length of time (several hours) at lower K levels. (The K_{Isc} for this material in sodium chloride solutions is about 10 to 15 $\text{ksi}\sqrt{\text{in.}}$ [15].)

Stress corrosion crack growth was monitored by means of a crack opening displacement gage of the clip-on type used in fracture toughness testing [20]. This gage was attached to the upper edge of the test specimen on the knife edges formed by the circular notch, as depicted in Fig. 4. As the crack propagated through the specimen, the crack opening displacement increased as a function of the crack length. The relationship among applied moment, crack length, and crack opening displacement was previously determined by performing a compliance calibration on a test specimen. This relationship is plotted in Fig. 5, in which the points represent the actual data from the compliance calibration, and the curve represents a least-squares fit to this data for the relation

$$\log \left[\frac{VBEW}{M} \right] = C \left[\frac{A}{W} \right] + D$$

where

- V = crack opening displacement, in.,
- B = gross specimen thickness, in.,

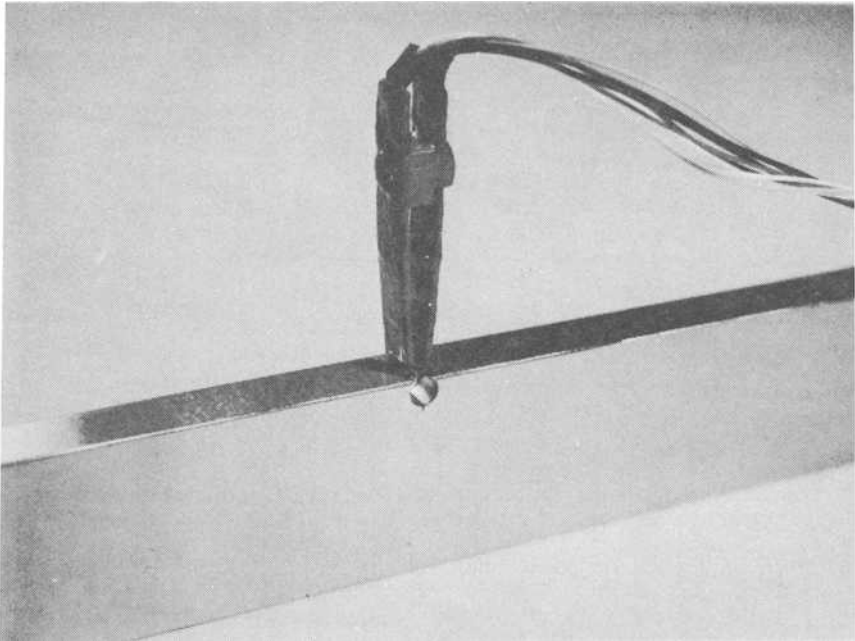


FIG. 4—Crack opening displacement gage attached to test specimen.

- E = Young's modulus, psi,
 W = specimen depth, in.,
 M = applied moment, lb · in.,
 C = a dimensionless constant,
 A = total crack length, including circular and straight notches, in., and
 D = a dimensionless constant.

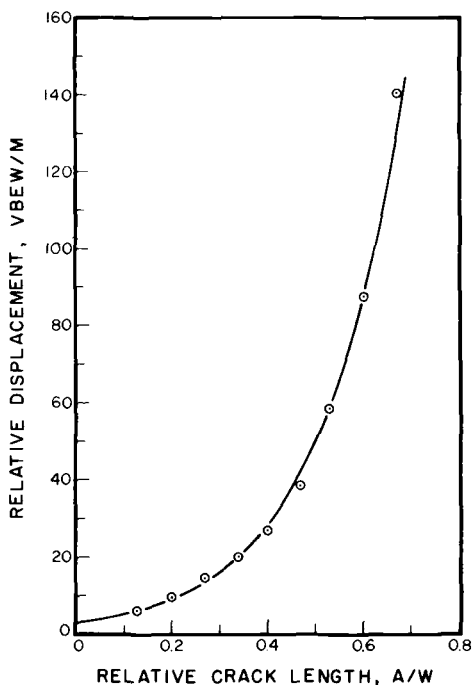


FIG. 5—Compliance relationship for side grooved cantilever bend specimens.

The electrical response of the gage was continuously recorded by means of a strip chart recorder. Data points were taken from the recorder chart at equal increments of gage response and converted to values of crack opening displacement by means of a prior calibration of the gage. The displacement values were then converted to crack lengths by means of the compliance relationship. The crack growth rate was determined by calculating the slope of the crack length-time curve at each data point.

The stress intensity factor corresponding to each data point was calculated by means of the equation

$$K = \left(\frac{6 M A^{1/2}}{B W^2} \right) \left(\frac{B}{B_N} \right)^{1/2} \left[1.99 - 2.47 \left(\frac{A}{W} \right) + 12.97 \left(\frac{A}{W} \right)^2 - 23.17 \left(\frac{A}{W} \right)^3 + 24.80 \left(\frac{A}{W} \right)^4 \right]$$

where

- M = applied moment, lb · in.,
- A = total crack length, including circular and straight notches, in.,
- W = specimen depth, in.,
- B = gross specimen thickness, in., and
- B_N = net specimen thickness between side grooves, in.

This equation is for single edge cracked plate specimens subjected to pure bending [11], modified by the factor $(B/B_N)^{1/2}$ to include the effect of the side grooves [21].

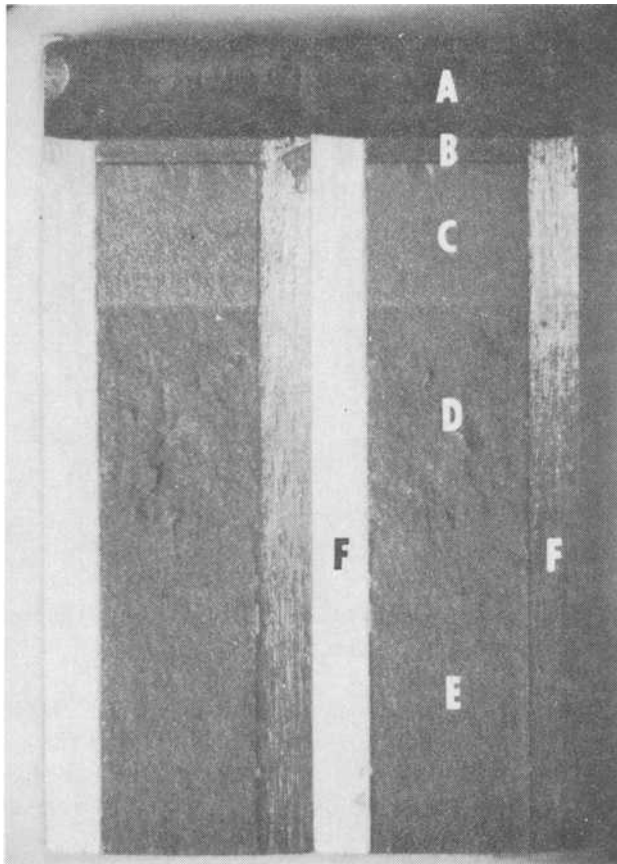
All the calculations were performed by a high speed digital computer. Graphs of crack length (A) as a function of time (T), and crack growth rate (dA/dT) as a function of stress intensity factor (K), for each stress corrosion test, were plotted by an automatic plotter connected to the computer.

Results and Discussion

General Shape of dA/dT - K Curves

Stress corrosion crack growth proceeded from the precrack length of 0.5 in. to a final crack length of 0.8 to 1.0 in., at which the specimens failed by rapid fracture. The stress corrosion fracture surface was very rough compared with the fatigue and rapid fracture surfaces, as shown in Fig. 6. Typical crack length-time plots are shown in Figs. 7 and 8. The plot in Fig. 8 indicates an incubation period of about 30 min preceding the commencement of stress corrosion crack growth. An incubation period was observed in some of the tests, but did not vary regularly with electrode potential.

A typical plot of dA/dT versus K is presented in Fig. 9. All of the dA/dT - K plots had this same general shape regardless of the applied potential. As K increases, dA/dT passes through several stages. At low K levels, dA/dT increases rapidly with increasing K (Stage I). At intermediate K levels, dA/dT is either independent of K , or only slightly K -dependent (Stage II). At higher K levels, dA/dT again increases rapidly with increasing K (Stage III). This



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|--------------------|--------------------------|
| A—Circular notch | D—Stress corrosion crack |
| B—Straight notch | E—Rapid fracture |
| C—Fatigue precrack | F—Side grooves |

FIG. 6—Typical fracture surface of stress corrosion test specimen.

stage is followed by the onset of rapid fracture, at which dA/dT rises abruptly.

Stage I of the dA/dT - K curves probably has little physical significance since it is associated with the commencement of stress corrosion crack growth from the existing fatigue precrack. The maximum K level in the final increment of fatigue precracking (15 ksi $\sqrt{\text{in.}}$) was kept well below the initial K level in the stress corrosion tests (25 ksi $\sqrt{\text{in.}}$) so that the initial stress corrosion crack growth rate would not be affected by the residual compressive stresses in the plastic zone at the tip of the precrack [22]. However, since the material in

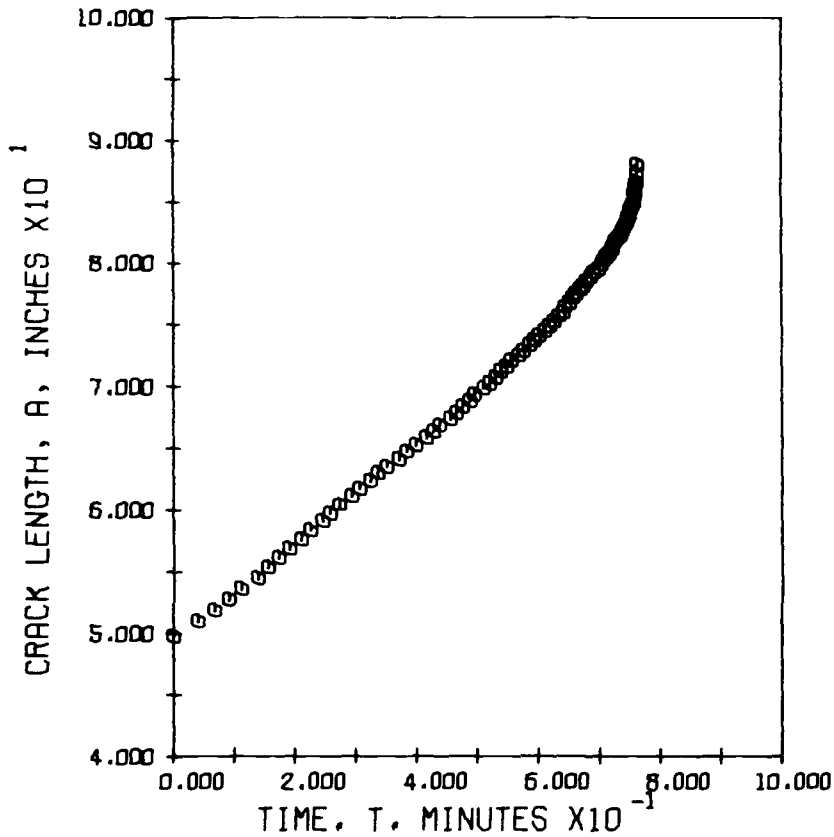


FIG. 7—Typical crack length-time plot for stress corrosion test with no incubation period.

this plastic zone has undergone cyclic plastic deformation, it is not representative of the material in the bulk of the specimen. This could affect the initial crack growth rate as well as the incubation period preceding the commencement of stress corrosion crack growth.

In addition, the commencement of stress corrosion crack growth from the precrack may not be uniform along the precrack front, so that the crack extends farther at some points along its front than at others. The rate of crack opening displacement, and thus the apparent crack growth rate, would then increase as the crack front became uniform. Thus, the apparent K -dependence of dA/dT in Stage I may simply be a manifestation of a transition from an unevenly extending crack front at the precrack tip, to a uniformly extending crack front.

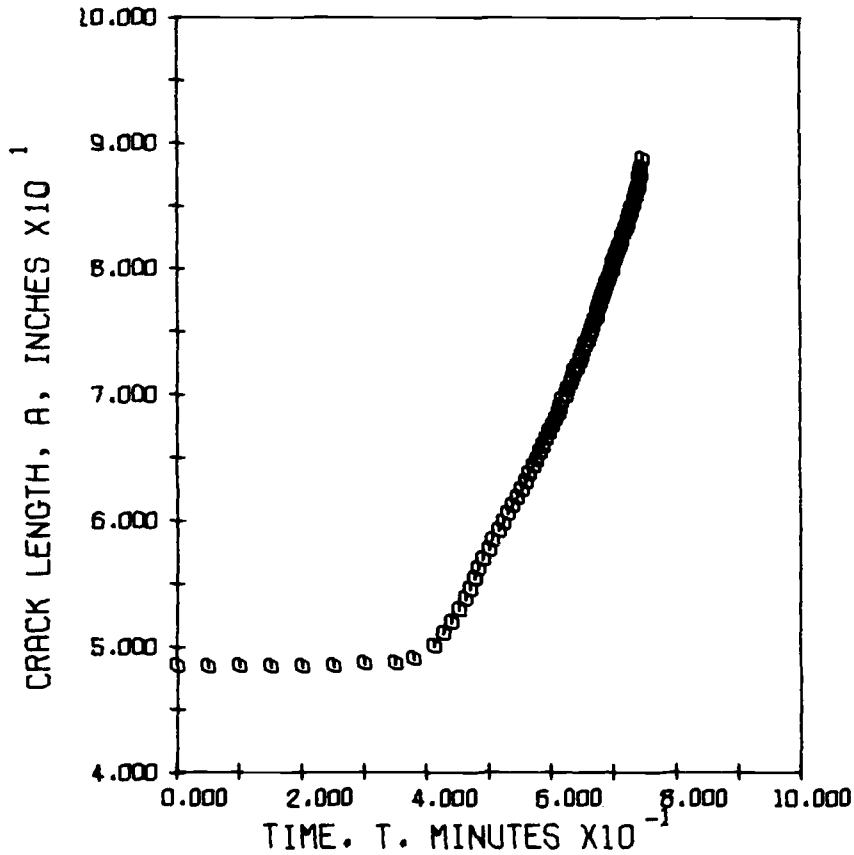


FIG. 8—Typical crack length-time plot for stress corrosion test with incubation period.

The occurrence of the crack growth rate plateau at intermediate K levels (Stage II) suggests that crack growth in this stage may be limited either by mass transport or by the kinetics of a reaction between the metal and the corrodent. From a purely mechanical standpoint, the crack growth rate would be expected to increase as the stress intensity at the crack tip is increased, as is the case in fatigue crack propagation [22]. The mass transport involved in limiting crack growth could be either the diffusion of hydrogen into the metal at the crack tip, or the migration of corrosive reactants down the length of the crack. (The impervious coating masking the sides of the specimen prevented direct access of the corrodent to the crack tip.) Alternatively, the crack growth rate may be controlled by the rate of some reaction at the crack tip, such as the adsorption of hydrogen on the metal surface.

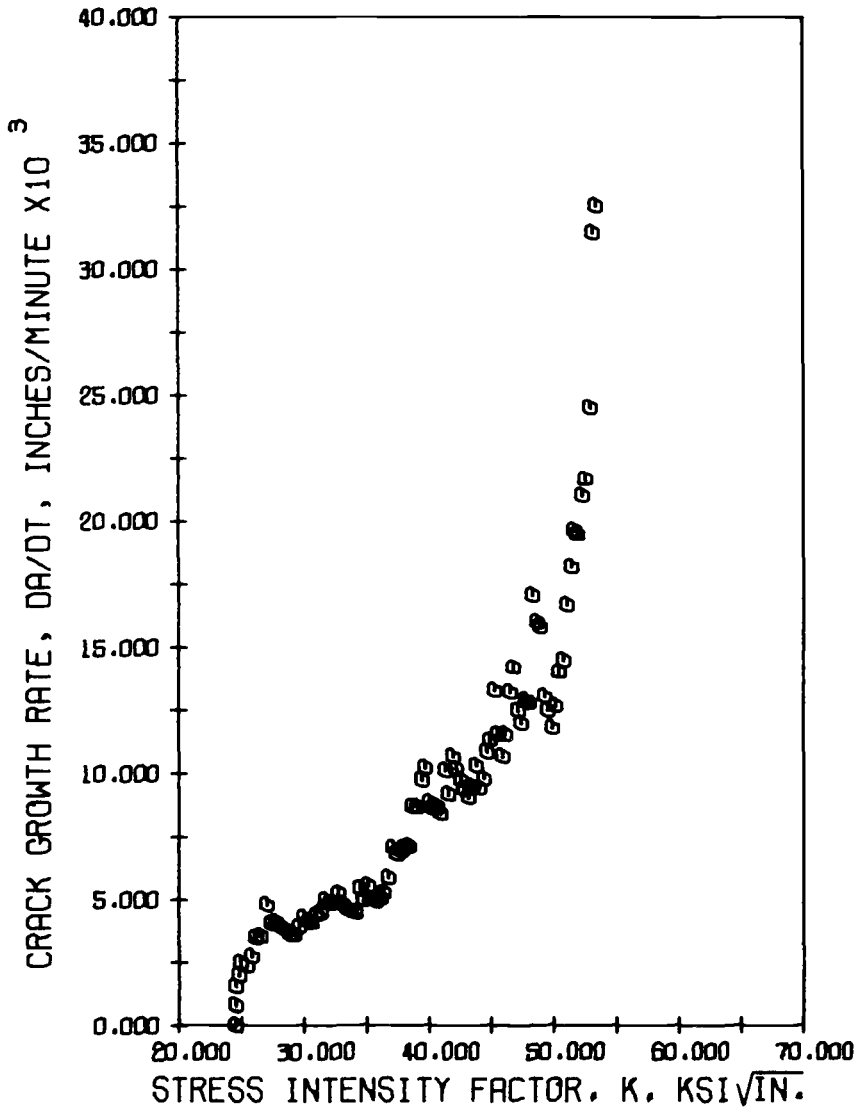


FIG. 9—Typical da/dt -K plot.

There is some evidence available which indicates that the crack growth rate in Stage II is controlled by mass transport rather than by reaction kinetics. In preliminary tests on two specimens with no side grooves and no coating masking the sides, polarized to -760 and -960 mV (versus SHE) in unbuffered 3.5 percent NaCl solution, the crack propagated more rapidly along the sides

of the specimens than in the interior, as shown in Fig. 10. The curvature of the stress corrosion crack front at the onset of rapid fracture (indicated by the arrows in Fig. 10) suggests that crack growth is mass transport-controlled.

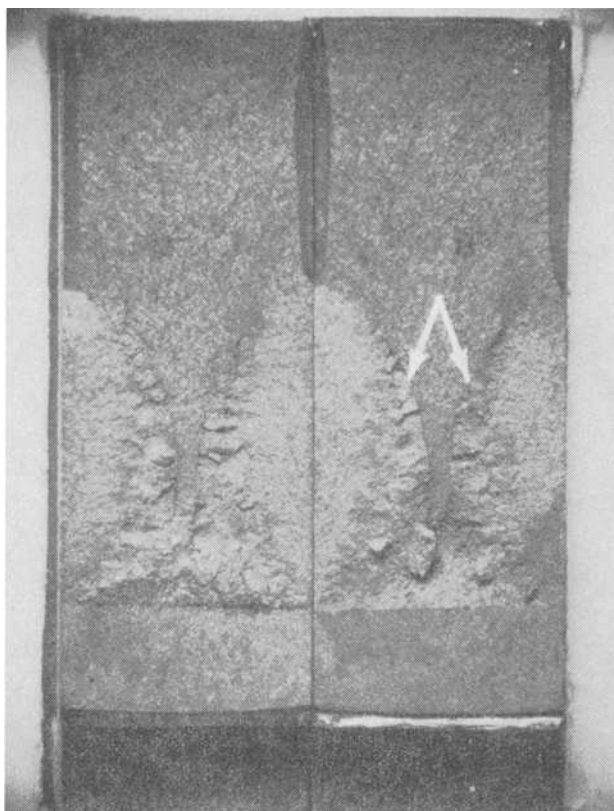


FIG. 10—*Fracture surface of specimen with no side grooves and no coating masking the sides, polarized to -960 mV (versus SHE) in unbuffered 3.5 percent NaCl solution.*

Mass transport-limited crack growth is apparently overridden by the mechanical factor in Stage III, where dA/dT increases rapidly with increasing K . Crack growth in this stage appears to be dominated by localized bursts of brittle rupture, as it is accompanied by audible acoustic emissions. Some of these bursts are quite large, as evidenced by the peaks preceding the onset of rapid fracture in Fig. 9. These bursts probably resulted from the local fracture toughness being exceeded at isolated locations along the path of the stress corrosion crack.

Secondary variations in dA/dT appeared in all of the dA/dT - K plots, indicating that crack growth proceeds irregularly. These variations may be due either to the inherently discontinuous nature of stress corrosion crack growth, or to secondary branching. The formation of nonpropagating branch cracks would temporarily increase the rate of crack opening displacement, and thus result in transitory increases in the apparent crack growth rate.

Reproducibility of dA/dT - K Curves

The stress corrosion test results are summarized in Table 2. The average dA/dT in the range $K = 30$ to 40 ksi $\sqrt{\text{in.}}$ is representative of the crack growth rate in Stage II which consists of a growth rate plateau. The K level at failure (rapid fracture) is equivalent to the fracture toughness of the metal, though the latter is measured more accurately under increasing load in accordance with the ASTM Test for Plane-Strain Fracture Toughness of Metallic Materials (E399-70T).

TABLE 2—Stress corrosion test results.

Specimen Number	Potential (vs. SHE), mV	Average Current mA	Avg. dA/dT from $K = 30$ to $K = 40$, in./min	K at Failure, ksi $\sqrt{\text{in.}}$
29	+240	18A ^a	0.0042	50
24	-110	3.0A	0.0055	55
25	-340	0.33A	0.0039	73 ^b
28	-340	0.50A	0.0037	52
26	-560	1.3C	0.0042	53
27	-560	1.3C	0.0032	57
21	-760	3.0C	0.011	54
23	-760	3.7C	0.0069	48

^aA indicates current was anodic;

C indicates current was cathodic.

^bApparent value.

The degree of reproducibility of the dA/dT - K curves can be determined by comparing the results for specimens tested at the same potential. With respect to the average dA/dT in the range $K = 30$ to 40 ksi $\sqrt{\text{in.}}$, the reproducibility is excellent for the two specimens tested at -340 mV (versus SHE), good for the two specimens tested at -560 mV, and only fair for the two specimens tested at -760 mV.

The reproducibility is generally poor for Stage III, partly because of the discontinuous nature of the brittle rupture bursts which characterize this stage, and partly because of the variation in the K level at failure.

With the exception of Specimen 25, the variation in K level at failure, 48 to 57 ksi $\sqrt{\text{in.}}$, is about the same as that normally found in fracture toughness values. In Specimen 25, at $K \sim 43$ ksi $\sqrt{\text{in.}}$, the crack began to branch on one side of the crack front, as indicated by the arrow in Fig. 11. This behavior reduced the actual K at the crack tip, so that the

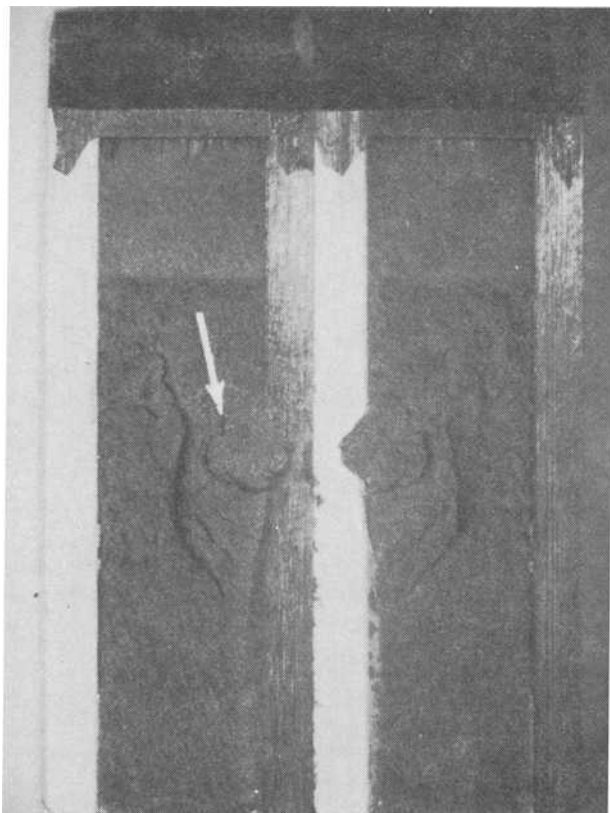


FIG. 11—Fracture surface of Specimen 25.

amount of slow crack growth was extended, and rapid fracture occurred at a higher apparent K level (73 ksi $\sqrt{\text{in.}}$)

Effect of Potential

The rest potential of the specimens in this corrodent was about -340 mV (versus SHE). (More positive potentials were anodic, whereas more negative potentials were cathodic.)

The electrode potential is a measure of the driving force for electrochemical reactions. Since stress corrosion cracking is governed, at least to some extent, by electrochemical reactions, the crack growth rate would be expected to vary with the applied potential. However, except at the very cathodic potential of -760 mV, the crack growth rate in Stage II was independent of potential, within the reproducibility of the dA/dT - K curves. This result implies that the electrochemical conditions at the tip of the stress corrosion crack are not the same as those outside the crack.

It has been recently observed that the electrochemical conditions (solution pH and electrode potential) at the tip of an advancing stress corrosion crack in AISI 4340 steel exposed to 0.6M NaCl solutions are favorable for hydrogen liberation regardless of the externally applied potential or the pH of the bulk solution [6]. Thus, in the present stress corrosion tests, as the potential was varied, the local pH at the crack tip apparently shifted to maintain the electrochemical equilibrium required for hydrogen liberation. However, the local potential at the crack tip also must have differed from the externally applied potential, since the potential of $+240$ mV is too anodic to permit electrochemical equilibrium favorable for hydrogen liberation. This difference in potential is attributed to the remoteness of the crack tip from the Luggin capillary probe. It has been experimentally demonstrated that a large potential gradient exists in crevices during potentiostatic anodic polarization [23]. This gradient is caused by the high resistance of the narrow electrolyte path. Thus, the local potential at the crack tip was not as anodic as the externally applied potential.

The crack growth rates at -760 mV are higher than those at the more electropositive potentials, which is probably indicative of increased hydrogen liberation.

The apparent shift in the crack tip pH as the potential is varied, despite a well buffered, agitated bulk solution, is indicative of the relative inaccessibility of the crack tip to the external solution. This inaccessibility is due to the geometry of a stress corrosion crack, and is undoubtedly enhanced by masking the sides of the specimen. The narrow cross section of the crack restricts mixing of the external solution with the microvolume of solution at the crack tip. This microvolume of solution is also likely to be buffered to its own pH level as a result of the electrochemical reactions occurring at the crack tip [6]. Thus variations in the chemistry of the bulk corrodent cannot be expected to affect the chemistry at the crack tip and hence, the crack growth rate.

Crack Branching

In stress corrosion tests on specimens without side grooves, the stress corrosion cracks began to branch into two diverging cracks after extending a short distance (~ 0.1 in.) beyond the fatigue precrack, at all potentials applied. Since it was not possible to obtain unambiguous crack growth rates

from the crack opening displacement measurements when the crack branched, side grooves were employed to maintain a single planar propagating crack. However, the side grooves were not effective in suppressing crack branching at very cathodic potentials (Fig. 12). As summarized in Table 3, deeper side

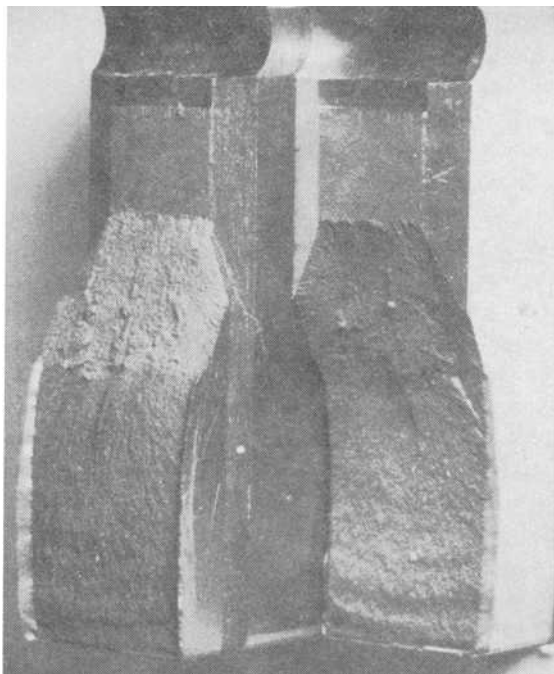


FIG. 12—Crack branching in specimen with 20 percent side grooves, polarized to -960 mV (versus SHE).

grooves were necessary to suppress branching as the potential was made more cathodic.

It has been proposed that two conditions are necessary for stress corrosion cracks to branch [13]:

1. The K level at the onset of branching must be at least twice K_{Isc} .
2. The crack growth rate must be constant.

These two requirements are based only on mechanical considerations. The high K level is required to provide sufficient force to drive two cracks, while the constant growth rate is needed so that one crack branch does not outrun the other. Both of these conditions were met in this study. However, the results indicate that tendency for crack branching is also electrochemically controlled, suggesting that this tendency is somehow related to the mechanism of stress corrosion cracking.

TABLE 3—*Effect of electrode potential on tendency for crack branching. S, crack grew straight. B, crack branched.*

Potential (vs. SHE), mV	Depth of Each Side Groove, % of Gross Specimen Thickness		
	0	10	20
anodic			
+680	...	S	...
+240	...	...	S
-110	...	S,S,S	S
-160	B,B	...	...
-260	B	...	...
-340	B,B	S	S,S
-560	...	...	S,S
-760	B	B,B	S,S
-960	B	...	B
cathodic			

Note: The specimens without side grooves were obtained from a different heat of 4340 steel.

Summary

Stress corrosion tests were conducted under well defined electrochemical and mechanical conditions on AISI 4340 steel (200-ksi yield strength level) in deaerated 3.5 percent sodium chloride solution buffered to pH 3.8. The results suggested that, at intermediate levels of stress intensity factor, stress corrosion crack growth is limited by mass transport, either in the metal or in the corrodent. At high levels of stress intensity factor, stress corrosion crack growth is apparently dominated by localized mechanical rupturing. The results also implied that the electrochemical conditions at the tip of the stress corrosion crack are not the same as those outside the crack. It was found that the tendency for the stress corrosion cracks to branch is electrochemically, as well as mechanically, controlled.

Acknowledgments

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Stress Corrosion Cracking of Copper Metals

REFERENCE: Thompson, D.H., "Stress Corrosion Cracking of Copper Metals," *Stress Corrosion Cracking of Metals—A State of the Art*, ASTM STP 518, American Society for Testing and Materials, 1972, pp. 39-57.

ABSTRACT: Four factors that cause stress corrosion cracking are sufficient stress, a suitable corrodent, a susceptible alloy, and time. The nature and sources of both applied and residual stress are discussed. The sources of residual stress that are peculiar to the brass industry are described. The copper (Cu) metals are listed in order of their relative susceptibility to stress corrosion cracking. Zinc (Zn) in Cu contributes to the probability of its cracking; nickel (Ni) in Cu metals tends to inhibit it. Stress corrosion cracking is not instantaneous, so time is a factor in its occurrence. Various methods for the prevention of stress corrosion cracking are discussed. Some examples of stress corrosion cracking in service are described. Probability is discussed in relation to its role of predicting the stress corrosion cracking of Cu metals. Testing of Cu metals for their resistance to stress corrosion cracking may employ loops or U-bends. Applied stress may be effected by dead weight loading or by the use of springs. Corrodents may be chemical solutions, natural environments (atmosphere, sea water) or exposure to service environments. The metallographic appearance of stress corrosion cracks in Cu alloys is described as are the crack paths in brass and in other metals.

Liquid metal embrittlement is similar to stress corrosion cracking but is thought not to be identical. The similarities and differences are discussed. Mercury (Hg) is used to test for the presence of residual stress in brass, however Hg is an extremely dangerous metal in contact with any Cu alloy. The possible sources of Hg are mentioned. A chiller which failed by Hg cracking is described. Other liquid metals may cause cracking of Cu alloys including low melting alloys which are used in tube bending.

KEY WORDS: stress corrosion cracking, copper alloys, external stresses, residual stresses, brasses, ammonia, embrittlement, failure, plastic deformation, transgranular corrosion, intergranular corrosion

Stress corrosion cracking (SCC) is a sudden catastrophic brittle failure, frequently of a ductile material, that is the result of the concomitant action of stress and corrosion. Copper (Cu) metals are subject to SCC as are most materials. Cu metals have the dubious honor of having been the first in which

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the phenomenon of SCC was recognized. The first mention in print was probably that of Sperry in *Brass World* in 1906 [1]. Although recent papers on SCC tend to be concerned with the newer metals – stainless steel or titanium (Ti) – papers on the SCC of Cu metals are still frequent. Neville Pugh of Illinois Institute of Technology has been co-author of at least five in the past five years [2-6]. Perhaps the outstanding paper on the subject was that of Moore, Beckinsale, and Mallinson [7] on “The Season Cracking of Brass and Other Copper Alloys” published in the *Journal of the Institute of Metals* in 1921. Much work has been done in the ensuing years but little has been learned about the practical aspects of the SCC of Cu metals since 1921; and since that classic paper contains no error of fact, it is still worthwhile to read.

Moore and his coworkers wrote of season cracking, a word used to describe the service failure of brass by SCC. One explanation of the source of this term is that during the British occupation of India, the officers observed that there was a rash of cracking failures of brass artillery shells during the monsoon season. The reason for this will be considered later.

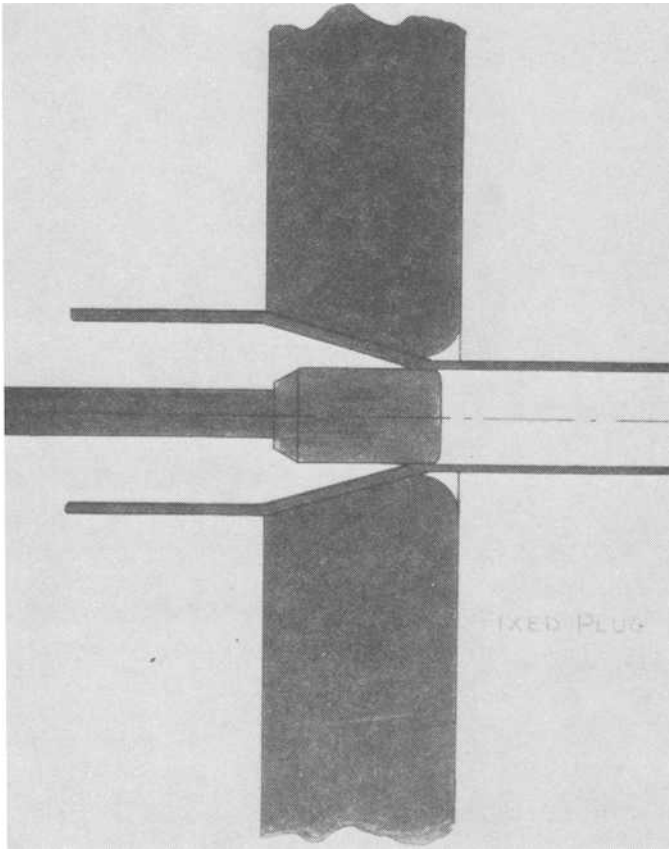
Factors in SCC

Four factors that control SCC are stress, corrodent, susceptibility of the metal, and time. High stress, the right corrodent, and a susceptible metal all increase the probability of SCC. They are causative, but time is a measure (a reciprocal one) of susceptibility. It is the dependent variable in the relationship.

Stress

Stress in copper metals is similar to that in other metals. However, there is applied, external, or what might be called “now” stress; hang a mass on a wire, calculate the force per unit area to get the stress – this is the “now” stress. This type is not a very important cause of SCC because structures are usually designed with full knowledge of the stresses, which are kept within reasonable bounds. The residual, or internal or what might be called “then” stress is caused by plastic deformation that was carried out in the past and from which the stress is a residual. Bend a piece of brass around a mandrel into a U-shape. The residual stress is minor. Hold the legs together and the residual stress is appreciable. Metal in the form of a closed curve may have this kind of stress; a loop, or bowl or tube may have great residual stress. Here are a couple of examples that might occur in the brass industry.

Seamless tubing is formed by cold drawing. Big tubes are made into little tubes by pulling them through a die, and simultaneously over a plug (Fig. 1). A reduction in the outside diameter, controlled by the size of the die, is known as “drop.” Reduction in the wall thickness controlled by the size of the annular space between the die and the plug is known as “pinch.” When a

FIG. 1—*Tube drawing.*

tube is sunk, that is, drawn through a die without a plug, the outside diameter is reduced but the wall thickness is not, and in fact may be increased (Fig. 2). It is all drop and no pinch. This tube will have enormous residual stress and other factors being favorable, will be highly subject to SCC. Figure 3 shows a tube that was sunk in this manner and was exposed to a cracking environment. The opposite obtains when the outside diameter is not reduced but the thickness is. This will produce a minimum amount of residual stress. It is all pinch and no drop. Occasionally tubes will be put into service in this condition, relying on the absence of residual stress to avoid stress corrosion cracking.

One item that is frequently made of brass is screw shells such as are used in sockets, plug fuses, or lamp bases. Not only are these deep drawn so as to produce a hoop stress but they have a thread rolled into them as well. Cold drawn rods may have high residual stress. A small wire that is drawn so that it is cold worked throughout its cross section probably has little stress, but a

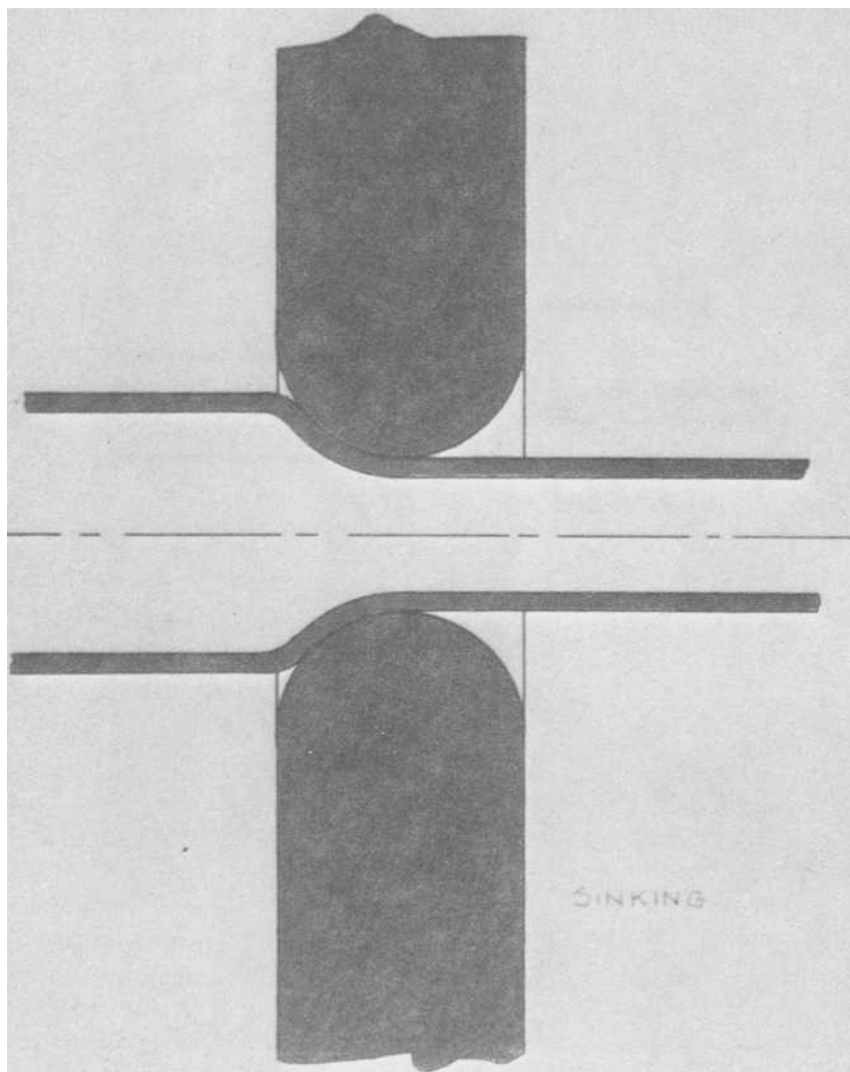


FIG. 2—*Tube sinking.*

large rod that has been worked on the outside but not at the center will have high residual stresses that may split it longitudinally. Figure 4 shows a hex rod that was cracked in an ammonia atmosphere.

Corrodents

The corrodents that will crack Cu metals are different from those that crack other metals. Before discussing them it is important to draw the

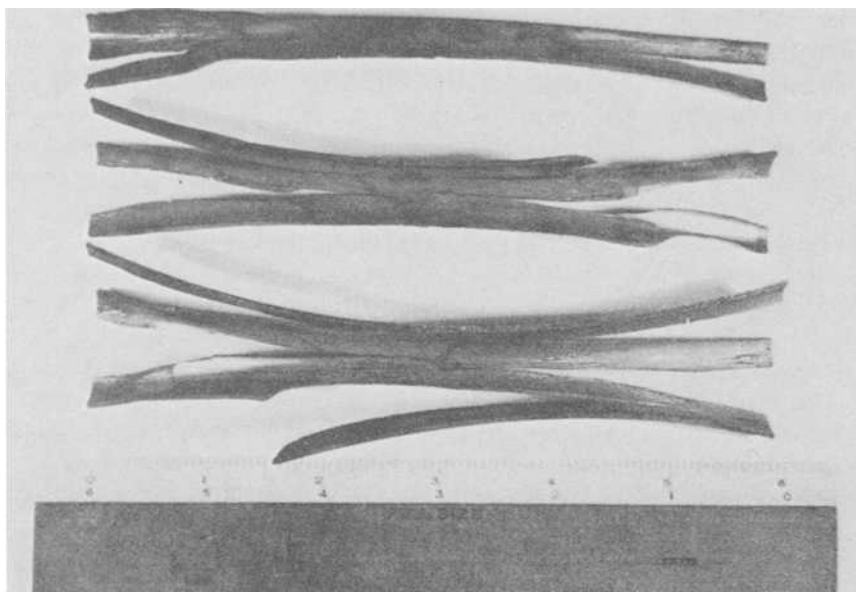


FIG. 3—Cracked tube that had been sunk.

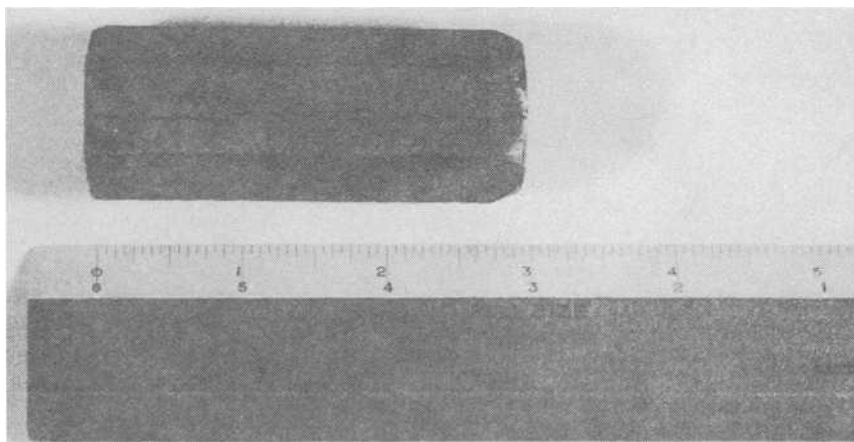


FIG. 4—Hex rod cracked in NH_3 .

distinction between SCC and liquid metal embrittlement. They are similar in many respects but different in many others. Since to discuss them together would hopelessly confuse them, mention of liquid metal embrittlement will be deferred until later. There have been claims that many corrodents will cause the SCC of Cu metals. I shall include in this discussion only those that I have

personally used to crack brass in the laboratory. Far and away the most important one is ammonia (NH_3). NH_3 is unique because it does not cause cracking in any other metal system; the NH_4^+ ion appears not to cause cracking in a stable salt such as $(\text{NH}_4)_2\text{SO}_4$. In a salt in which it disassociates, like $(\text{NH}_4)_2\text{CO}_3$ to form NH_3 , cracking will occur. Pugh considers $\text{Cu}(\text{NH}_3)_x^{++}$ ion is needed for the SCC of Cu metals. X is usually four or five. NH_2 groups also cause cracking or are easily converted to NH_3 . Amines and sulfamic acid both cause cracking. Dry NH_3 will not cause SCC of brass. This was abundantly demonstrated by the one-time successful use of brass valves and gauges on tanks of anhydrous NH_3 . It is probably true that the SCC of Cu metals will not occur in the absence of oxygen (O_2) or an oxidizing agent. It has been stated [9] that carbon dioxide (CO_2) is also a requisite. Thus air rather than O_2 is necessary. Practically, moisture is of the utmost importance. When other factors are favorable, a very small amount of NH_3 (present almost anywhere) is sufficient to cause cracking. Hence the controlling factor may be moisture and cracking may appear to be caused by the presence of a condensed moisture film. Other than NH_3 the most effective agents causing cracking are the fumes from nitric acid or moist nitrogen dioxide. Sulfur dioxide will also crack brass but there are both maximum and minimum concentration limits that must be exceeded and the action is slow in any event.

Resistance of Cu Metals to SCC

There is not enough information on the relative resistance of the many Cu alloys to SCC. Experience tells us that Cu and cupro nickel (Cu-Ni) are highly resistant to cracking (if not immune) and that brass is not very resistant, especially if it contains 30 to 40 percent zinc (Zn). Many alloys were tested by a rather simple laboratory loop test. The results are shown in Table 1 [6]. Whereas the relative positions of these alloys can hardly be taken as established fact in this or any other environment, the ranking is in general similar to what can be expected in service, and provides a guide in the choice of an alloy for a specific application.

Figure 5 shows the time to 50 percent relaxation (a measure of resistance to cracking) plotted against the Zn content of Cu-Zn alloys. Obviously the resistance is rapidly reduced with increasing Zn content. Alloys containing Cu, Zn, and a third element are spotted on the figure indicating the beneficial effect of nickel (Ni) and probably of lead (Pb).

Pure metals are said to be immune to SCC and this is true of Cu in the practical sense. Pugh [4] has, however, cracked 99.999 percent Cu in the laboratory. (Uhligh and Duquette [11] maintain that what Pugh observed was not, in fact, SCC). DHP Alloy 122, which contains 0.015 to 0.040 percent phosphorus (P), is not immune to SCC. Under an applied load in the laboratory it can be cracked rather readily. In service, where residual stress is usually not high because of the tendency of the metal to creep, cracking is rare but not unknown. Of all the millions of pounds of hard drawn DHP Cu

water tube in service, there has been one well authenticated instance of SCC. unknown. Of all the millions of pounds of hard drawn DHP Cu water tube in service, there has been one well authenticated instance of SCC.

Time

The fourth factor involved in SCC, the one which is a measure of resistance, is time. SCC may occur in as little as a few minutes in an accelerated laboratory test or it may take years. Specimens have cracked after exposures of ten years in controlled tests.

Prevention of SCC

The prevention of SCC depends on control of the causative factors. These factors are stress, corrodent, and susceptible metal. The corrodent may be divided into three parts – NH_3 , O_2 and moisture, thus giving five essential factors – stress, susceptible material, NH_3 , O_2 , and moisture. If any of these is completely absent, SCC will not take place. One obvious method of preventing SCC is to shield the metal from the corrodent. This is frequently not successful. Antique car buffs and old timers may remember that long ago automobile headlights had Ni plated brass rims that season cracked despite the Ni plate. Occasionally one sees a chrome plated cocktail shaker that has cracked although it was plated with chromium, presumably over Ni. It may be more effective to keep susceptible materials away from concentrations of NH_3 and particularly of moisture. Heating of warehouses to prevent thermal cycling and consequent moisture condensation may be required. Desiccated packaging is also effective. The case of the cracked cartridge cases during the monsoon season, the wet season, is an example.

Relief of residual stress by annealing is probably the most common way of avoiding SCC. Residual stress in metal will be completely relieved by a recrystallizing anneal. A relief anneal at just the right temperature, for just the right length of time, will relieve stresses but will not soften the metal. This is tricky and very difficult to do on a production basis; also it does not relieve all the stresses. Nevertheless this is a not uncommon procedure. Brass screw shells are always subjected to a relief anneal. Of course there are cases where relief annealing is impossible. A cartridge case is loaded with propellant and is finally crimped around the bullet. Relief of stresses by annealing is out of the question. The other common method of avoiding SCC is by alloy selection. If cartridge brass (70 percent Cu – 30 percent Zn) cracks, substitute red brass (85 percent Cu – 15 percent Zn). If red brass cracks, substitute copper. If an admiralty condenser tube (79 percent Cu – 29 percent Zn – 1 percent Sn) cracks substitute Cu-Ni. Unfortunately, the better material is always more expensive.

Examples of SCC

Instances of SCC that have occurred in service are not uncommon. Several

655	Silicon Bronze (A)	354.0	...	...	...	...	...	3.10	1.10	...
110	Tough Pitch Copper	>2000.0 ^b	...	...	...	...	...	...	...	...
715	Cupro Nickel, 30 percent	>2000.0 ^b	...	...	...	...	...	30.00	0.60	0.50 Fe

^aBalance copper.

^bNo relaxation at end of 2000 h.

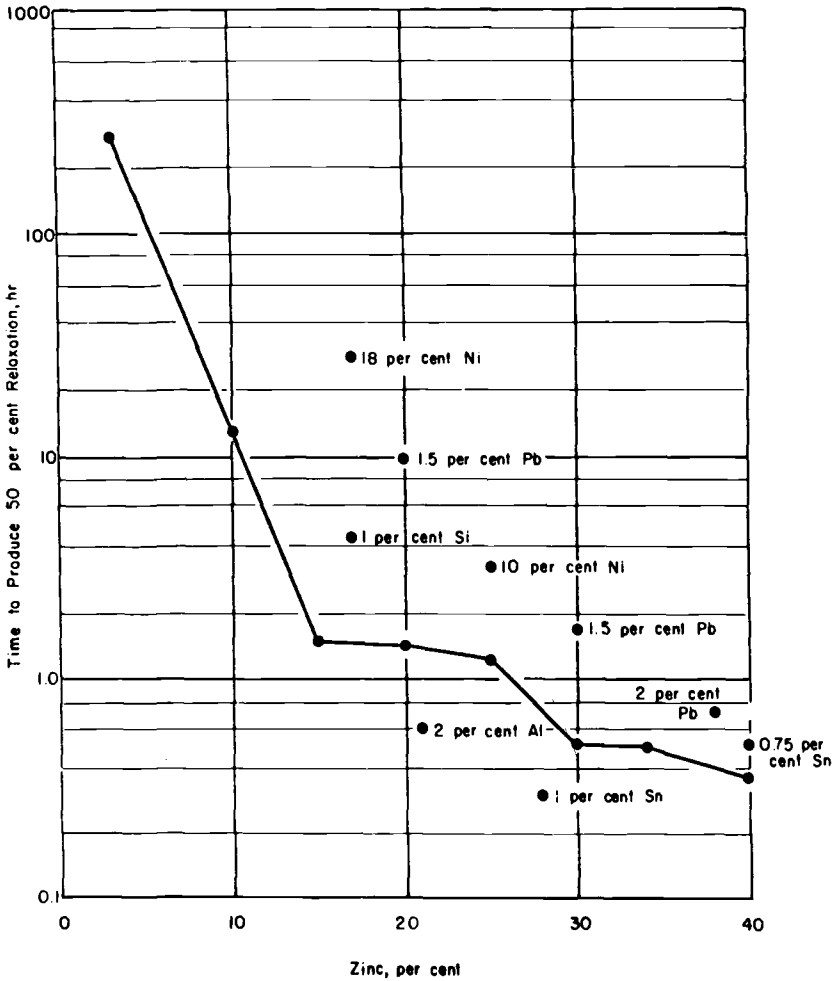


FIG. 5—Stress corrosion cracking of Cu-Zn alloys.

cases occur each year but the discussion will be limited to those cases that have something informative about them. One that happened a good many years ago involved the brass screw shells that have been mentioned. It was then the practice to form the shells in one building and then to truck them to another building where they were relief annealed in a muffle furnace. Production on Friday afternoon might have to wait until Monday morning to be annealed. This normally caused no problem, but one Monday morning it was discovered that thousands of the shells had cracked over the weekend. The explanation was that in being trucked from one building to another the shells had to go outdoors. It was a cold New England winter so the shells were chilled. The second building was warm and it was moist because of pickling and cleaning operations. A film of moisture was thus condensed on

each shell. The factors were there — high residual stress, a susceptible metal, air, moisture, everything except NH_3 . It did not take much of the latter to cause the damage.

In another instance aluminum (Al) bronze welding wires were layer wound on spools, with appreciable stress. The wires had been given some cold work to make them stiff enough to be pushed through the welding gun. The spools of wire were stored in an unheated storehouse. Again it is reasoned that temperature changes caused moisture condensation that initiated the extensive damage that ensued. The spools looked like old straw hats, with broken wire ends sticking out in all directions.

Another example that was quite different involved a hard drawn Cu water tube that went under the boardwalk in Atlantic City from the Convention Hall to a beachside lavatory. The line was lagged with animal hair felt. This became damp, the protein decomposed with the formation of NH_3 resulting in a unique failure of copper water tube.

Another similar case occurred in a hospital in Poughkeepsie, New York. The water lines were hard drawn red brass pipe. The cold water lines were also lagged with animal hair felt and decomposition resulted in extensive cracking, much like the Atlantic City case.

Probability of SCC

A probabilistic approach to this subject makes sense. If the probability of the existence of the several factors is high, the probability of rapid failure is then high. If one of the factors has a low probability, this may be offset by a high probability of another factor. Expressed mathematically:

$$P_c = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{O}} \cdot P_{\text{O}_2} \cdot P_\sigma \cdot P_{\text{alloy}}$$

where

$$\begin{aligned} P_c &= \text{probability of rapid cracking,} \\ P_{\text{NH}_3} &= \text{probability of high } \text{NH}_3 \text{ concentration,} \\ P_{\text{H}_2\text{O}} &= \text{probability of the presence of moisture,} \\ P_{\text{O}_2} &= \text{probability of adequate } \text{O}_2, \\ P_\sigma &= \text{probability of a high stress, and} \\ P_{\text{alloy}} &= \text{probability of a susceptible alloy} \end{aligned}$$

In the case of the Cu water tube, P_σ was low but other probabilities were high and cracking occurred. In the case of the screw shells, NH_3 was low but the other factors overcame that and cracking occurred rapidly and liberally.

Test Methods

There are many test methods for assessing the resistance (or susceptibility)

of Cu metals to SCC. Essentially they consist in subjecting the metal to all the factors that cause SCC. To accelerate the test so that it can be accomplished in a finite time, the factors have to be made as severe as possible — just varying the one that is under study. A simple test is shown in Fig. 6. The

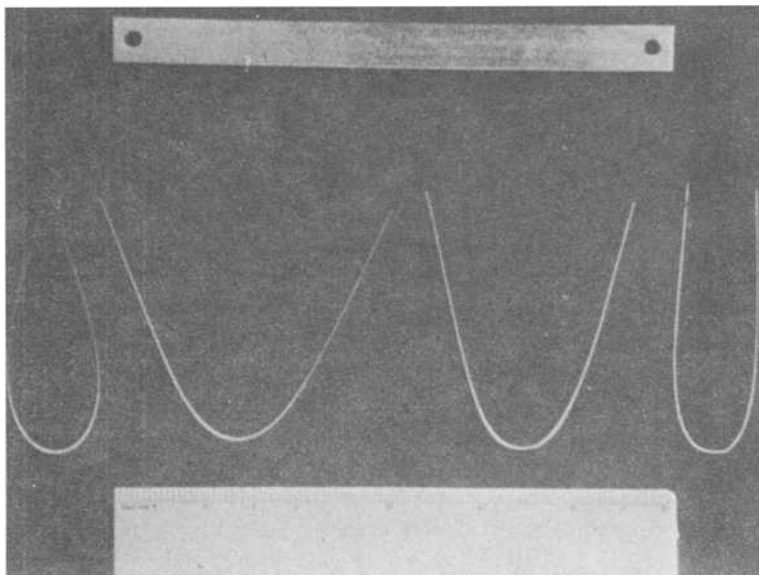


FIG. 6—*The loop test for stress corrosion cracking specimens.*

straight specimen at the top is bent into a loop and held by a twist of Cu wire as shown at the left. If the ends are released they spring out to the form shown next on the right. Now if the restrained metal loop is exposed to a severe corrodent, and again the ends are released, it collapses as shown in the next photograph. Finally a longer exposure causes further collapse. In this case the metal was 70-30 brass and the corrodent was moist NH_3 atmosphere such as is formed if a quantity of concentrated ammonium hydroxide (NH_4OH) is placed in the bottom of a closed container. Figure 7 shows two loops — one of 70-30 brass and one of 70-30 Cu-Ni. NH_4OH was admitted to the jar and 20 minutes later Fig. 8 was taken. The brass has cracked; the Cu-Ni has not. Such a test is simple, quick, and cheap. It will measure the relative resistances of different alloys to SCC; will show the effect of heat treatment or of corrodent, or measures taken to reduce the incidence of SCC. Since the stress is unknown and essentially unknowable, it will not relate SCC to stress and as in such specimens the stress is a function of the strength, it will not show the relation between metal strength and SCC. To do this, applied loads must be used. Figure 9 shows a device for applying a tensile

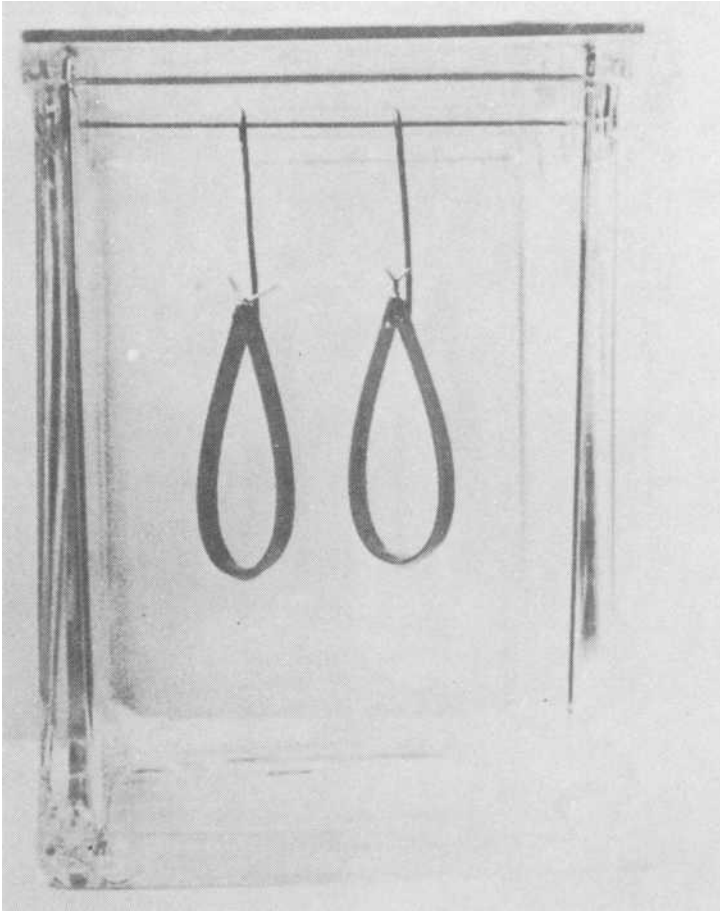


FIG. 7—*The loop test for stress corrosion cracking—start.*

load to a small brass specimen by the use of a spring. The lower part of this unit would be immersed in either a liquid or gaseous NH_3 environment. Failure of the specimen will cut off the current to an electrically operated timer.

Little has been done or at least described in the literature, on the SCC of Cu metals in any specific environment other than those deliberately obtainable in the laboratory. One such environment is natural outdoor atmosphere. Mattsson et al [10] exposed 63-37 brass cups to both accelerated laboratory environments and to:

1. bold and sheltered outdoor urban atmosphere in Sweden,
2. bold and sheltered outdoor rural atmosphere in Sweden,

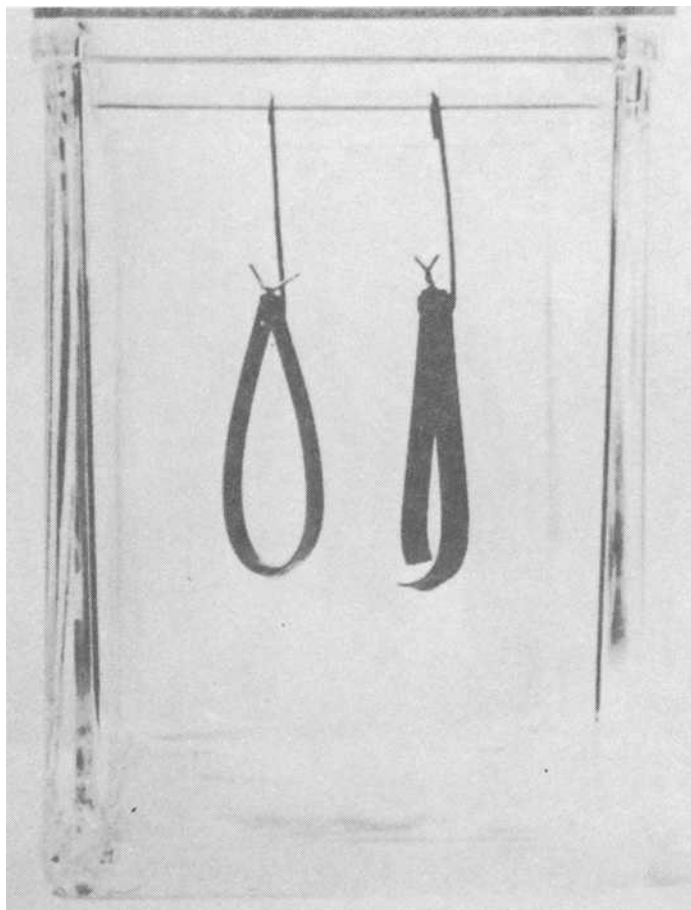


FIG. 8—*The loop test for stress corrosion cracking—after a failure.*

3. bold and sheltered outdoor marine atmosphere in Sweden, and
4. heated and unheated indoor storage.

Exposures were for up to 61 months. The type of atmosphere was as variant as was the temperature at which the cups were annealed following drawing, but only one alloy was included. An atmospheric test was carried out at the Research and Technical Center of the Anaconda American Brass Co. Loops like those described above were made from 19 different Cu alloys and were exposed outdoors in Waterbury, Conn. under bold and sheltered conditions. After ten years there were relatively few failures. The following alloys cracked at the bold exposure site: Muntz Metal 280, Phosphor Bronze (A) 510, Arsenical Admiralty 443, Naval Brass 464, Nickel Silver 18 percent 752, Ambraloy 687 (Arsenical aluminum brass). Only the admiralty, naval brass,

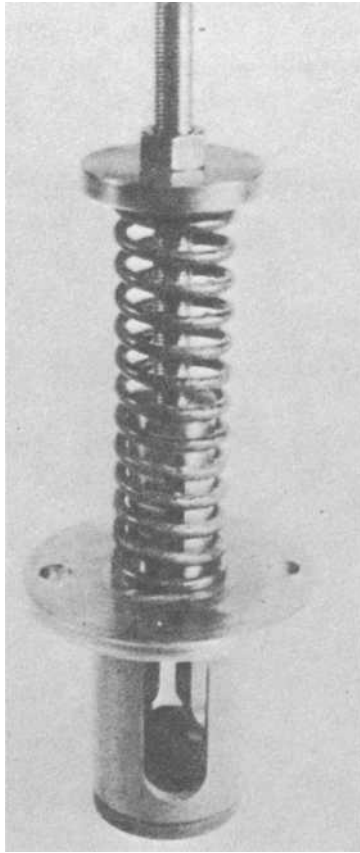


FIG. 9—*Spring loaded stressing device for stress corrosion cracking.*

nickel silver cracked in the sheltered location. These results correlate fairly well with the result of accelerated tests except for the phosphor bronze and nickel silver which would be expected to have better stress corrosion resistance than, say, Cartridge Brass 260. The point of this discussion is that although a number of laboratory tests on the SCC of Cu metals has been described, correlation of these accelerated tests with exposure to any natural environment has been minimal.

Crack Paths

The paths of stress corrosion cracks in Cu metals may be intergranular or transgranular. Usually cracks in brass are intergranular although changes in cold working or the chemistry of the corrodent may effect a change to transgranular cracking. From a practical standpoint a notable exception is the

characteristic behavior of admiralty and aluminum brass. These common condenser tube alloys are essentially brasses to which have been added tin (Sn) in one case and Al in the other. Cracking failures of these alloys seem always to be transgranular. Figure 10 shows a photomicrograph (X500) of

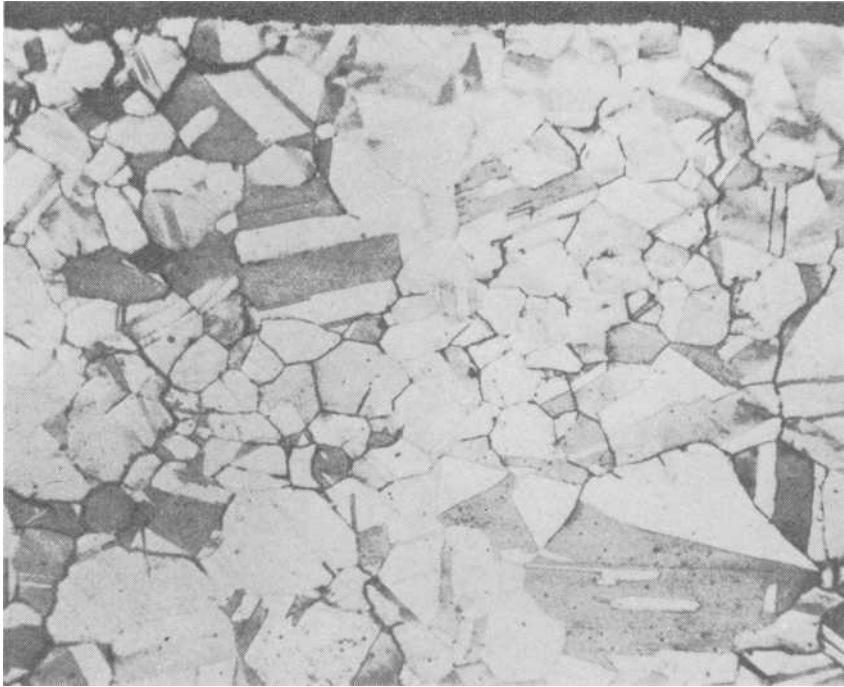


FIG. 10—*Intergranular cracking of brass (X500).*

70-30 brass that was cracked in service; the cracks are intergranular. Figure 11 is a similar picture of arsenical admiralty; the cracks are strikingly transgranular. Aside from theoretical interest this difference in crack paths is of practical importance. There is some tendency to interpret intergranular cracks in brass as being stress corrosion cracks and transgranular cracks as being fatigue cracks, when trying to assess the cause of a service failure. This will lead to a false conclusion that admiralty and aluminum brass always fail by fatigue. These alloys are quite susceptible to SCC; identification of the cause of the service failure cannot be based on an observation of crack paths alone.

NH₃ and Hg

Most SCC failures are ascribed to the action of NH₃, even when very little NH₃ is present in the environment that caused cracking. When examining metals that have failed by SCC, the absence of NH₃ among the corrosion

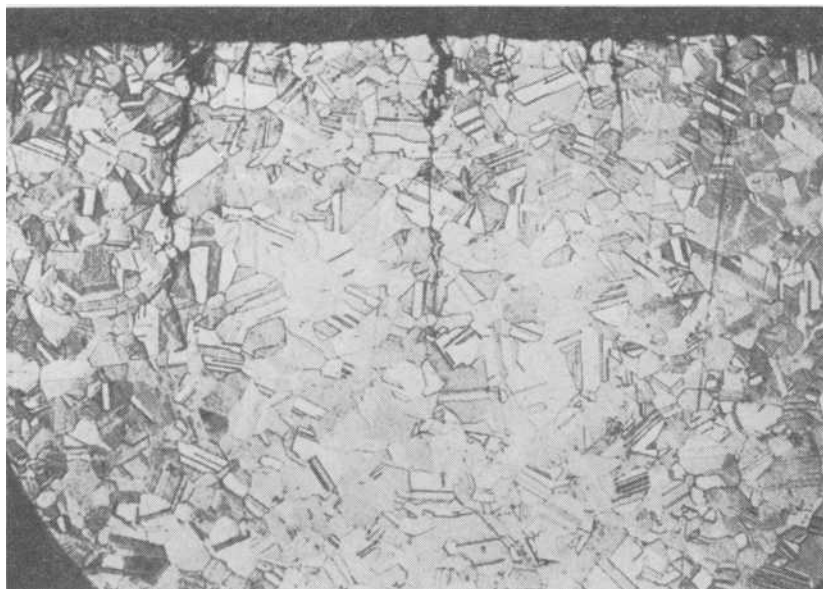


FIG. 11—*Transgranular cracks in admiralty (X500).*

products is not proof that it was not, in fact, the guilty corrodent, for ammonia salts tend to be fugacious and have fled before analysis has a chance to detect them. Mercury (Hg) on the other hand forms a stable amalgam on the metal surface. Failures that are caused by Hg are always identifiable. For these reasons it is believed that most failures are caused by NH_3 unless Hg is found among the corrosion products. Both NH_3 and Hg cause stress cracking but it is desirable to differentiate between them. Call the NH_3 cracking SCC and the Hg cracking liquid metal embrittlement. Hg is used in ASTM Mercurous Nitrate Tests for Copper and Copper Alloys (B154-71). The test consists in immersing the specimens to be tested in an acid solution of mercurous nitrate (HgNO_3) for a definite period. Hg plates out on the surface of the copper metal and liquid metal embrittlement then proceeds. This test is "for the purpose of detecting in copper or copper base alloy products the presence of residual (or internal) stresses that might bring about the failure of the material in service or storage through stress corrosion cracking." Figure 12 shows the results of a HgNO_3 test on the hex rod that was shown in Fig. 4. Note that the HgNO_3 test is not one for assessing the susceptibility of metals to SCC but its purpose is the detection of stresses that might cause SCC. Confusion on this point has led to the improper use of the HgNO_3 test for measuring the susceptibility of a metal to SCC. Actually metals display drastic differences in their reactions to NH_3 and Hg. Stressed 70-30 brass will crack readily in solutions of either NH_3 or mercurous salts, but Cu-Ni, which verges

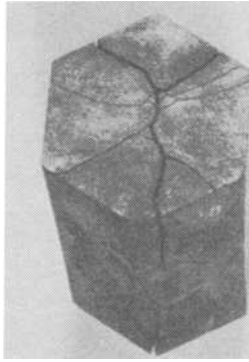


FIG. 12—Hex rod cracked in Hg.

on immunity to SCC, will, under some circumstances, crack when immersed in HgNO_3 solution. It follows that susceptibility to Hg cracking is not evidence of susceptibility to SCC. Hg should be kept away from Cu metals (particularly brasses under stress) in any and all circumstances. This brings to mind another failure that was the result of a lack of appreciation of the facts, a failure that was very expensive. A small brass heat exchanger had been manufactured. It was vacuum tested using a Hg manometer to check the vacuum. A slug of Hg was accidentally allowed to enter the heat exchanger. This was known and the heat exchanger was opened and the Hg was cleaned out, presumably perfectly. The heat exchanger was one of four that were used as chillers in the air conditioning of a submarine. It was installed outboard of the keel on the lowest deck. After the vessel was completed and launched, the system was pressure tested and it was found that the chiller leaked. The only way to remove the chiller was to cut holes through every deck from the top of the submarine to the bottom, remove and replace the chiller, and to repair weld all the decks. The chiller was, of course, the victim of liquid metal embrittlement from Hg. The dire warning is never trust Hg in contact with any Cu metal. Avoid the use of Hg-containing instruments in testing Cu-metal structures.

Other liquid metals are less important causes of failure than Hg. Low melting alloys used for filling tubes that are to be bent may cause embrittlement of the tubes. Bending causes residual stresses. Heating with a torch to liquefy the metal may cause a cracking failure. Cu-Ni tubes have been inadvertently cracked in this manner.

Summary

To summarize:

1. SCC is caused by the simultaneous action of stress and corrosion.
2. Stress may be residual or applied ("then" or "now" stresses).

3. The commonest corrodent is NH_3 with water vapor and air.
4. Resistance of Cu metals is as follows:
 - a. *Low Resistance*: (1) brass containing over 20 percent Zn, and (2) brass containing over 20 percent Zn and small amounts of Pb, Sn, or Al such as leaded brass, naval brass, admiralty, or aluminum brass.
 - b. *Intermediate Resistance*: brasses containing less than 20 percent Zn, such as red brass, commercial bronze, and gilding; aluminum bronze, nickel silver, or phosphor bronze.
 - c. *High Resistance*: silicon bronze, phosphorized copper.
 - d. *Very High Resistance*: cupro nickel and tough pitch copper.

Prevention may be achieved by denying to the metal any of the factors that cause SCC. Most commonly this is done by annealing or by alloy selection. Liquid metal embrittlement is similar to stress corrosion, but it is not identical.

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Stress Corrosion Cracking Behavior of Nickel and Nickel Alloys

REFERENCE: Boyd, W.K. and Berry, W.E., "Stress Corrosion Cracking Behavior of Nickel and Nickel Alloys," *Stress Corrosion Cracking of Metals—A State of the Art*, ASTM STP 518, American Society for Testing and Materials, 1972, pp. 58-78.

ABSTRACT: This paper presents a discussion of the susceptibility to stress corrosion cracking of nickel and alloys containing substantial additions of nickel. The occurrence of cracking in various environments such as chloride solutions and salt environments, hydrofluoric and hydrofluorosilicic acid, high temperature water and steam, caustic solution, mercury, mercuric salts and liquid metal embrittlement are discussed. Also discussed are the mechanism of stress corrosion cracking and the prevention of stress corrosion cracking in nickel alloys.

KEY WORDS: stress corrosion cracking, nickel, nickel alloys, failure, hydrofluoric acid, transgranular corrosion, intergranular corrosion, boilers, sea water, chemical cleaning, steam, alkalies

One important class of materials for both high temperature and corrosion service is the family of alloys containing appreciable amounts of nickel. The literature contains considerable evidence to show that as the nickel content is increased, particularly for alloys containing iron-chromium-nickel, susceptibility to stress corrosion cracking markedly decreases. The well known curve of Copson [1] relating the cracking time in 42 percent magnesium chloride as a function of nickel content is shown in Fig. 1.

As the nickel content of the alloys is increased to 25 percent and above, time to failure is markedly increased. At about 45 percent nickel, the alloys do not crack in the commonly used boiling 42 percent magnesium chloride test solution. However, this is not to say that nickel-base alloys, *per se*, do not suffer from stress corrosion cracking. In fact, over the years, a number of environments have been identified as promoting cracking of nickel and nickel

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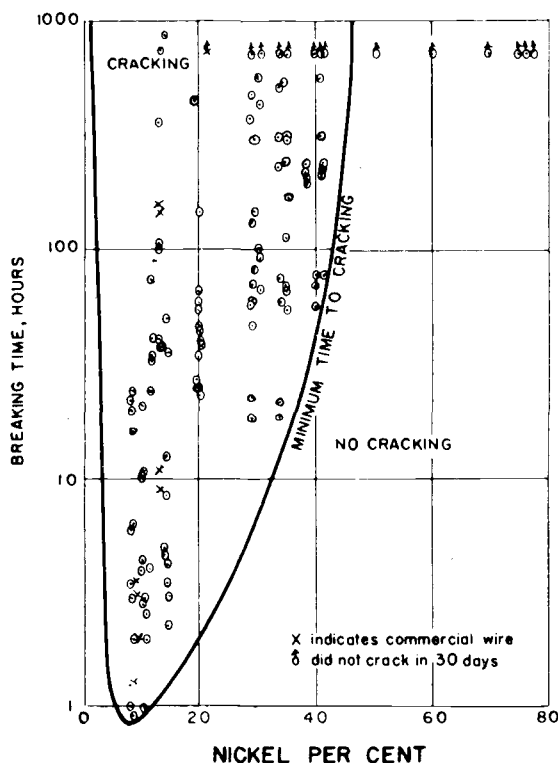


FIG. 1—Breaking time of iron-nickel-chromium wires in boiling 42 percent magnesium chloride [1].

base alloys. Some of the first incidents of stress corrosion cracking of nickel and high nickel alloys were encountered in high temperature caustic soda and caustic potash solutions and in molten caustic where they are the preferred material of construction. Cracking of certain nickel-copper, nickel-chromium-iron, and nickel-chromium-molybdenum-iron alloys has been observed under somewhat special conditions in fluorosilicic acid, hydrofluoric acid and mercury and mercuric salt solutions. More recently evidences of cracking have occurred in high temperature salt solutions, and in high temperature water and steam, contaminated with trace amounts of oxygen, lead, fluorides, or chlorides or both. A form of embrittlement akin to stress corrosion cracking, at least in part, is exhibited by some sensitized nickel base alloys upon contact with chromic acid solutions and polythionic acids.

The mode of fracture in nickel base alloys is predominately intergranular. The exceptions seem to be the cracking of cold-worked nickel-copper alloys in hydrofluoric acid and those occurring in Incoloy 800 and related alloys containing less than 40 to 50 percent nickel when exposed to boiling 42 percent MgCl_2 . High temperature, high purity water contaminated with lead

salts may also induce transgranular working of Inconel 600. Photomicrographs of typical stress corrosion cracks for several alloys are shown in Figs. 2 and 3.



FIG. 2—Intergranular stress corrosion cracking of Monel 400 in steam ($\times 100$).

This paper presents a discussion of the susceptibility to stress corrosion cracking of nickel and alloys containing substantial additions of nickel. Typical alloy compositions are shown in Table 1. Since stainless steels and similar alloys containing lesser amounts of nickel are the subject of other papers in this series, their behavior is only referred to in this paper to illustrate more clearly the behavior of the high nickel alloys.

Occurrence of Cracking of Nickel Alloys in Various Environments

Chloride Solutions and Salt Environments

The results of a series of studies to determine the stress corrosion cracking



FIG. 3—*Intergranular stress corrosion cracking of Inconel 600 in high temperature water (X 70).*

behavior of binary iron-nickel alloys in caustic and chloride solutions was reported by Copson [1]. The alloys contained from 0 to 100 percent nickel and were exposed as U-bend specimens to two environments; namely boiling 33 percent sodium hydroxide containing 0.13 percent lead oxide and 0.13 percent sodium chloride; and boiling 42 percent magnesium chloride.

After a 14 day exposure period, the cracks were clearly visible in the 5 and 9 percent nickel irons, whereas metallographic examinations were required to reveal cracks in the 0 percent and 2 percent alloys. No cracks were found in either pure nickel or the 28 percent nickel-iron alloy. Similar type results as to the effect of nickel content were observed in the boiling 42 percent magnesium-chloride environment. Cracks were found in the 2 percent, 5 percent, and 9 percent nickel irons with the 9 percent nickel alloy being the most severely cracked. No evidence of stress corrosion cracking occurred for the 0 percent, 28 percent, 42 percent, and 100 percent nickel alloys.

TABLE 1—Nominal chemical composition of typical commercial nickel and nickel base alloys.^a

Designation	Ni	C	Mn	Fe	S	Si	Cu	Cr	Al	Ti	Others
Nickel 200	99.5 ^b	0.08	0.18	0.2	0.005	0.18	0.13	...	...	...	...
Nickel 201	99.5 ^b	0.01	0.18	0.2	0.005	0.18	0.13	...	...	...	...
Nickel 205	99.5 ^b	0.08	0.18	0.10	0.004	0.08	0.08	...	...	0.03	Mg 0.05
Nickel 211	95.0 ^b	0.10	4.75	0.38	0.008	0.08	0.13	...	...	...	...
Nickel 220	99.5 ^b	0.04	0.10	0.05	0.004	0.03	0.05	...	...	0.03	Mg 0.05
Nickel 230	99.5 ^b	0.05	0.08	0.05	0.004	0.02	0.05	...	...	0.003	Mg 0.06
Nickel 270	99.98	0.01	<0.001	0.003	<0.001	<0.001	<0.001	<0.001	...	<0.001	Co <0.001
											Mg <0.001
DURANICKEL Alloy 301	96.5 ^b	0.15	0.25	0.30	0.005	0.5	0.13	...	4.38	0.63	...
PERMANICKEL Alloy 300	98.5 ^b	0.20	0.25	0.30	0.005	0.18	0.13	...	...	0.40	Mg 0.35
MONEL Alloy 400	66.5 ^b	0.15	1.0	1.25	0.012	0.25	31.5	...	...	...	...
MONEL Alloy 404	54.5 ^b	0.08	0.05	0.25	0.012	0.05	44.0	...	0.03	...	...
MONEL Alloy R-405	66.5 ^b	0.15	1.0	1.25	0.043	0.25	31.5	...	...	...	...
MONEL Alloy K-500	66.5 ^b	0.13	0.75	1.00	0.005	0.25	29.5	...	2.73	0.60	...
MONEL Alloy 502	66.5 ^b	0.05	0.75	1.00	0.005	0.25	28.0	...	3.00	0.25	...
MONEL Alloy 401	42.5 ^b	0.05	1.6	0.38	0.008	0.13	Bal.	...	...	...	...
INCONEL Alloy 600	76.0 ^b	0.08	0.5	8.00	0.008	0.25	0.25	15.5	...	...	...
INCONEL Alloy 601	60.5	0.05	0.5	14.1	0.007	0.25	0.50	23.0	1.35	...	...
INCONEL Alloy 625	61.0 ^b	0.05	0.25	2.5	0.008	0.25	...	21.5	0.2	0.02	Mo 9.0 Cb + Ta 3.65
INCONEL Alloy 702	79.5 ^b	0.05	0.50	1.0	0.005	0.35	0.25	15.5	3.25	0.63	...
INCONEL Alloy 706	41.5	0.03	0.18	40.0	0.008	0.18	0.15	16.0	0.20	1.75	Cb + Ta 2.9
INCONEL Alloy 718	52.5	0.04	0.18	18.5	0.008	0.18	0.15	19.0	0.50	0.90	Mo 3.05 Cb + Ta 5.13
INCONEL Alloy 721	71.0 ^b	0.04	2.25	6.5	0.005	0.08	0.10	16.0	...	3.05	...
INCONEL Alloy 722	75.0 ^b	0.04	0.50	7.0	0.005	0.35	0.25	15.5	0.70	2.38	...
INCONEL Alloy X-750	73.0 ^b	0.04	0.50	7.00	0.005	0.25	0.25	15.5	0.70	2.50	Cb + Ta 0.95
INCONEL Alloy 751	72.5 ^b	0.05	0.5	7.00	0.005	0.25	0.25	15.5	1.20	2.30	Cb + Ta 0.95

INCOLOY Alloy 800	32.5	0.05	0.75	46.0	0.008	0.50	0.38	21.0	0.38	0.38	...
INCOLOY Alloy 801	32.0	0.05	0.75	44.5	0.008	0.50	0.25	20.5	...	1.13	...
INCOLOY Alloy 802	32.5	0.35	0.75	46.0	0.008	0.38	...	21.0	0.58	0.75	...
INCOLOY Alloy 804	41.0	0.05	0.75	25.4	0.008	0.38	0.25	29.5	0.30	0.60	...
INCOLOY Alloy 825	42.0	0.03	0.50	30.0	0.015	0.25	2.25	21.5	0.10	0.90	Mo 3.0
NI-SPAN-C Alloy 902	42.25	0.03	0.40	48.5	0.02	0.50	0.05	5.33	0.55	2.58	...
NIMONIC Alloy 75	77.6	0.10	0.45	0.50	0.007	0.45	0.05	20.5	0.20	0.35	...
NIMONIC Alloy 80A	74.5	0.05	0.50	0.55	0.007	0.30	0.05	20.5	1.25	2.35	...
HASTELLOY B	61	0.05	1.0	5	1.0	1.0	...	1	...	...	28Mo 0.3V 2.5 Co
HASTELLOY C	54	0.08	1.0	5	1.0	1.0	...	15.5	...	...	16Mo 4W 2.5 Co
HASTELLOY F	47	0.05	1.5	17	1.0	1.0	...	22	...	...	6.5Mo, 1W, 2Cb 2.5 Co&Ta
HASTELLOY X	47	0.10	1.0	18	1.0	1.0	...	22	...	...	9Mo 1.5 Co

^a Compositions obtained from the Handbook of Huntington Alloys, Huntington Alloys Products Division, International Nickel Company and from Haynes Stellite Company, Division of Union Carbide.

^b Plus cobalt.

The effect of the nickel additions in both tests is quite similar, in that susceptibility to cracking increases with increasing nickel content reaching a maximum at around 9 percent. With larger nickel contents, the alloys appear to be immune to stress corrosion cracking.

It is interesting that the mode of fracture for the nickel-irons was primarily intergranular in the case of the boiling caustic solution, while transgranular branching cracks similar to those of austenitic stainless steels were found for the specimens exposed to the boiling 42 percent magnesium-chloride solutions.

Uhlig, [2] in a discussion of Copson's paper, suggested that in view of the sensitivity of the 9 percent nickel irons to hydrogen stress cracking that this could account for the fracture in the magnesium chloride. Other experiments involving cathodic protection seem to preclude hydrogen stress cracking. However, more definitive experiments are needed to completely eliminate hydrogen as a factor in the cracking mechanism.

A group of high strength steels which are of interest to the aerospace industry are the maraging steels which contain from 18 to 25 percent of nickel. These high alloy steels, as pointed out in another lecture in this series, are susceptible to stress corrosion cracking in marine and industrial atmospheres as well as in tap water, sea water, or distilled water. They are also susceptible to hydrogen stress cracking. Stress levels above 50 percent of the yield strength are required to initiate cracking in many of the alloys.

A newly developed high strength alloy, Multiphase (35Ni-35Co-20Cr-10Mo), is capable of developing strengths of 300 ksi. Research studies to date have indicated that this alloy is highly resistant to seawater and marine atmospheres which rapidly promote stress corrosion cracking failures in maraging and high strength low alloy steels [3].

The boiling 42 percent magnesium chloride test is widely used to study the stress corrosion cracking of the austenitic stainless steels. For example, Type 304 stainless steel will crack in the environment in 2 to 4 h. As previously pointed out (Fig. 1), as the nickel content is increased, longer times are required for the onset of cracking. A companion study has been made by Scarberry et al [4] in boiling MgCl_2 with commercial iron-chromium-nickel alloys having nickel contents over the range of those reported for the experimental alloys described in Fig. 1. The results of this study are presented in Table 2. They are in agreement with Copson's study, namely that this class of alloy is immune to stress corrosion cracking in boiling 42 percent MgCl_2 when the nickel content of the alloy is greater than 40 to 50 percent.

In the course of their studies, Neumann and Griess [5] exposed Inconel 600 and Incoloy 804 in magnesium chloride. Inconel 600 did not crack during a 125-h exposure whereas the Incoloy 804 (44 percent Ni) alloy cracked in less than 100 h. Small additions of titanium, columbium, and copper do not appear to have any significant effect on cracking time of the high nickel alloys. On the other hand, Staehle [6] in his work at The Ohio State University found that small additions of molybdenum to Fe-Cr-Ni alloys

TABLE 2—*Stress corrosion cracking in boiling 42 percent magnesium chloride [4].*

Alloy	Nickel Content, percent	Time to Cracking
Type 304 stainless steel	9	2 h
Type 316 stainless steel	12.5	43 h
Incoloy alloy 800	31	140 h
Incoloy alloy 825	42	No cracking in 30 days
Incoloy alloy 901	42	No cracking in 30 days
Hastelloy alloy C	51	No cracking in 30 days
Inconel alloy 625	62	No cracking in 30 days

containing 50 percent nickel significantly reduced time to cracking. This detrimental effect of molybdenum appears to hold for higher nickel compositions of the Inconel 600 type. Similar effects of molybdenum have been noted for nickel-base alloys exposed to high temperature water and are discussed in a subsequent section [7,8].

As in the case of austenitic stainless steels, nitrogen additions to high nickel alloys cause them to become susceptible to cracking in the magnesium chloride test. In our laboratory, high nitrogen containing Inconel 600 compositions were found to be highly susceptible to stress corrosion cracking in 42 percent magnesium chloride.

Nickel-copper alloys such as Monel 400 are a preferred material of construction for salt plants. Evaporators are commonly lined with nickel-copper alloy. The alloy has good resistance to the concentrated salt brines at temperatures of about 130 C (265 F) and is not susceptible to stress corrosion cracking. Stainless steels on the other hand would crack rapidly under these service conditions.

Titanium alloys in contact with dry sodium chloride are well known to exhibit hot salt cracking at temperatures between 288 C (500 F) and 540 C (1000 F). Because of the potential use of high strength nickel alloys in the supersonic transport, studies have been conducted to explore the susceptibility of Inconel 722 and Inconel X-750 to elevated temperature stress corrosion cracking in the presence of chloride salt. Inconel X-750 appears to exhibit some susceptibility to chloride salt stress corrosion cracking at temperatures of 565 C (1050 F) and 675 C (1250 F) [9]. At higher temperatures, cracking is questionable. In other studies, Kirchner and Ripling [10] found no indication of cracking of Inconel 722 at 455 C (850 F) at a stress level of 40 ksi.

Some intergranular attack was noted for austenitic stainless steels exposed to sodium chloride in the temperature range 500 to 700 C (1020 F to 1300 F). Pickering et al [11] however, did not find any evidence of stress corrosion cracking but only intergranular attack. Thus, the cracking at 675 C (1250 F)

of austenitic alloys may be stress accelerated intergranular attack rather than hot-salt cracking as encountered with titanium.

Hydrofluoric and Hydrofluorosilicic Acid

Nickel, nickel-copper, and copper base alloys have excellent records in fluorosilic and hydrogen-fluoride service. Nevertheless, several cases of cracking of the high nickel alloys have been documented in hydrofluoric acid environments.

At the first symposium on stress corrosion cracking held in 1944, Frazer [12] described the cracking of cold drawn Monel 400 alloy tubing which had been exposed to a solution containing approximately 25 percent H_2SiF_6 at temperatures approaching 50 C (120 F). Since that time, other such failures have been documented and confirmed in the laboratory by Copson and Cheng [13]. The Monel 400 tube was full hard, and the cracking followed an intergranular path.

Five case histories of the failure of Monel 400 in hydrofluoric acid (liquid and vapor) also were documented by Copson and Cheng. These failures were transgranular instead of the normal intergranular expected for nickel alloys. Laboratory investigations suggested that stress corrosion cracking was most likely to occur in the vapor phase when air and moisture were present. Total immersion studies in nonaerated mixtures of 48 percent hydrofluoric acid and 30 percent hydrofluorosilicic acids did not initiate cracks in Monel 400 or Monel K-500 after an exposure period of 30 days. Copson and Cheng also studied the cracking behavior of a number of other nickel base compositions in hydrofluoric acid. These data are summarized in Table 3. In general, the susceptibility to cracking was directly related to the hardness of the materials. Cold-worked or aged materials which give rise to higher hardness were the most susceptible to cracking. Both intergranular and transgranular cracking were noted depending on the alloy. Duranickel 301 cracked in an intergranular manner as did the aged-hardened Inconel X-750 material, whereas Inconel 600 specimens developed numerous shallow transgranular cracks.

A particularly interesting facet of this research was the fact that cracking occurred in the environments where the corrosion rates were high, in fact in some instances the Monel 400 specimens were covered with a layer of copper. Generally, cracking is encountered only in relatively noncorrosive environments. The observation of the high corrosion rate suggested that the cracking might be associated with hydrogen, generated by the corrosion, entering the metal. In this respect, a cathodic current applied to the specimen might differentiate between electrochemical stress corrosion cracking and hydrogen stress cracking. Cathodic currents of 2.6 A/dm² caused cracking of the age-hardened Monel K-500 U-bend specimens. However, the cracking resulting from the cathodic charging was intergranular instead of transgranular as obtained during the stress corrosion cracking experiments. The fact that cracking did occur is an indication that hydrogen might be involved. On the

TABLE 3—Results of stress corrosion cracking studies of nickel alloys in hydrofluoric acid vapor [13].

Material	Condition	Hardness		No. of Tests	First Observed Cracking Days
		VHN 30pd	Rockwell C		
Monel K 500	Hot-Rolled	148-210		3	2 to 6
Monel K 500	Aged		32	1	5
Monel 400	Annealed	109-136		23	4 to 15
Monel 400	Cold-Rolled	250		2	6 to 15
Monel 400	Welded			17	4 to 14
Monel 400 1% Si	Cold-Rolled	293		1	15
80 Ni, 15 Cu	Annealed	147		1	5
Nickel 200	Cold-Rolled	232		1	14
Duranickel 301	Hot-Rolled	204		1	None ^a
Duranickel 301	Cold-Rolled		28-29	2	49 ^b
Duranickel 301	Aged		37-41	6	4 to 9
Inconel 600	Cold-Rolled	295		2	14 to 15
Inconel X-750	Hot-Rolled	198	12	1	None ^c
Inconel X-750	Cold-Rolled		29-36	6	None ^d
Inconel X-750	Aged		31-45	9	4

^a 14 day test.^b Three other specimens were not cracked at 14 days when the tests were stopped.^c 49 day test; one other specimen was not cracked at 14 days when the test was stopped.^d Three 14 day and three 49 day tests.

other hand, the differences in the fracture mode suggest that hydrogen *per se* is not entirely responsible for the transgranular cracking in hydrofluoric acid vapors.

The cracking of Monel 400 in hydrofluoric acid solutions containing Cu^{++} ions has been studied by Graf [14]. He found a similarity between the cracking of nickel-copper alloys in fluoride environments and the cracking of brass in commercial solutions. The stress corrosion cracking susceptibility of the Monel 400 was strongly dependent on the CuF_2 content of the hydrofluoric acid. The greater the CuF_2 , the shorter the time to failure.

High Temperature Water and Steam

The nickel base alloys, and particularly Inconel Alloy 600, have found increasing use in high temperature water and steam because their resistance to stress corrosion cracking is much better than that of the austenitic stainless steels when chloride contamination occurs in the system. This problem has been most frequent in nuclear reactors of the pressurized water type which use shell-and-tube type heat exchangers to generate steam. High purity water (primary water) heated by the reactor core flows inside the tubes and boiler water is outside the tubes (shell side). The accidental introduction of chlorides and air into the boiler water has produced stress corrosion cracking in austenitic stainless steel tubes. The cracks are usually found in the tubes at

the crevices between the tubing and the tube sheet as shown in Fig. 4. In these areas, high heat throughout causes localized evaporation of the boiler water. The chlorides which may run only a few ppm in the boiler water are concentrated many-fold in the crevice. The high chloride level, the presence of oxygen, and high tensile stress from the tube expanding operation combine to cause stress corrosion cracking of the stainless steel.

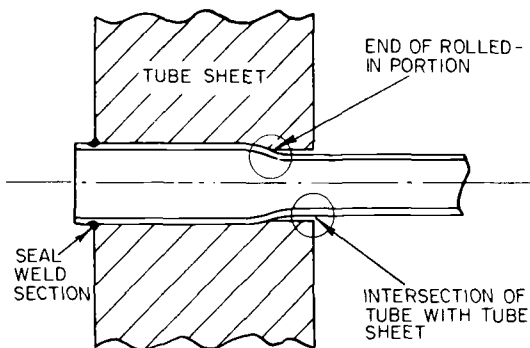


FIG. 4—Areas susceptible to stress corrosion cracking in austenitic stainless steel tube-to-tube sheet joints.

Cracking may also occur in crevices beneath tube support plates in the same manner as described above. Cracking may also occur on fully exposed tubes under active boiling or steam blanketing conditions.

Nickel base alloys have been substituted for austenitic stainless steels in these applications because of the better resistance of nickel base alloys to chloride stress corrosion cracking. The performance of these nickel base alloys has been evaluated under boiler water conditions with varying amounts of chloride, in high temperature seawater to simulate an accidental condition, and in reactor primary cooling water since the inside of the tube is exposed to this environment.

Boiler Water—Most boiler water studies have been conducted in 500 to 600 F water containing 40 to 300 ppm phosphate ion and pH 10 to 11 to simulate boiler water treatment and 0 to 500 ppm chloride ion and 0 to 8 ppm oxygen (at room temperature) to simulate accident conditions. The tests have been conducted in model heat exchangers or in autoclaves tilted every 30 min or so to produce a concentrating condition in the vapor space. Specimens in the autoclave tests were usually U-bends although some bent beams and tensile specimens have been used at loadings less than yield strength.

Unalloyed Nickel 200, Inconel 600, Monel 400, Inconel X-750, and Hastelloy C have not cracked under the above described conditions in tests running several thousand hours, although some pitting occurred in the nickel and Monel 400 [15-20]. The austenitic stainless steels exhibited extensive stress corrosion cracking under these same conditions.

However, certain high nickel (32 to 42 percent) alloys are not completely resistant to stress corrosion cracking in high temperature water containing oxygen and small concentrations of chloride. The results presented in Table 4

TABLE 4—*Stress corrosion cracking behavior of several alloys in water containing 100 ppm chloride and 50 ppm oxygen at 300 C (572 F) [5].*

Alloy	pH	Observations
Incoloy	2.8	Cracks < 500 h
	6.5	Small cracks after 2000 h ^b
	10.5	No cracks 2000 h ^a
Incoloy 804	2.8	Small cracks after 2000 h ^b
Inconel	2.8	No cracks 2000 h ^a
	6.5	No cracks 1000 h ^a
	10.5	No cracks 1300 h ^a
Incoloy 825	2.8	Cracks < 300 h
	6.5	Cracks < 100 h
	10.5	One complete failure and one small crack 1500-2000 h

Four specimens per test.

^aDuration of test.

^bCracks were not visible at end of test but were found on sectioning the specimens.

indicate that highly stressed Incoloy 804, and Incoloy 825 crack in 300 C (572 F) water containing 100 ppm chloride and 50 ppm oxygen particularly at low pH [5,21]. Resistance to cracking under these conditions increases with increasing pH. Inconel 600 did not crack at any pH level (2.8 to 10.5) in these studies.

Possibly the above 32 to 42 percent nickel alloys would not crack in chloride contaminated boiler water, because of the inhibiting effect of the phosphate ion in the boiler water. Tests have shown that austenitic stainless steels have not cracked in 3000 h in 300 C (572 F) water containing 300 ppm phosphate at pH 10.5 whereas with no phosphate addition cracks initiated within 100 h in this environment [5]. A similar inhibiting effect would probably occur with these high nickel-25 to 45 percent iron-20 to 30 percent chromium alloys which apparently behave more like the austenitic stainless steels than Inconel 600 (77Ni-7Fe-16Cr) under these conditions.

Seawater—Nickel base and high nickel alloys exhibit some degree of stress corrosion cracking in natural or synthetic seawater at 260 C (500 F). Published results are somewhat conflicting. Studies in 288 C (550 F) natural seawater at a velocity of 10 fps produced cracking in Monel 400 and Inconel 600 but not in Inconel X-750 or Hastelloy C in 24 days' exposure [19,22]. None of these alloys cracked in a similar exposure at 177 C (350 F) [19].

On the other hand, tilting autoclave tests in synthetic seawater at 288 C (550 F) have produced the following results [23]:

Inconel 600 — no cracking in 20 specimens in 39 days,

Hastelloy C — 7 of 10 specimens cracked within 32 days,

Hastelloy X — 10 of 10 specimens cracked within 5 days,

Ni-13Cr-14Fe-9Mo weld overlay — 4 of 4 specimens cracked within 8 days.

Twenty of 20 Type 347 stainless steel specimens failed within 3 days in these tests. None of the above nickel alloys failed when exposed 77 days fully submerged in static autoclaves to the above environment although 20 of 20 Type 347 stainless steel specimens failed within 4 days.

Inconel 600, Inconel X-750, and Inconel weld overlays did not crack in the following tilting autoclave test [7]: two 100-h periods in aerated boiler water at 260 C (500 F), 500 ppm Cl^- , 4 to 6 ppm oxygen, 225 ppm PO_4 , pH 10.3 followed by two 360-h periods in aerated synthetic seawater at 288 C (550 F). Type 304 stainless steel and Types 308 and 309 weld overlays cracked in this test.

In yet another test in synthetic seawater at 260 C (500 F), Inconel weld overlays containing 12Cr-9Mo-13 to 21Fe cracked within 8 days' exposure [24].

The stress corrosion cracking susceptibility of nickel alloys in high temperature seawater has been related to the mean atomic diameter of the Alloy [7,8]. No cracking was observed in Ni-Cr-Fe alloys with a mean atomic diameter $<2.539\text{\AA}$. The critical mean atomic diameter for Ni-Cr-Fe alloys decreased with increasing molybdenum content in the alloys. This observation has not been studied extensively and its significance with respect to mechanism of cracking is not yet known.

Primary Water—The primary coolant in water cooled reactors is high purity neutral water or deionized oxygen free water adjusted to pH 9-10 with LiOH or NH_4OH . Both types of coolants are used in pressurized water reactors. Boiling water reactors use neutral high purity water and because of radiolytic decomposition reach an equilibrium of ~ 0.2 ppm oxygen (and an equivalent amount of hydrogen) dissolved in the water.

There has been at least one instance of an Inconel 600 tube cracking in the primary coolant of an operating reactor [25]. The cracking occurred in a crevice and could have been caused by concentration of the LiOH (used for pH control) due to localized boiling. Subsequent laboratory tests in 1M LiOH and in high purity water at 220 C (420 F) failed to produce cracking in the stressed Inconel samples and no conclusions were made as to whether the cracking was caused by high purity water or concentrated LiOH.

However, laboratory tests conducted in Saclay, France, in 1959, indicated that 80Ni-20Cr and 78Ni-14Cr-8Fe alloys cracked in high purity degassed water at 350 C (662 F) [26]. Subsequent tests produced cracking in Inconel 600 and Hastelloy B but not in Incoloy 800 [27,28]. Other laboratories produced cracking of Inconel 600 in high purity water after ~ 6000 -h

[29,30] and 10 000-h exposure [31]. The latter was on cold-worked spring material. On the other hand, a number of investigators have failed to crack highly stressed Inconel 600 in high purity water of pH 10 simulated primary coolant water [25,31-35].

The possibility that contaminants in the water may have caused the cracking has been investigated. Dissolved oxygen in the water and lead contamination in the water or on the specimen have been found to cause cracking in the inner specimens (crevice area) of double U-bends of Inconel 600, Inconel 625, Incoloy 800, Type 304 stainless steel, and Type 347 stainless steel [36]. As little as 5 percent oxygen in the headspace of the autoclave at room temperature was sufficient to cause cracking. Sensitized specimens in this study exhibited deeper cracks, but cracks were initiated in both sensitized and solution treated material in the 18 week period. Only those specimens with plastic strain (U-bends) cracked under these conditions.

Despite the evidence for contaminants, there is a growing amount of data indicating that highly stressed Inconel 600 will crack in high purity water under certain conditions. These conditions are not yet well defined but appear to include the following:

1. The specimens are thermally cycled and dried a number of times before failure eventually occurs after months of exposure. This suggests that the oxide film probably cracks during cooling and drying. Then upon subsequent exposure to high temperature water, the stress corrosion crack initiates in the fresh metal exposed by the crack in the oxide film. The large cathodic area of the oxide surface in relation to the small anodic area of freshly exposed metal provides a large potential difference to initiate stress corrosion cracking. The role of time may be to grow the oxide to a critical thickness which will crack.

2. Pickled specimens crack more readily [30]. Heavy pickling produces incipient grain boundary attack. The pickling solution usually contains HF. Since fluorides are only sparingly soluble, there is a good possibility that metal fluorides are retained in the attacked grain boundaries. Subsequent exposure to high temperature water could cause the metal fluorides to hydrolyze and cause fluoride stress corrosion cracking of the Inconel 600. A significant observation is the fact that grain boundary attack initiated in Monel 400 and Inconel 600 by pickling will propagate upon subsequent exposure to high temperature water even though the specimens are not stressed [37,38]. This fact is often overlooked in actual service conditions.

Steam—Laboratory tests in pure steam at 649 C (1200 F) have produced stress corrosion cracking in Inconel 600 [27]. On the other hand, in chloride contaminated steam at temperatures to 343 C (650 F) Inconel 600, Incoloy 800, and Hastelloy X did not exhibit stress corrosion cracking whereas Types 304, 316, and 347 stainless steels cracked within two weeks [39,40].

Insufficient data are available for supporting conclusions as to the susceptibility of nickel base alloys to stress corrosion cracking in steam. However, it should be noted that nickel alloy expansion bellows (usually Inconel 600) are

used in steam crossover lines in power plants and cracking failures are limited to those conditions of caustic carryover from the boiler water.

Monel 400 bellows also are often used in steam service. A number of undocumented reports exist on Monel 400 bellow failures that have been attributed to stress corrosion cracking in steam. Frazer [12] in his review of nickel alloy behavior cites an incident of the cracking of a Monel 400 gasket in steam service. For the most part, the rather sketchy information suggests that the failures may be related to contaminants in the steam.

In a recent oral presentation, Scarberry [41] has indicated that Monel 400 boiler feedwater tubes exhibit intergranular stress corrosion cracking in amine treated waters. In laboratory studies, with highly stressed specimens, cracking occurred in the vapor above 1M NH_4OH at 500 F only when there was oxygen present.

Caustic—In further discussion of caustic cracking, Frazer indicated that cold-worked nickel base alloys will crack in concentrated caustic solution at high temperature [12]. The usual means of correcting the problem is to stress relieve the cold-worked part.

Studies have been conducted in 1 molal LiOH at 218 C (425 F) and 355 C (636F) in connection with the possibility of concentrating the LiOH used to adjust the pH of the primary coolant water in pressurized water reactors [25,42]. No cracking occurred in specimens stressed to 95 percent of the 218 C (425 F) yield strength and exposed 6800 h to 1 molal LiOH at 218 (425 F) [25]. On the other hand, 1 of 10 welded Inconel 600 capsules failed by cracking in or near the weld after 88 days in 1 molal LiOH at 335 C (636 F) [42]. The other 9 specimens did not crack in exposures ranging from 88 to 180 days.

NaOH apparently is more aggressive than LiOH as evidenced by the results listed for welded Inconel 600 capsules exposed to 1 molal NaOH at 335 C (636 F) in companion tests to those described above [43].

<u>Failures</u>	<u>No Failures</u>
1 - 45 Days	1 - 180 Days
1 - 70 Days	
1 - 80 Days	
1 - 145 Days	
1 - 165 Days	

The stress corrosion cracks in the above five specimens occurred in or near the welds.

Mercury, Mercuric Salts, and Liquid Metal Embrittlement

Liquid metal embrittlement of a wide variety of alloy systems by mercury and mercury amalgams and salts is well documented. Examples of alloys suffering such embrittlement are copper base alloys, high strength aluminum alloys, low alloy high strength steels, and titanium alloys, to name a few. A

mercuric nitrate stress corrosion cracking test is used to demonstrate the existence of residual stresses in brasses and is also useful for the 70-30 and 90-10 cupronickel alloys. Mercury and mercury salts will also crack highly stressed Monel 400 [12].

In addition to these examples of liquid metal embrittlement, DeVries et al [44] suggested that Monel 400, Nickel, and Hastelloy B were subject to cracking in molten lithium at 315 C (600 F). Copson [45] cites the case of an Inconel 600 tube bundle from a fatty acid heater which was dipped in molten lead at 430 C (800 F) to remove carbonaceous material. The bundle was then heated to 540 C (1000 F) for 10 to 15 min. After the tube was placed back in service at 340 C (650 F) cracks developed in the hairpin bends and were identified as intergranular cracking caused by molten lead. The effects of small lead additions in high temperature water were discussed in a previous section.

Other Environments

Nickel and nickel base alloys are resistant to a number of solutions known to promote cracking of other alloys. For example, nitrate solutions which readily initiate cracking in carbon steels are quite innocuous to nickel base alloys. The same is true for ammonia solutions which are responsible for the well known season cracking of brass. Even the nickel-copper alloys are immune to ammonia cracking.

Sulfide cracking as occurring in carbon steels is unknown in the case of nickel alloys. However, nickel alloys are particularly susceptible to attack by sulfur compounds at high temperatures which may result in embrittlement of the nickel alloys.

There have been several cases of stress corrosion cracking of Inconel 600 in solutions where sodium sulfide was suspect [46]. One such case occurred in a vacuum evaporator equipped with Inconel 600 tubes which was used for the second effect evaporation of a sodium sulfide liquor from 10 to 20 percent concentration at 85 C (185 F). Metallographic examination of the failed tube revealed cracking associated with severe intergranular attack. There were carbides at the grain boundaries, and the tube exhibited a high degree of cold work.

The other incident involved an Inconel 600 spring, which also was sensitized and cold-worked. Failure occurred in contaminated steam which may have contained sodium sulfite and alkaline phosphate from the boiler water treatment.

Another failure of nickel alloys which has been termed stress corrosion cracking is the intergranular attack observed in polythionic acids. The attack has been observed in both stainless steels and nickel alloys. Samans [47] found that the intergranular attack developed in stainless steels sensitized in the temperature range 425 to 925 C (800 to 1700 F). The Incoloy 800 and Inconel 600 alloys evinced attack after a quench followed by a 4-h sensitizing

treatment at 650 C (1200 F). Unsensitized specimens do not exhibit the cracking. This fact plus the observation that intergranular attack will occur on the sensitized specimens in the absence of stress casts considerable doubt as to whether the attack is a true case of stress corrosion cracking. Most likely, describing that attack as stress assisted intergranular attack is more appropriate.

Mechanism of Stress Corrosion Cracking in Nickel Base Alloys

Over the years, considerable research effort has been directed toward providing a better understanding of the mechanism of stress corrosion cracking. These efforts have included carbon steels, stainless steels, aluminum and titanium alloys, but surprisingly little effort has been exclusively devoted to elucidating those mechanisms operative in nickel and nickel base alloys. Perhaps this stems from the fact that considerable information is available for Fe-Ni-Cr alloys, much of which may be directly applicable to nickel and its alloys. However, it would be interesting to learn the mechanism of cracking of high nickel alloys in high purity water or in high temperature water containing oxygen.

The effect of nickel additions in reducing susceptibility to cracking of alloy systems has been attributed to an increase in stacking fault energy which in turn gives rise to a change in dislocation arrangement from coplanar to clustered; the latter being more resistant to stress corrosion cracking. This increase in stacking fault energy of nickel would account for the predominately intercrystalline cracking of nickel base alloys. On the other hand, alloys having clustered arrays of dislocation are susceptible to stress corrosion cracking and both intergranular and transgranular cracking have been observed in the same nickel alloy depending on the environment and the condition of the alloy.

Graf [48] has suggested that the tendency to stress corrosion cracking of homogeneous alloys is present when the amount of the more noble constituent present in the alloy lies between 0 and 50 percent. As the noble metal is added, susceptibility to stress corrosion cracking increases to a point and then begins to decrease as more and more noble nickel is present in the alloy and finally immunity is observed. The contrasting factor in the cracking mechanisms is the plating out or enrichment of the noble element on the walls of the crack to provide the electrochemical driving force for the dissolution of the yielding metal at the apex of the crack. When the concentration of noble metal reaches a critical level, the potential differences no longer exist and corrosion behavior is controlled by the surface dissolution of the alloy alone. The curve of Fig. 1 certainly resembles those drawn by Graf, even though all the nickel alloys shown are not homogeneous. In many instances, the cracking of nickel alloys follows the amount of noble alloy constituent along the lines outlined by Graf. However, there are a number of exceptions. First, not all the alloys in Fig. 1 are homogeneous. Secondly, X-ray diffraction, magnetic

methods, and chemical techniques have not been successful in establishing the existence of the presence of metallic nickel deposits or patches within a crack. Thus, it is difficult to establish the applicability of Graf's theory.

The possibility that hydrogen produced by the cathodic portion of the corrosion reaction may play some role in the cracking process, has been postulated for a number of metallic systems. Also, some evidence exists that in some environments hydrogen may be an important factor in nickel alloys. However, more research is needed to establish its true role.

In any event, there seems little doubt that as in other metallic systems, the mechanism of cracking in nickel alloy systems involves a continuing dissolution process. Certainly, slip step emergence or lattice disarrays could initiate local dissolution. However, once started, explanations must take into consideration the role of nickel in the role of repassivation of the yielding metal and its contribution to explain Staehle's restricted lateral dissolution criteria [49]. The answer to why nickel alloys crack in high purity, high temperature water should go a long way to elucidating those combinations of processes at work in nickel alloys which can be used to constitute an overall stress corrosion cracking mechanism for nickel base alloys.

Prevention of Stress Corrosion Cracking in Nickel Alloys

As in the case with other metals and alloys, the best method of preventing stress corrosion is reducing tensile stress. In nickel alloys this is often accomplished by reducing residual stresses. For example, an annealing treatment at 850 C (1560 F) will effectively reduce the occurrence of cracking in nickel weldments in caustic service. Copson and Cheng [13] demonstrated that an annealing treatment for 1 h at 600 to 650 C (1100 to 1200 F) would reduce cracking tendencies of Monel 400 in hydrofluoric acid service.

Similarly, control of the environment is also an effective technique for minimizing stress corrosion cracking. Elimination of oxygen or full immersion or both to prevent contact with vapors will reduce the incidence of cracking of high nickel alloys in hydrofluoric acid service.

There is also some evidence that water treatments and pH control techniques used in boiler and nuclear water may be a contributing factor to the observation that high nickel alloys exhibit superior stress corrosion cracking behavior in these environments, especially in the presence of a few ppm of chloride which crack stainless steel. This also suggests that environmental control may be effective in preventing cracking in high purity oxygenated water.

Summary

Nickel base alloys are highly resistant to chloride stress corrosion cracking which plagues stainless steels. For Fe-Cr-Ni alloys, nickel contents of more than 50 percent are quite immune to cracking in boiling 42 percent magnesium chloride.

Cracking of nickel and nickel base alloys is encountered in high temperature caustic solutions and molten caustic and hydrofluoric acid vapors containing air and moisture.

There are a number of instances of cracking of Incolloys, Inconels, and related nickel base alloys in high temperature water and steam, some of which can be explained on the basis of contaminants in the system. On the other hand, the factors contributing to the cracking of Inconel 600 in degassed high purity water or high temperature water containing oxygen have not yet been defined.

This summary of the occurrences of stress corrosion cracking of nickel alloys should provide the engineer with a measure of degree criteria which should reduce the probability that stress corrosion cracking will occur in a given service application.

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Testing Methods for Stress Corrosion Cracking

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ABSTRACT: Stress corrosion testing methods are discussed from a general point of view with an emphasis on the desirability of standardization. The usefulness of smooth, notched, or precracked specimens is compared and some results using the different types are presented. Some precautions that should be taken are described: these include avoidance of crevice corrosion, galvanic effects, or hydrogen embrittlement results. Finally, since it is possible to find some type of environment that will crack almost every engineering alloy, it is important to use realistic loading methods and test media that relate to material serviceability for a particular application.

The work of ASTM Committee G-1 on Corrosion of Metals in preparing recommended practices for various test specimens such as C-ring, bent beam, tension, U-bend, and precracked specimens is summarized; as is, similar work with environments such as the boiling MgCl_2 test.

KEY WORDS: stress corrosion, stress corrosion tests, galvanic corrosion, hydrogen embrittlement, concentration cell corrosion, alloys, surface properties, deflection, corrosion environments, coatings

In a very comprehensive state-of-the-art paper on stress corrosion testing, Craig et al pointed out that a problem with most stress corrosion investigations is the lack of standardized testing methods [1]. This makes correlation of data from one investigator to another difficult if not impossible. The first attempts to take some steps toward standardization have been published in an earlier publication [2-4]. This paper is essentially an update of one of the earlier papers [2].

The earlier paper on stress corrosion testing methods described differences in stressing under conditions of constant deflection or constant load, primarily with smooth specimens. The suggestion was made that the choice of stressing method was best dictated by the reason behind conducting the stress corrosion tests. In that paper and in this, the discussions are aimed primarily

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at stress corrosion testing of a practical engineering type.

Tests are still conducted both under constant deflection and constant load, but there is an increased awareness of the complexities of the stress state particularly under constant deflection, leading to a more enlightened interpretation of test results.

For the past several years the main point of discussion has centered on the usefulness of smooth specimens versus precracked. Again, it is my opinion that the reason or purpose behind conducting a stress corrosion investigation should dictate the approach.

The reasons behind conducting a stress corrosion investigation previously presented [2] can be grouped under the broad headings of alloy development or environmental effects. Alloy development would include:

1. Evaluation of a metal or alloy, or various heat treatments of one alloy for susceptibility to stress corrosion in certain environments.

2. Comparison of stress corrosion susceptibilities of several alloys.

3. Establishment of engineering data to be used for design purposes. Environmental effects would include:

1. Study of environments for their influence on the stress corrosion behavior of various alloys.

2. Evaluation of a specific service requirement for the possibility of stress corrosion.

3. Determination of the effectiveness of coatings or other protective measures for reducing stress corrosion of susceptible metals and alloys.

For alloy development both smooth and precracked specimens should be used in order to obtain a complete picture of the susceptibility to stress corrosion.

For environmental and coating studies important considerations should be selection of a specimen type and a stressing method which provides reproducibility of stress pattern and stress level from one specimen to another, and more important, is the selection of a material known to be susceptible to stress corrosion cracking. In materials which exhibit anisotropic stress corrosion behavior, the direction known to show the greatest susceptibility should be used.

To study environmental effects a more complete characterization of stress corrosion behavior is obtained if stress raisers are also taken into consideration, so preferably both types of specimens should be used. If time or economy dictates only one type, precracked or notched specimens are preferable. These simulate stress raisers such as screw threads, sharp fillets, fatigue, and weld cracks or other flaws which may be introduced into a component during its manufacture or design, while others such as pits may naturally develop during exposure to a corrosive environment.

For a specific service requirement the part should be tested under the type of stress that will most nearly duplicate that to be encountered in service, if known. If not known, and maybe even if it is, consideration should be given to testing under the most severe conditions the part will ever see.

Test Specimens

Descriptions of the most commonly used types of specimens are available elsewhere [1,2]. An excellent summary of stress corrosion testing with precracked specimens has also been written [5].

A wide variety of precracked specimen configurations are available classified with respect to the relationship between K_I which is the stress intensity factor for opening mode and crack extension. The analysis in terms of K_I is potentially applicable to actual structures as well as test specimens, but the significance of such data with respect to structural design has not been fully established. This is because it is difficult to analyze the size and distribution of stresses in components of complex geometry.

Precracked specimens are particularly useful for titanium and those high strength steels which do not have a tendency to pitting attack. Leckie and Loginow have presented a comparison of results obtained with HY-80, HY-130(T), 12Ni and 18Ni maraging steels using smooth and precracked specimens in several environments [6]. The precracked specimens frequently showed failure whereas the smooth did not.

Table 1 presents results obtained on an H-11 steel in 3½ percent NaCl using different types of specimens. Most of the specimens were stressed at 168

TABLE 1—Results on H-11 steel using different types of specimens
(240 ksi strength levels).

Electrolyte — 3½ percent NaCl, Constant Immersion		
Type of Specimen	Stress Level, ksi	Hours to Failure (Number of Specimens)
Smooth Tensile	168.8	125, 206, 367
Notched Tensile	75% N.T.S. 168.8	8, 12, 5 33, 112, 225
Smooth C-Ring	168.8	No Failure 1058 (3)
Notched C-Ring	168.8	840 (2) 1300
Bent Beam	168.8 112.5	Broke Overnight (3) 20, 44, 46
U-Bend	Above Y.S.	900 (3) (012 in. Decarb) 75, 86, 95 (Decarb removed)

ksi or approximately 75 percent of the yield strength. Failures occurred with all the specimens except for the smooth C-ring — only the times to cracking varied. For tests conducted at stress levels below the yield strength, the bent beam appeared to be the most sensitive specimen and the results showed the least scatter.

The variation in times to cracking with the smooth and notched tensiles probably reflects the time required in a smooth specimen for a pit to develop a sufficient stress concentration or for the chemistry within the pit to change to conditions required for cracking, as described by Brown [7].

Results on the first set of U-bend specimens were puzzling because of their unexpectedly long life. Metallographic examination of cross sections revealed the presence of a decarburized surface approximately 0.012 in. in depth. Removal of this surface by grinding after heat treatment decreased the time to cracking by a factor of ten. Decarburization may deserve consideration as a protective measure.

With an aluminum alloy with two different heat treatments, the type of specimen did not play such a great role (Table 2). C-rings and tension

TABLE 2—Results of alternate immersion test in 3½ percent NaCl
(Short transverse specimens from 3-in. thick plate, stressed 75 percent of yield).

Specimen Type	Time to Cracking, Average of 3 Specimens	
	7075-T651	7075-T7351
C-Rings	16 Days	No failure in 30 days
1/8-in. Diameter Tensiles	2 Days	No failure in 30 days

specimens, both short transverse specimens tested under constant strain, produced the same result — only the times to failure were different. The tension specimen with its uniaxial loading was obviously the more severe type.

Surface Preparation

Surface preparation plays an important role in the results of stress corrosion tests. Most specimens have machined or ground surfaces. Either machining or grinding can produce physical, structural, or chemical changes in the surface layers which are not necessarily reproducible from specimen to specimen. Also care must be taken not to overheat the surface during these operations to avoid metallurgical changes.

Paxton and Proctor have written a review paper on the effect of machining and grinding on the stress corrosion cracking susceptibility of a wide variety of alloys [8]. They conclude that, although the subject has not really been sufficiently investigated, most machining and grinding operations result in

residual surface tensile stresses to some extent. These residual stresses in general decrease the resistance to stress corrosion cracking.

Some investigators prefer electropolishing or chemical or mechanical removal of the as-machined surface, others prefer to degrease the surface. The influence of surface preparation was demonstrated by Cochran and Staehle using 310 stainless steel wires [9]. Mean cracking times varied by as much as a factor of 4 with different surface preparations. They found less scatter in results when the surfaces were chemically prepared rather than manually prepared. Kohl found times to failure were 4 times longer with electrolytic polishing than with machining [10]. These results lend credence to the presence of residual stresses from machining which would be removed by electropolishing or chemical means.

Cocks, on the other hand, in studying aluminum alloys, found that electropolished specimens failed faster than those tested with as-machined surfaces [11]. He contends that machining produces a surface damaged layer within which the grain boundary structure has been destroyed. This layer must be penetrated and grain boundaries exposed before the stress corrosion process can begin since stress corrosion failures in aluminum alloys are always intergranular. Removal of this layer by electropolishing decreased times to failure by a factor of five. In any case it is undoubtedly the induction or initiation period that is most affected by surface preparation.

Results of stress corrosion tests on ground versus chemically milled surfaces are presented in Table 3. A chem-milled surface increased the susceptibility of

TABLE 3—Results of U-bend stress corrosion tests
on H-11 steel in 3½ percent NaCl.

Type of Surface	RMS	Time to Failure, h
Ground	2-8	221, 245, 269
Chem-Milled	20-24	10, 19, 27
Chem-Milled and Shot Peened		90, 209, 24 ^a

^aEdges not deburred.

an H-11 steel in 3½ percent NaCl to stress corrosion cracking over a machine milled surface. This may seem to be an inconsistency in view of the previous statement about removal of machined surfaces increasing life. However, metallographic examination revealed that the ground surface contained numerous nicks and gouges, but these were shallow and rounded. Chem-milling produced fewer but deeper and sharper notches which would increase

susceptibility to stress corrosion cracking in a notch sensitive H-11. Shot peening provided some improvement but failure times were still shorter than with ground specimens. It may be that sufficient precautions were not taken to remove all the sharp edges produced by the peening prior to forming the U-bends. The edges of the specimen that failed in 24 h were left as shot peened. The other two were abraded to remove sharp edges but perhaps not enough.

In reporting stress corrosion results, the method used to prepare the surface of the specimens for test should be mentioned. The ASTM recommended practice for C-rings specifies a 30-rms finish.

Protection Against Galvanic and Crevice Effects

Care must always be exercised to avoid galvanic effects between specimens, stressing fixtures, and exposure racks. This is necessary not only to avoid galvanic protection of the stressed area but also to prevent crevice corrosion. In some cases, crevice effects can also provide galvanic protection to the stressed area, but in other cases, it may give rise to hydrogen embrittlement by the cathodic corrosion product, hydrogen. Protection can readily be applied by means of suitable coatings or insulators, but the materials should be carefully selected so that they will neither contaminate the corroding medium or be deteriorated by it. However, the use of insulating bushings will not necessarily prevent crevice corrosion. Crevices could exist between the bushing and specimen. Also, crevice corrosion does not necessarily develop corrosion products in the crevice. Crevices have been known to act as a cathode and thereby accelerate the corrosion of the noncrevice surfaces. (The presence of crevices can be particularly critical with alloys that exhibit passivity such as stainless steels and titanium.)

Inspection for Cracking

Some materials will tend to fracture or crack in a way that is easy to detect, particularly if stressed at a high level, or if notch sensitive. Frequently, though, with lower applied stresses or with more stress corrosion resistant alloys, cracking begins slowly and is difficult to detect. Small cracks may initiate at multiple sites and an arbitrary decision must be made as to when a specimen should be considered to have failed. Usually, it is preferable to consider a specimen has failed when the first crack is detected either with the naked eye or at a low magnification (X10 to X15). If doubt exists, record the date the suspected crack was first noted, continue exposure and watch for further growth to confirm the first observation.

Metallographic and fractographic examination is frequently used to verify the visual observation and to determine the mode of failure (intergranular or transgranular).

Replication and Reproducibility of Results

A problem that arises in outlining a stress corrosion test program is to decide the number of replicate specimens required to adequately characterize stress corrosion behavior. The ideal approach is to test specimens over a range of applied stresses. At least four specimens should be tested at each stress level. If statistical comparison is to be made, ten or more specimens are preferable. Sprowls has provided some guidelines in this regard and also in interpretation of results [4]; rather than delve deeply into this aspect here, those interested are referred to this excellent coverage of the subject.

On the subject of reproducibility Frank LaQue has stated that while reproducibility is a necessary feature of any method of test that gives reliable results, it can also be a characteristic of a procedure that gives consistently wrong answers [12]. One test can be as consistently wrong as another can be consistently right.

LaQue's point was that a relationship has to be established between a laboratory test and performance in the service environment towards which the test is directed — a very important point in stress corrosion testing.

Reproducibility of results within a single laboratory is frequently difficult to obtain, but from laboratory to laboratory, even more difficult. Croucher has reported on a joint test program conducted by 15 companies [13]. It involved four steels, two specimen configurations, and two environments. For precipitation hardening stainless steels, the bent beam specimen provided more reproducible results than the C-ring; a 20 percent salt spray environment produced better reproducibility than a 3½ percent NaCl alternate immersion test. Humidity is an important variable in the alternate immersion test and if not controlled could produce variations in results.

Five laboratories participated in an ASTM interlaboratory test program of an Al-Zn-Mg-Cu alloy using C-rings and alternate immersion in 3½ percent NaCl. The C-rings were from the same source and all were machined at the same place. The reproducibility of results within a laboratory was good, and three of the five laboratories showed good agreement.

Standardization of Test Methods

ASTM Subcommittee G01.06 on Stress Corrosion Testing has prepared recommended practices on U-bends, bent beam, and C-ring specimens. Also being written are recommended practices for tension and precracked specimens. These contain dimensions, descriptions of stress states, formulas for calculating stresses, and guidelines in the use of the specimens.

The same approach is used for standardizing on environments. Polythionic acid and boiling MgCl_2 procedures have been prepared and task groups on hot salt testing for titanium and environments for stress corrosion testing of copper and magnesium alloys have been formed.

Efforts such as these are important if stress corrosion testing is to become a science rather than an art. More careful investigations into the effects of all possible variables in any test method should be encouraged because these also make an important contribution toward achieving this goal.

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The Resistance of Wrought High Strength Aluminum Alloys to Stress Corrosion Cracking

REFERENCE: Brown, R.H., Sprowls, D.O., and Shumaker, M.B., "The Resistance of Wrought High Strength Aluminum Alloys to Stress Corrosion Cracking," *Stress Corrosion Cracking of Metals—A State of the Art, ASTM STP 518*, American Society for Testing and Materials, 1972, pp. 87-118.

ABSTRACT: An up to date review of the stress corrosion cracking performance of wrought high strength aluminum alloys is presented. Special emphasis is placed on factors of microstructure and its directionality and the effect of ancillary alloying elements, and environmental factors.

Examples of typical service problems encountered with stress corrosion cracking of high strength aluminum alloys are described along with means of combating them, such as peening, coatings, or the use of special stress corrosion resistant alloys.

KEY WORDS: stress corrosion cracking, aluminum alloys, failure, crack initiation, intergranular corrosion, crack propagation, residual stress, Alclad

Most wrought high strength aluminum alloys are susceptible to stress corrosion cracking (SCC) to varying degrees ranging from relatively high susceptibility to virtual immunity, depending upon temper, manufactured form, and magnitude and direction of tensile stress relative to the grain structure. Instances of stress corrosion failure of aluminum alloy structures have resulted from sustained residual or assembly tensile stresses acting in the short transverse direction in relation to the grain structure at the surface of a part. In contrast, longitudinal tensile stresses, even those approaching the yield strength, have rarely caused stress corrosion problems.

Stress corrosion cracking in aluminum alloys typically occurs along grain boundaries whereas cracking associated with mechanical fractures resulting from fatigue, creep rupture, tensile overload, etc. generally is transgranular. Although the microstructures of most aluminum alloys in tempers that are susceptible to stress corrosion cracking are characterized by localized decom-

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position of solid solution at the grain boundaries, the degree of susceptibility is not predictable by the structural features revealed by either light or electron microscopy. Other requisites for the stress corrosion cracking of a given alloy composition and microstructure are a specific environment and a sustained tensile stress at the surface.

The continued successful utilization of wrought high strength aluminum alloy products depends upon the proper use of reliable corrosion data and the proper analyses of structural components and their assembly by the design engineer. This paper provides up to date information on the stress corrosion characteristics of wrought high strength aluminum alloys.

Four Agents in Stress Corrosion Cracking

Stress corrosion investigators do not agree on a definition of stress corrosion cracking and consequently definitions appearing in books and glossaries generally are broad. The definition given in the *Corrosion Handbook* [1], "Cracking resulting from the combined effect of corrosion and stress," is a broad definition and actually covers a variety of chemical-mechanical failures. H.R. Copson [2] restricted the stress to "static tensile stress" and then classified stress corrosion cracking failures into four types. However, the classification still covered such a broad range of causes and mechanisms that stress corrosion cracking has come to have different meanings to different people.

It is advantageous to have a classification of these varied failures to assist in cataloging service failures and to determine suitable preventative measures. This is a matter of great practical importance to materials engineers and designers because methods for avoiding each type of failure generally are different. Another proposed classification based on the chemical-mechanical characteristics of the failures is given in Table 1.

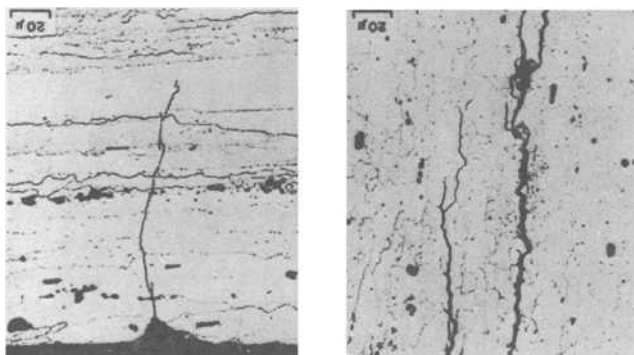
Type 1 is stress corrosion cracking and is defined as cracking that is initiated by directional chemical or electrochemical attack or both synergized by sustained tensile stress at the surface. To obtain the specific result of stress corrosion cracking, four primary agents must be concurrently contributing:

1. a specific alloy composition,
2. a unique microstructure resulting from metallurgical processing,
3. a tensile stress at exposed surfaces, and
4. a specific environment.

Type 2 is corrosion fatigue which is cracking that is initiated by cyclic stressing synergized by chemical or electrochemical attack or both. An important distinction between Types 1 and 2 in aluminum alloys is the mode of cracking: stress corrosion cracks are characteristically intergranular, whereas corrosion fatigue cracks, even if they should initiate at a site of intergranular corrosion, are characteristically transgranular (Fig. 1).

TABLE 1—*A classification of delayed cracking failures.*

Type	Cause of Cracking	A Stress	B Oxidation Reduction	Interaction A and B	Type of Failure
1	Stress Corrosion	Sustained Tension	Yes	Synergistic	Chemical Mechanical
2	Corrosion Fatigue	Inter- mittent	Yes	Synergistic	Chemical Mechanical
3	Area Reduction by Corrosion	Sustained	Yes	Additive	Mechanical
4	Hydrogen Embrittle- ment	Sustained	No	None	Mechanical
5	Fatigue	Inter- mittent	No	None	Mechanical
6	Creep Cracking	Sustained Tension	No	None	Mechanical
7	Liquid Metal Penetration	Sustained	No	None	Mechanical

FIG. 1—*Comparison of a typical intergranular stress corrosion crack (SCC) and a typical transgranular fatigue crack in a 7XXX series high strength aluminum alloy. Keller's Etch.*

Type 3 is a mechanical type failure that sometimes is confused with true stress corrosion cracking. This type of mechanical failure occurs only under severe corrosive conditions with the applied stress having no appreciable effect

upon either the rate or the geometry of the corrosive attack. The distinction between these two types of failure is of considerable practical significance, however, because the methods of combating them are quite different. Whereas, the relatively simple procedure of applying a protective coating will suffice to prevent the corrosion that may cause a mechanical failure, the prevention of stress corrosion cracking requires a much more sophisticated approach. Moreover, a corrosion induced mechanical failure may occur with alloys that are highly resistant to stress corrosion cracking (Type 1).

Types 4, 5, 6 and 7 will not be discussed since oxidation reduction of the parent metal is not directly involved in the cracking process. There may well be an electrochemical aspect associated with failures by hydrogen embrittlement cracking.

Alloy Composition and Microstructure

Stress corrosion cracking has not been reported in the use of pure or commercially pure aluminum or in commercial alloys of the Al-Mn, Al-Si, Al-Mg with <3 percent Mg, Al-Mg₂Si and Al-Si-Mg types. Although some alloys in the two latter types (6XXX series) can under certain special metallurgical conditions be rendered susceptible to stress corrosion cracking in laboratory tests [3], such special conditions can easily be avoided in commercial practice. Stress corrosion resistant tempers have been developed for alloys in the Al-Mg system (5XXX series) containing more than 3 percent Mg. However, most wrought high strength heat treatable aluminum alloys of the Al-Cu (2XXX series) and the Al-Zn-Mg (7XXX series) types are susceptible to stress corrosion cracking to varying degrees depending upon temper, manufactured form, and magnitude and direction of tensile stresses. The copper free Al-Zn-Mg alloys differ from the others in the heat treatable group, however, in that they are not as amenable to tempering to a stress corrosion resistant condition, and they display a susceptibility to stress corrosion cracking in a much wider range of environments. The nominal compositions and typical tensile properties of the high strength alloys to be considered below are given in Table 2.

Aluminum alloys in tempers that are susceptible to stress corrosion cracking are characterized by microstructures wherein there has been a localized decomposition of solid solution at the grain boundaries; in most instances the presence of identifiable precipitation in the grain boundaries can be established. Because stress corrosion cracking occurs along the grain boundaries any degree of anisotropy of the grain structure can have a marked influence upon stress corrosion performance. Therefore, alloying additions or metallurgical treatments that affect the precipitation of alloy constituents or the shape of the metal grains can markedly influence the resistance of an alloy to stress corrosion cracking.

The specific roles of grain boundary precipitates and the solid solutions in

the grain margins and hence the exact location of the localized corrosion path depend upon the alloy composition, the metallurgical condition, and upon the chemical nature of the environment. Moreover, knowledge of electrochemical relationships of alloy phases (Fig. 2) has enabled the stress corrosion resistance of certain alloys to be predicted from the microstructures. By the integration of this electrochemical knowledge [4] and metallographic knowledge, metallurgical practices have been devised to produce tempers to impart stress corrosion resistance to several aluminum alloys [5, 6].

The terms "susceptible alloy" or "susceptible microstructure" are meaningless to the intelligent use of high strength aluminum alloys. Figures 3 and 4 show electron micrographs illustrating the difficulty in correlating structures with stress corrosion resistance. The structures shown are for commercially fabricated forgings and 1 and 2-in. thick plate, the stress corrosion data are for short transverse tests. Structures of 7075 alloy in the W, T6, and T73 tempers are shown in Fig. 3. The structure representative of the maximum strength T6 temper differed from that of the W temper principally by the high density of zone formation in the T6. The T73 temper, overaged in comparison with the T6, exhibited zones of larger size with greater inter-particle spacing and some platelets of M' and M-phase precipitate. A few residual quenched-in dislocations also are present. The T73 temper is virtually immune to stress corrosion cracking in chloride environments, whereas, parts in the T6 and W tempers are susceptible at low stresses when tested in the short-transverse direction. Thus, the type of structure shown in Fig. 3c might be judged to be representative of a stress corrosion resistant metallurgical condition. However, Fig. 4 shows microstructures similar to that of 7075-T73 in an experimental temper of alloy 7079 and in alloy 7039, both of which are susceptible to stress corrosion cracking at low stresses in the short transverse direction.

Manufactured Products and Directional Grain Structure

One important factor in the stress corrosion behavior of heat treated aluminum alloys is the direction of tensile stressing in relation to direction of working and grain flow [7]. Figure 5 shows in three dimensions the microstructure of a heat treated aluminum alloy rolled plate. The direction parallel to the direction of rolling (working) has been termed longitudinal. The direction perpendicular to the rolling direction and parallel to the rolled surface has been termed the long transverse. The direction perpendicular to the rolled surface has been termed short-transverse. The direction of grain flow may be less simple in other products. The macroetched transverse section of an 8 in. by 8 in. by 24-in. hand forging of 7075-T6, shown in Fig. 6, although not typical of all hand forgings illustrates how complicated the metal flow can be. The variation in stress corrosion resistance, as affected by orientation of the test bar in relation to grain flow, is marked.

TABLE 2—Nominal composition and typical tensile properties of several wrought aluminum alloys.^a

Alloy and Temper	Nominal Composition, %						Tensile Strength, ksi	Yield Strength, 0.2%, ksi	Elongation In 2 in. %
	Si	Cu	Mn	Mg	Cr	Zn			
Al-Cu Alloys (2XXX Series)									
2011-T3	...	5.5	...	...	...	...	55	43	15
2011-T8	...	5.5	...	...	...	0.4 Pb, 0.4 Bi	59	45	12
2014-T6	0.8	4.4	0.8	0.5	...	0.4 Pb, 0.4 Bi	70	60	13
2024-T3	...	4.4	0.6	1.5	...	...	70	50	18
2024-T81	...	4.4	0.6	1.5	...	...	70	65	7
2219-T37	...	6.3	0.3	...	...	0.06 Ti, 0.18 Zr, 0.1V	57	46	11
2219-T62	...	6.3	0.3	...	...	0.06 Ti, 0.18 Zr, 0.1V	60	42	10
2219-T851	...	6.3	0.3	...	...	0.06 Ti, 0.18 Zr, 0.1V	66	51	10
2219-T87	...	6.3	0.3	...	...	0.06 Ti, 0.18 Zr, 0.1V	69	57	10
2020-T6	...	4.5	0.5	...	...	0.2 Cd, 1.1 Li	84	77	3
Al-Mg-Mn Alloys (5XXX Series)									
5454-O	...	...	0.8	2.7	0.12	...	36	17	22
5454-H34	...	...	0.8	2.7	0.12	...	44	35	10
5083-O	...	...	0.7	4.45	0.15	...	42	21	22
5083-H321	...	...	0.7	4.45	0.15	...	46	33	16
Al-Mg-Si Alloys (6XXX Series)									
6061-T6	0.6	0.27	...	1.0	0.20	...	45	40	12
Al-Zn-Mg Alloys (7XXX Series)									
7039-T6	...	...	0.27	2.8	0.20	4.0	66	55	13
7039-T63	...	...	0.27	2.8	0.20	4.0	63	53	13

Al-Zn-Mg-Cu Alloys (7XXX Series)									
7075-T6	...	1.6	...	2.5	0.30	5.6	...	83	73
7075-T76	...	1.6	...	2.5	0.30	5.6	...	78	68
7075-T73	...	1.6	...	2.5	0.30	5.6	...	73	63
7178-T6	...	2.0	...	2.7	0.30	6.8	...	88	78
7178-T76	...	2.0	...	2.7	0.30	6.8	...	83	73
7079-T6	...	0.6	0.20	3.3	0.20	4.3	...	78	68
7001-T6	...	2.1	...	3.0	0.30	7.4	...	98	91
7001-T75	...	2.1	...	3.0	0.30	7.4	...	84	72

^a Sources: *Aluminum Standards and Data*, 3rd ed., Aluminum Association, Jan. 1972 and *Aluminum*, K. R. Van Horn, Ed., Vol. 1, Chapter 9, American Society for Metals, 1967.

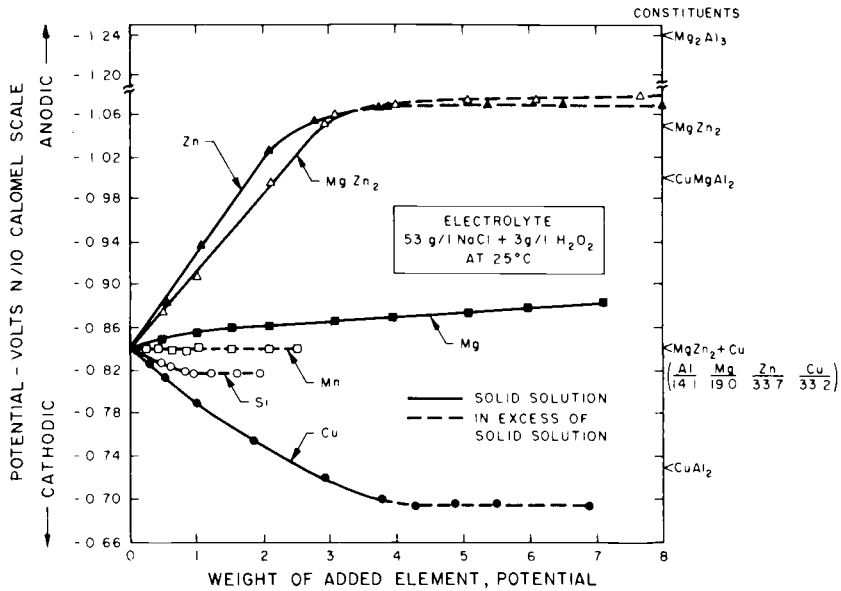
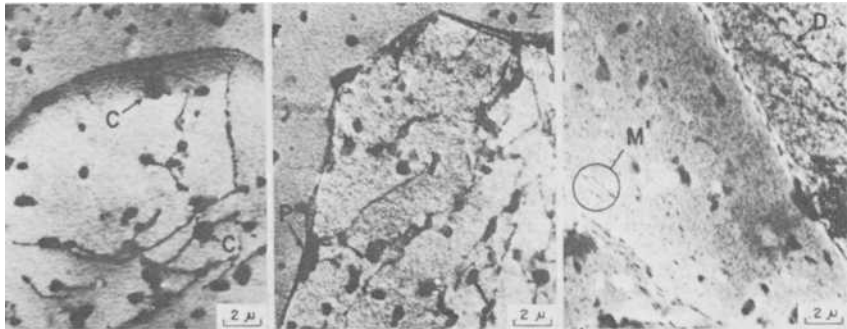


FIG. 2—Electrode potentials of aluminum solid solutions and constituents [4].



(a) 7075-W

(b) 7075-T6

(c) 7075-T73

FIG. 3—Electron transmission micrographs of thin foils from 2-in. thick rolled plate heat treated and cold water quenched in the laboratory. In all three samples there are numerous particles of Cr-rich constituent (C) with dislocations pinned to some of these particles in the 7075-W and T6. Some residual quenched-in dislocations also are present in the T73. The structure of the T6 temper differs from that of the W temper principally by the high density of zone formation in the T6. The T73 temper shows zones of larger size than the T6 and precipitated platelets of M' phase (M'). Short-transverse specimens stressed and exposed 84 days to the 3.5 percent NaCl alternate immersion test were susceptible to SCC at stresses as low as 15 percent Y.S. for the W (8 ksi) and T6 (11 ksi) tempers, but were resistant at stresses as high as 75 percent Y.S. (46 ksi) for the 7075-T73.

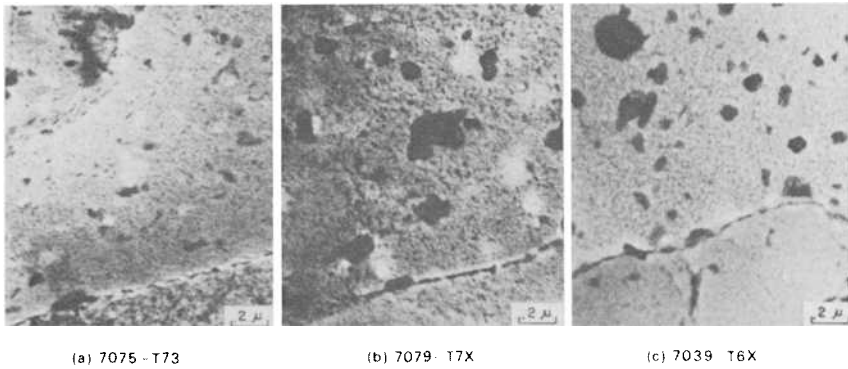


FIG. 4—Electron transmission micrographs of thin foils from thick metal sections. In all three instances there is evidence of grain boundary precipitation with precipitate-free grain margins and relatively large zones in the grain bodies. Yet the resistance to SCC in an 84-day 3.5 percent NaCl alternate immersion test varied widely: short-transverse specimens of 7075-T73 were resistant at an applied stress of 75 percent Y.S. (46 ksi), the 7079-T7X was susceptible at 75 and 50 percent Y.S. (25 ksi), and the 7039-T6X was susceptible at stresses of 75, 50, and 25 percent Y.S. (13 ksi).

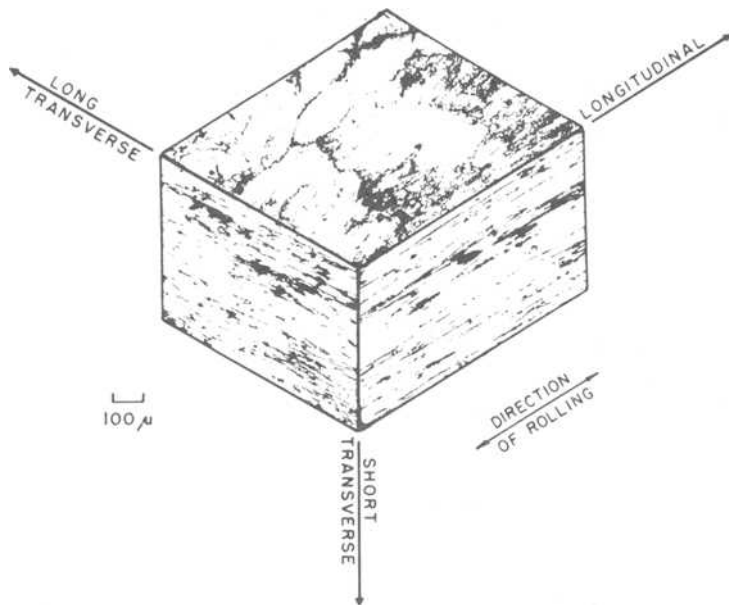


FIG. 5—Composite micrograph of the grain structure near the midplane of 1½-in. thick rolled plate of 7075-T6 alloy. The relatively long, wide, and thin fragmented (unrecrystallized) grains are typical of the grain structure of thick plate of most other commercial high strength aluminum alloys. Keller's Etch.

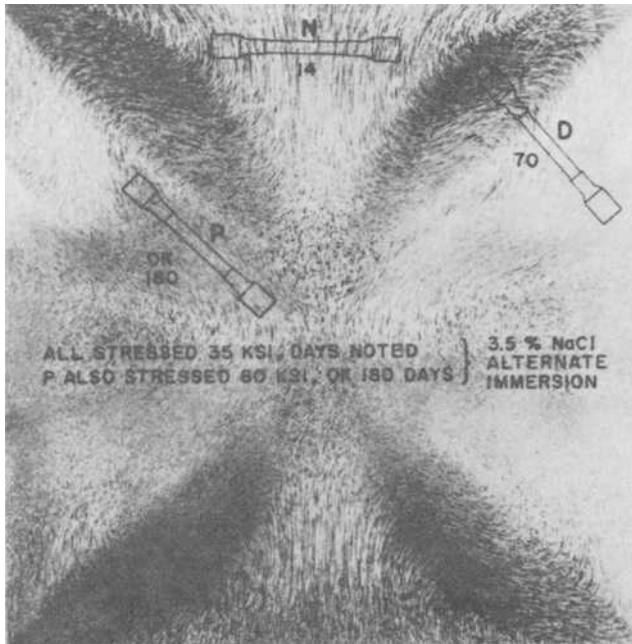


FIG. 6—Superimposed on a photograph (X0.5) of a macroetched transverse section of a special 8-in. square hand forging of 7075-T6, fabricated to produce a complex grain flow, are the outlines of three stress corrosion specimens along with their days to failure in the 3.5 percent NaCl alternate immersion. These specimens showed widely different stress corrosion resistance, as would be expected in view of their orientation to the grain structure. Noteworthy is the high order of resistance of specimen (P).

Figure 7 demonstrates that if the high degree of resistance to stress corrosion cracking in the long transverse direction of a highly oriented grain flow is sacrificed in order to improve the resistance in the short transverse direction by reducing the degree of orientation, improvement in the short transverse direction is small, whereas the threshold in the long transverse direction is decreased markedly [3].

The stress corrosion resistance in the three principal directions identified in Fig. 5 is to a great extent controlled by the morphology and shape of the grains, which in turn is related to composition and fabricating history. In conjunction with other metallurgical phenomena, the ancillary elements often have a remarkable effect upon the grain shape in heat treated wrought aluminum alloys. For example, in Fig. 8 (left) the quaternary aluminum-zinc-magnesium-copper alloy plate had equiaxed recrystallized grains [8]. The addition of 0.17 percent manganese did not appreciably change the grain shape, and a relatively low resistance to stress corrosion in all directions was

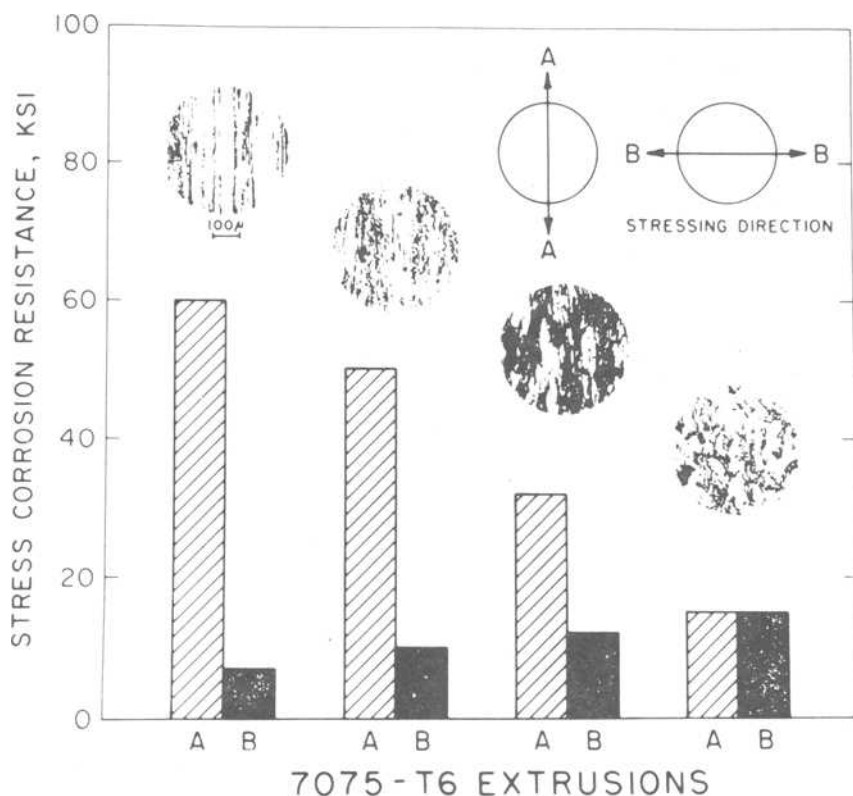


FIG. 7—The stress corrosion resistance is expressed in terms of a threshold stress (defined on page 103) determined in the 3.5 percent NaCl alternate immersion test, and the photomicrographs (Keller's Etch) show grain structures with various degrees of directionality. The micrograph at the left represents the longitudinal and the short-transverse directions relative to the grain flow. The resistance to SCC was highest when this most oriented grain structure was stressed in the (A) direction (longitudinal) and lowest when this same structure was stressed in the (B) direction (short transverse). The other three micrographs represent transverse sections. It is evident that as the degree of directionality decreases in the transverse sections (going from left to right) the increase in resistance to SCC in the (B) direction (short transverse) is small compared to the large decrease in resistance in the (A) direction (long transverse). In symmetrical round or square sections where there is neither a long or short transverse direction (micrograph at the right) there is equally low resistance to SCC in directions (A) and (B).

observed for both alloys in the T651 temper. However, the stress corrosion performance in the longitudinal direction was materially improved by increasing the manganese to 0.53 percent. It will also be noted that increasing the manganese content caused the grains to be less equiaxed and more platelike. The addition of either 0.09 percent zirconium or 0.19 percent chromium effected greater retardation of recrystallization resulting in even a more distinct platelike grain formation. This change in grain shape resulted in

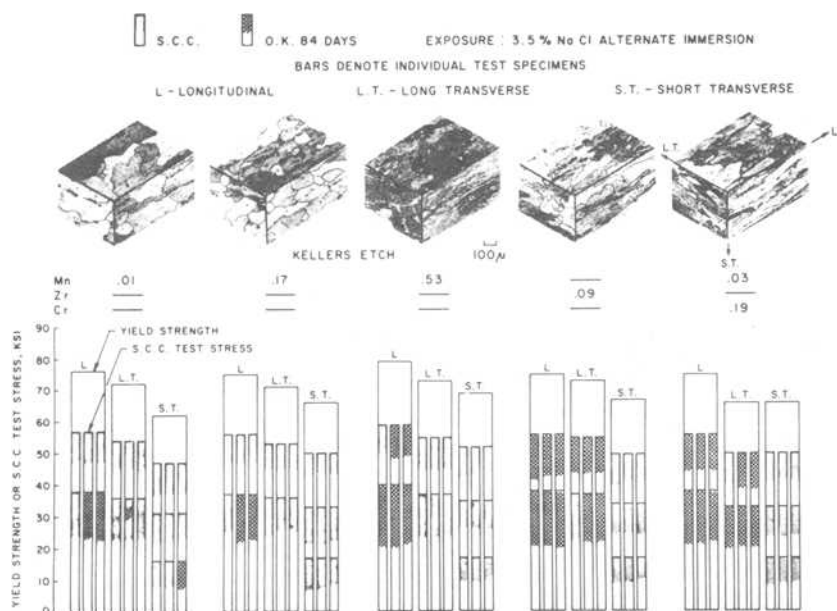


FIG. 8—Tests were made on 3-in. thick plate of five 7075-type alloys with the following composition in common: 5.59-6.05 Zn, 2.43-2.53 Mg, 1.38-1.62 Cu, 0.07-0.11 Fe, 0.05-0.06 Si. All plates were heat treated to a T651 condition with the standard practice for 7075 alloy. Note that elongated platelike grains improve stress corrosion performance in longitudinal and long transverse directions.

a further improvement in stress corrosion performance of the T651 temper, not only in the longitudinal but also in the long transverse direction.

Figure 9 shows that the difference in stress corrosion resistance between the three different directions in the five different alloys is materially reduced when the plates are artificially aged to the T7351 type temper, although the grain shape is the same as in the T651 temper. It will be noted, however, that the improvement in stress corrosion resistance is accompanied by a substantial reduction in mechanical properties.

Environmental Factors and Stress Corrosion Testing

Experimental evidence has shown that stress corrosion cracking is the result of the synergistic interaction of mechanical and oxidation reduction phenomena. That is, in combination with the mechanical processes, there is a chemical reaction that occurs on a relatively small scale that results in the oxidation of the alloy along some highly localized path, and the reduction of an element or compound in the environment. Hence, in the absence of an oxidant, stress corrosion cracking would not be anticipated; that is, if the

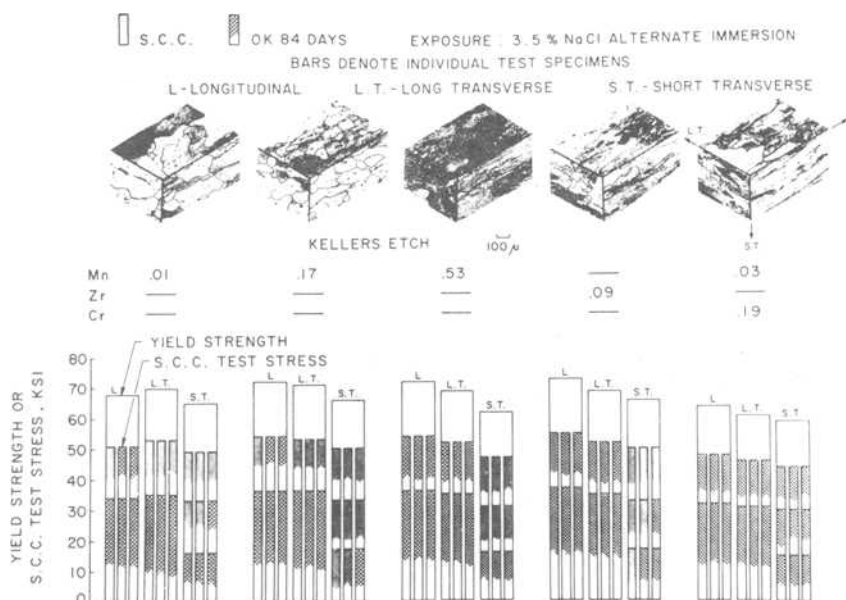


FIG. 9—Effect of grain shape of the same materials shown in Fig. 8 on the stress corrosion performance in the T7351 temper. Although there was an improvement with the T7351 over the T651 temper for all five alloys, there was also an appreciable sacrifice in yield strength associated with the T7351 temper.

environmental conditions were a vacuum or an inert gas, stress corrosion should not occur.

Most normally encountered environments will contain water (H_2O) in the form of liquid or vapor; in this sense the environment will be aqueous. In the broadest sense it need not be, but could contain other reducible inorganic or organic compounds. However, since the nonaqueous condition would represent a condition not usually encountered, the discussion will be limited to aqueous environments. Figure 10 can be used as an introduction to the effect of environment on stress corrosion specimen life [9]. Short-transverse tensile bars 1/8 in. in diameter from 3-in. thick 7039-T651 plate were exposed, stressed to 75 percent of the short transverse yield strength. Stress corrosion cracking occurred in chloride containing solutions in less than a month. Although the specimens had a life of about 10 months in a mild laboratory atmosphere, the life was on the order of about 3 days outdoors in the industrial atmosphere at New Kensington, Pennsylvania. The fact that similar specimens have not cracked after immersion for six years in a highly refined mineral oil would seem to offer sufficient evidence that an oxidant is required to cause stress corrosion cracking.

Data such as shown in the previous figure have caused some to comment that since water alone can cause stress corrosion cracking, water is a specific

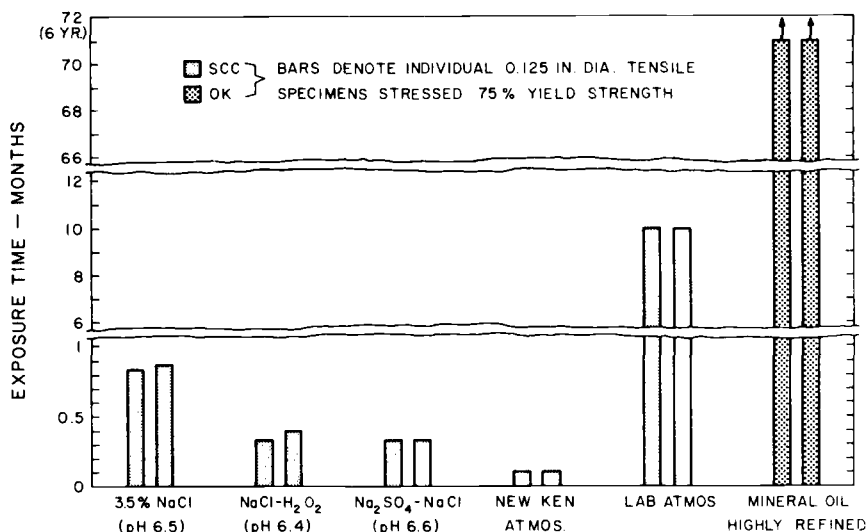


FIG. 10—Short transverse tests in 3-in. thick 7039-T651 alloy plate.

stress corrosion cracking agent [10]. Such a generalization neglects the fact that many aluminum alloys that are susceptible in aqueous chloride solutions do not stress corrosion crack in distilled water. In addition some aluminum alloys will stress corrosion crack in aqueous media, but a specific combination of additional ions or compounds must be present.

Figure 11 indicates the performance of five aluminum alloys stressed to 75 percent of their short transverse yield strengths and exposed to six aqueous solutions (pH 7). These data demonstrate that at least one out of three specimens of 7039-T63 failed in less than sixty days when exposed to one-normal solutions of NaCl, NaBr, NaI, NaF, NaNO₃ and Na₂CrO₄ [11]. In contrast 7075-T651 failed only in chloride and bromide solutions and the 2219-T37 failed only in the chloride solution. It is noteworthy that the 2219-T87 and the 7075-T73 did not stress corrosion crack in any solution. Thus, the effects of the specific nature of the environment can vary with alloy composition and temper.

This type of information becomes important in devising suitable accelerated stress corrosion tests for evaluating the stress corrosion susceptibility of new aluminum alloys and tempers. Many types of accelerated stress corrosion test media have been used for investigating the resistance to stress corrosion cracking of aluminum alloys [12, 13], most of which utilize sodium chloride solutions in some way. A test procedure that has found widespread usage involves alternate immersion in 3.5 percent sodium chloride solution. This test has been used for many years at Alcoa Research Laboratories and has been found to correlate well with outdoor atmospheric environments for most

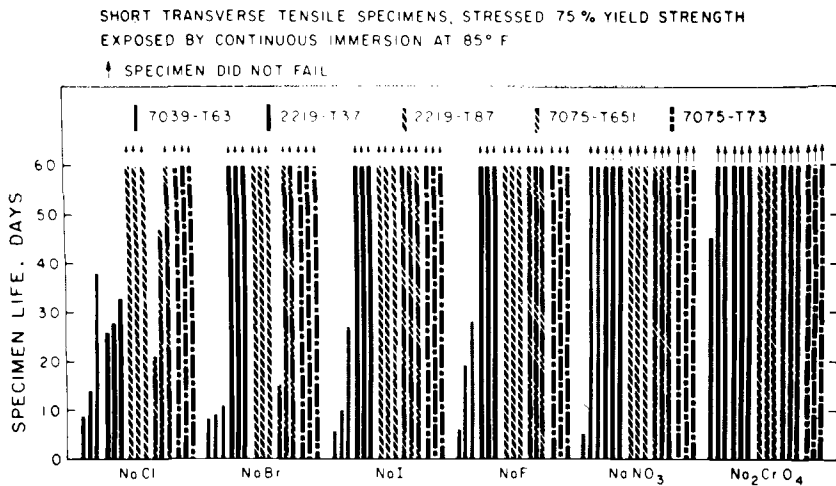


FIG. 11—Stress corrosion cracking of aluminum alloys in neutral aqueous solutions.

types of aluminum alloys. The alternate immersion cycle used is one hour, with a 10-min period of immersion followed by 50 min of drying in air. The 3.5 percent NaCl solution was made with sodium chloride of 99.7 minimum percent NaCl, 0.1 maximum percent NaI plus City of New Kensington tapwater containing <200 ppm total solids. The solution pH ranged between 6.4 and 7.2. Evaporation losses were made up regularly by the addition of tapwater, and a change of solution was made each month. The alternate immersion apparatus (illustrated in Ref 7) is located indoors with ambient temperature and humidity of the laboratory atmosphere. The various 3.5 percent NaCl alternate immersion test data presented in this paper were obtained under the above conditions. The current practice is to make the salt solution with A.C.S. Reagent Grade Sodium Chloride and deionized water, and to perform the test in a room with the atmosphere controlled at 27 ± 1 C (80 ± 2 F) and 45 ± 6 percent relative humidity, per Federal Method 823.

The variability that may be obtained in results with this test even under the more closely defined and controlled conditions stipulated in Method 823 of Federal Test Method Standard 151b and now used in many laboratories was discussed by Craig et al [14] and Sprowls [15].

While the 3.5 percent NaCl alternate immersion test is a reliable test for most types of aluminum alloys, it has been shown to be not as critical as exposure to an industrial atmosphere for Al-Zn-Mg alloys containing less than about 1 percent copper [14, 16, 17]. In Fig. 12 is shown an example in which the relative susceptibility to stress corrosion cracking of 7039 alloy in two tempers in New Kensington atmosphere was not reliably predicted by a

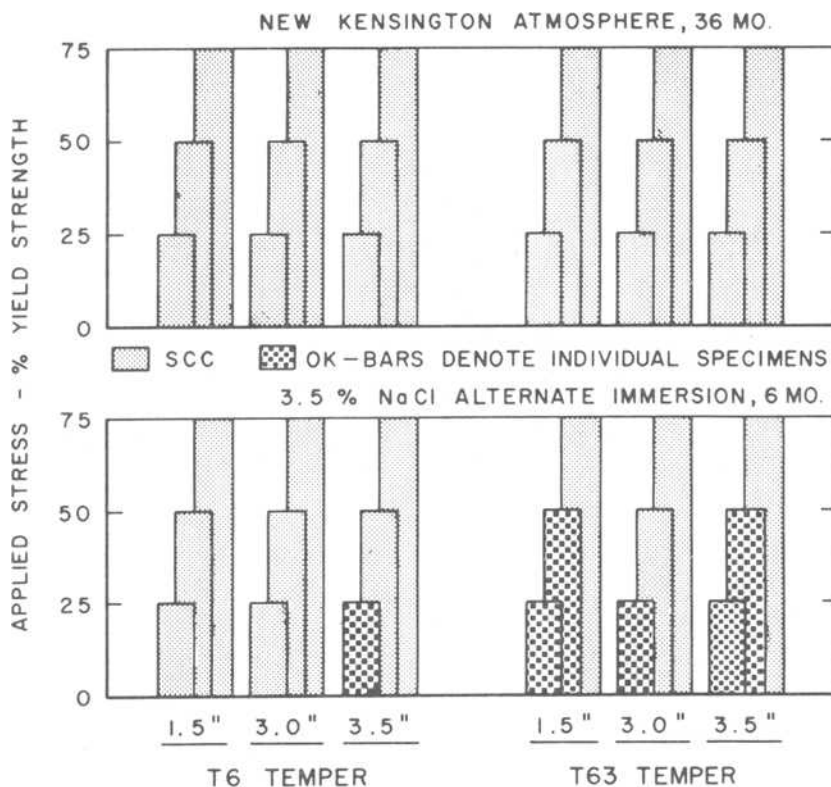


FIG. 12—Comparison of 7039-T6 and 7039-T63 alloy plate.

6-month exposure to the test conditions described above. Further consideration of the 3.5 percent NaCl alternate immersion test is given in the next section.

The stress corrosion performance in an unusual environment emphasizes the significance of the specificity of the environment required in some instances to cause stress corrosion cracking. Figure 13 illustrates a high resistance to stress corrosion cracking of 7075-T7351 in NaCl and the relatively low resistance of 2024-T351 in the same medium. However, there resulted a strikingly different behavior when the environment was inhibited red fuming nitric acid at 75 C (165 F). In this instance stress corrosion cracking did not occur in the case of 2024-T351, whereas 7075-T7351, normally considered highly resistant, failed. Further emphasis of the specificity of the environment was shown by the fact that 7075-T651 was susceptible in both media and 2024-T851 was resistant in both media.

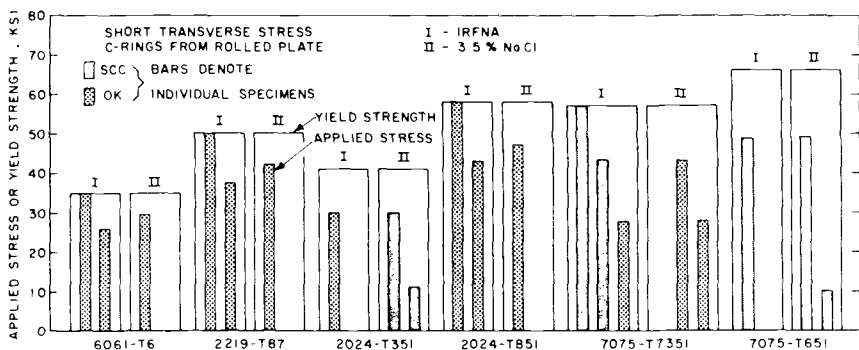


FIG. 13—Comparison of resistance to stress corrosion cracking of various alloys in inhibited red fuming nitric acid at 165 F and in 3.5 percent NaCl alternate immersion.

Stress Corrosion Threshold Stress (Intensity)

Most investigators agree that for stress corrosion cracking to occur, tensile stresses at the surface of the alloy are required. Furthermore, most investigators agree that the tensile stresses must be sustained for relatively long periods of time. It is important to realize that these surface tensile stresses must be present for sufficient duration to permit relatively slow chemical or electrochemical reactions or both to occur. Since in general terms the rate of growth of a purely mechanically produced fracture is much more rapid than rates of reaction between chemicals and alloys, it becomes almost obvious that the tensile stress must be of prolonged duration to permit the chemical and mechanical phenomena to produce their mutual interaction. One of the most useful methods of describing the susceptibility (or the resistance) of an alloy and temper to stress corrosion cracking is in terms of a "threshold" stress. The "stress corrosion threshold" usually is defined as the lowest value of sustained tension stress that will cause stress corrosion cracking under given test conditions (the implication being that stresses below the threshold are safe stresses). The actual existence of a threshold stress for the stress corrosion cracking of a highly susceptible material remains controversial because it is difficult to obtain experimental proof. However, it is unnecessary to resolve this point for the purpose of conducting stress corrosion cracking tests to predict the serviceability of an alloy and to compare the resistance to stress corrosion cracking of one alloy with another. Physical limitations of test equipment govern the accuracy with which a stress corrosion cracking "threshold stress" can be determined; and the selection of test environment, type of test specimen, method of loading, and duration of test determine the magnitude of the "threshold." Therefore, in dealing with threshold stresses, the specific test conditions must be associated with the threshold stress data.

The procedure for determining a threshold stress is illustrated in Fig. 14 by the data obtained for the relatively new stress corrosion resistant T76 (T76510, etc.) temper for 7075 and 7178 alloy products. Test specimens loaded to various stress levels are subjected to a suitable corrosion test, and a stress corrosion cracking threshold stress, as indicated tentatively by the dashed lines, is estimated.

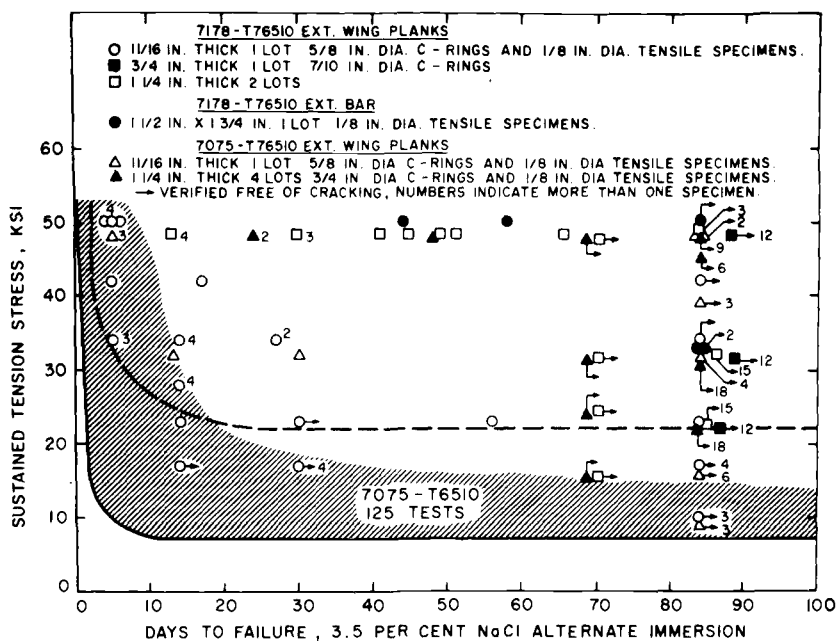


FIG. 14—Specific test data for the relatively new stress corrosion resistant T76 (T76510, etc.) temper for 7075 and 7178 alloy extrusions were plotted on the background of test data defined by the cross-hatched area for the established 7075-T6510 material. The dashed line was drawn to indicate an estimate of the highest sustained tension stress at which short transverse specimens would not stress corrosion crack in the 3.5 percent NaCl alternate immersion test.

Figure 14 also compares the stress corrosion cracking of 7075-T76510 and 7178-T76510 extrusions with 7075-T6510 (one of the older tempers for this alloy) stressed in the short transverse direction relative to grain flow. This information showed that in a large number of tests if a stress of about 7 ksi was exceeded in the short transverse direction, stress corrosion cracking of 7075-T6510 was likely to occur. However, a limited number of tests made on extrusions in the new T76510 temper show that no stress corrosion cracking occurred until a stress of 25 ksi was exceeded. It is also important to note that 7178-T76510 has a tensile strength almost the same as 7075-T651.

It has been established through many years of stress corrosion testing 7075 and 7178 alloy products that the results of an 84 day alternate immersion test in 3.5 percent NaCl predict reliably the performance to be expected after extended exposure to a seacoast atmosphere [7]. Although there is a greater incidence of stress corrosion cracking failures of specimens of these alloys in the 84 day alternate immersion test than in long time exposures to an industrial atmosphere, the 3.5 percent NaCl alternate immersion test nevertheless can be considered an excellent testing procedure for predicting stress corrosion performance both in seacoast and industrial atmospheres. The relationship of this laboratory stress corrosion test with atmospheric service type environments is shown by an examination of the data in Fig. 15.

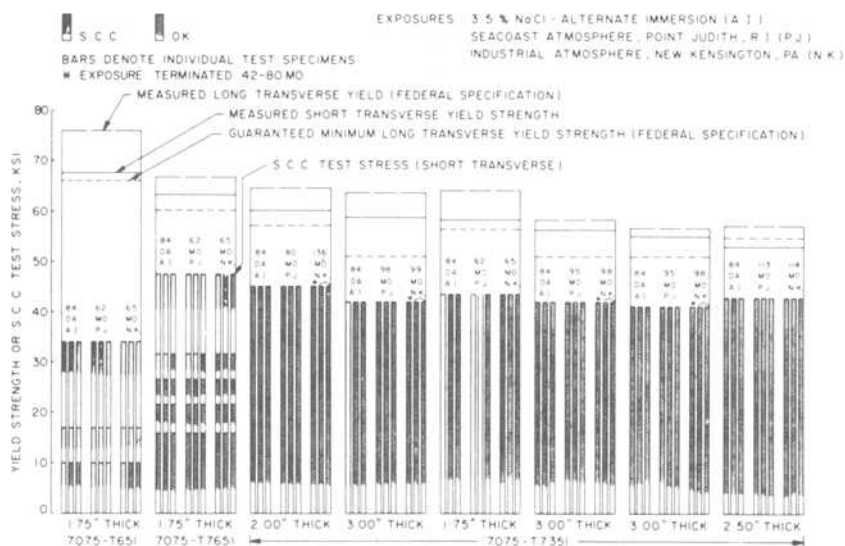


FIG. 15—Effect of temper on yield strength and stress corrosion performance—short transverse stress.

Attempts to correlate the stress corrosion resistance of aluminum alloys with various mechanical properties have been unsuccessful. For example, there is little support for a generalized relationship between tensile strength or fracture toughness and the resistance to SCC. Although Fig. 16 suggests a possible relationship between the stress corrosion threshold in the longitudinal direction and the tensile yield in this direction, certainly no relationship exists between these characteristics when data for the short transverse direction are examined.

Likewise, data in Fig. 17 comparing measurements of fracture toughness, as determined by unit propagation energy or tear strength yield strength ratio,

with SCC threshold stress does not indicate a simple relationship between these characteristics.

Stress Intensity – Fracture Mechanics Analyses

After a sharp notch resulting from a corrosion fissure or a minute stress corrosion crack has initiated in a stressed specimen or component, there is developed at the tip of the fissure or crack a highly localized concentration of stress that is difficult to quantify with a high degree of accuracy. The magnitude of the concentrated stress can be large and becomes of more significance to the initiation and propagation of a stress corrosion crack than is the nominal stress. Thus, while the nominal stress may be related to the initiation of stress corrosion and of stress corrosion cracking, the concentrated stress at the tip of the incipient fissure or crack may relate more directly to the propagation of a crack. From the viewpoint of fracture mechanics, considerable significance is ascribed to the stress situation in the vicinity of a stress concentrator, and this stress situation generally is characterized by a "stress field intensity factor" [18]. This term, denoted K_I , is the quantity representing the combined effect of crack (fissure, or flaw) dimensions and nominal stress field which influences the mechanical behavior of the crack. If the initiation and propagation of a stress corrosion crack is considered as a form of "subcritical flaw growth," then it is appropriate to inquire whether or not the mechanical aspects of stress corrosion cracking are better characterized by the gross section (nominal) stress or the local stress at the tip of a fissure, as described by the stress intensity factor.

Because of the relatively long periods of time required (and often the uncertainty) to develop stress concentrators, many investigators have turned to the use of "precracked" specimens and the use of fracture mechanics analyses of the stress intensities [19]. Stress corrosion evaluations of alloys with stress intensity concepts were first found to be advantageous for ferrous and titanium alloys. Considerable work is currently in progress in various laboratories to determine the merit of this method of testing aluminum alloys [20-23]. The most promising procedure for comparing aluminum alloys and tempers appears to be by the use of diagrams of stress corrosion crack propagation rate versus applied stress intensity as shown in Fig. 18 from the work of M.V. Hyatt [21]. Although the full diagram is required to describe the performance of an alloy, numbers derived from the diagrams, such as the "highest sustained crack propagation rate at a specified range of stress intensity" and the "threshold stress intensity factor" can be used to make comparisons [23, 24].

Service Performance

The sources of sustained tension stresses at the surface that cause stress corrosion cracking in aerospace structures rarely result from operating loads

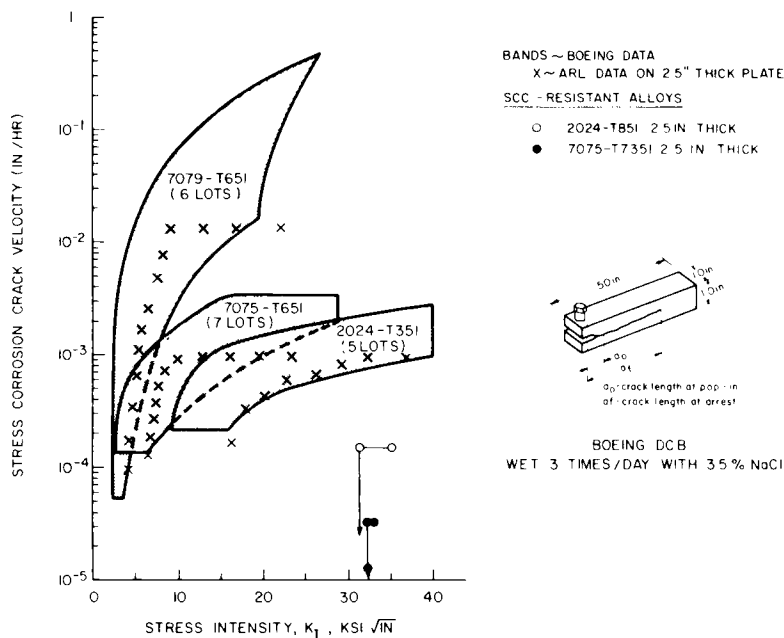


FIG. 18— K_I -rate data for short transverse (S-L) tests of plate 1 to 4.5-in. thick.

that are anticipated in the design. The stresses anticipated by the designer are usually sufficiently low, and the loads resulting from operating conditions are usually of such short duration in aircraft that stress corrosion cracking is not a result. Practically all difficulties encountered by stress corrosion cracking result from stresses that are not anticipated or considered by the designer. Hence, the main problems created by stress corrosion cracking result from tensile stresses that are introduced during fabrication of a part, during heat treatment of a part, or during the assembly of parts.

Forming, swaging, joggling, and bending are fabrication operations that can leave residual tensile stresses on local areas of the alloy surface of sufficient intensity to permit stress corrosion cracking to occur in a susceptible alloy if the service environment is of that particular specific composition as to permit stress corrosion fissures to develop. An example of stress corrosion cracking of a tube of 2024-T3 alloy that has been swaged at room temperature is shown in Fig. 19. The problem could have been prevented by either one of two ways. One way would have been to artificially age the swaged 2024-T3 tube to the T81 temper. Although the stresses would be slightly reduced by artificial aging, they would still remain at a substantial level. However, the T81 temper is resistant to stress corrosion cracking in most natural or service environments. Another approach would have been to swage the 2024 tube in the O temper and heat treat after swaging to the T42 temper. Care must be

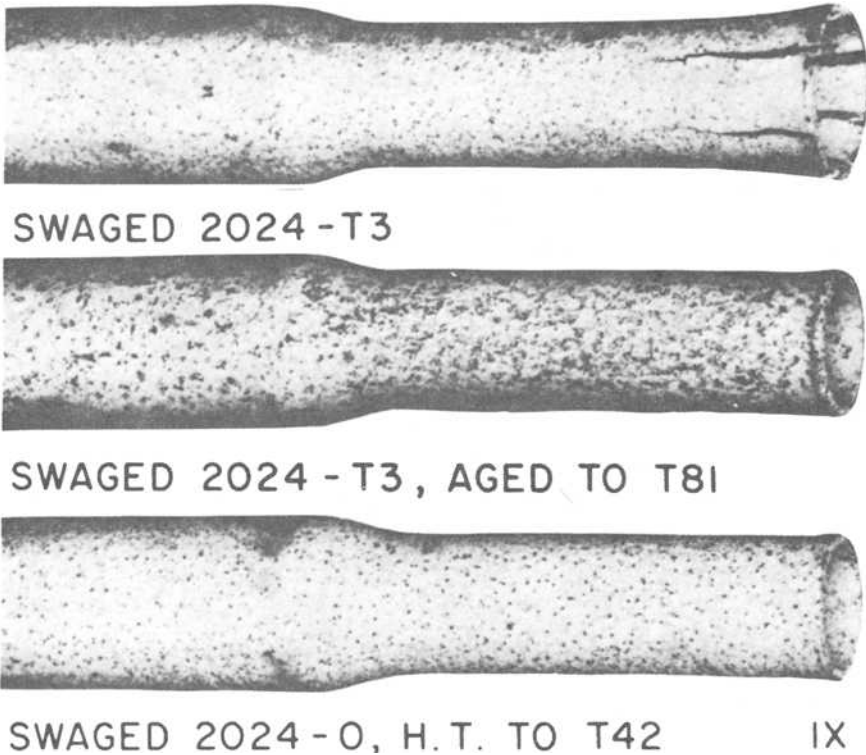


FIG. 19—Swaged tube ends of various tempers of 2024 alloy exposed to 3.5 percent NaCl solution by alternate immersion for 84 days. (Corrosion products chemically removed after exposure).

exercised in the latter approach to be sure excessive grain growth does not occur on post-swaging heat treatment.

Quenching from the solution heat treating temperature can introduce sufficient residual tensile stresses in a part to result in stress corrosion cracking. Although the portion of the part that is in tension generally is below the surface of the part during the quenching operation, machining operations can expose surfaces that have sufficiently high residual tension stresses to cause stress corrosion cracking. This is especially true where the direction of the tension stress is normal to the direction of grain flow, for example, the parting plane region of a die forging. Figure 20 is a photograph of a machined die forging of 7075-T6 alloy after exposure to the 3.5 percent sodium chloride alternate immersion test. Note the stress corrosion crack in the hollow machined boss. This crack is parallel to the metal flow lines of the parting plane and, hence, is a short transverse failure, and reproduces the failure of such a part in service. Since some reduction in mechanical properties

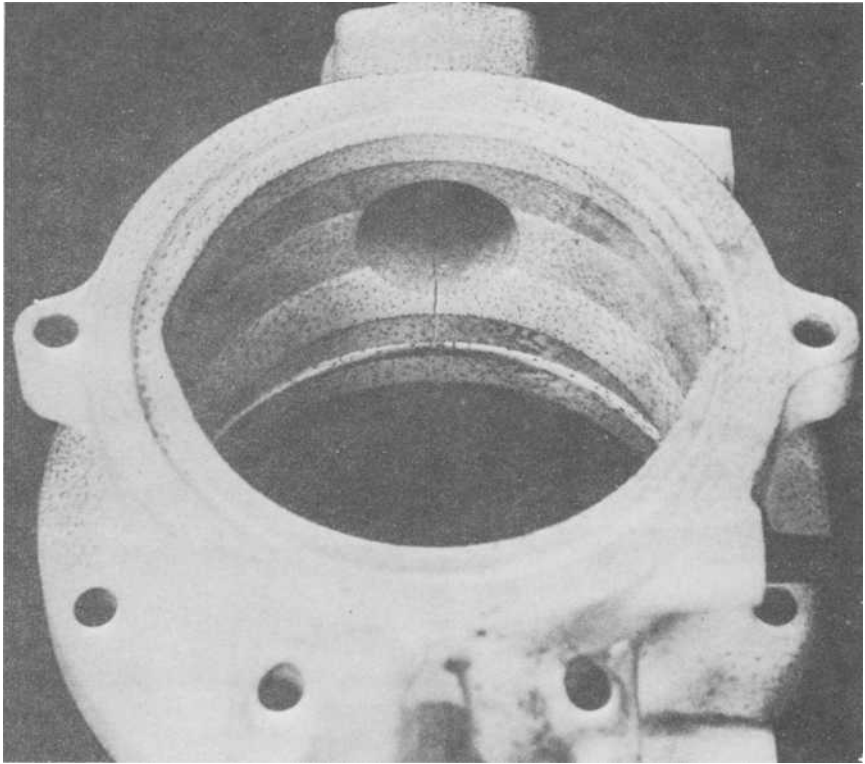


FIG. 20—Machined die forging of 7075-T6 alloy showing extent of cracking into forward boss after an exposure of 18 days in the 3.5 percent NaCl solution by alternate immersion. This crack is parallel to the metal flow lines of the parting plane and hence is a short transverse failure (Magnification approximately $\times 1$).

was acceptable, the part was changed to 7075-T73. This material with a high resistance to stress corrosion cracking (that is, a high threshold stress level, even in the short transverse direction), did not suffer this type of failure, as illustrated in Fig. 21. Other methods needed to control stress corrosion of such a part will be discussed later.

Assembly stresses, such as misalignments between holes of two parts joined by fasteners, interference fits caused by inadequate tolerance control, the use of tapered fasteners without sufficient dimensional control, etc., are examples of the manner in which residual tensile stresses can be introduced during shop assembly. Figure 22 shows a drawn tube of 7075-T6 alloy into the end of which solid aluminum alloy plugs were interference fitted. The forcing of the plugs created a circumferential sustained tensile stress in the wall of the 7075-T6 tube. Delayed cracking developed in the wall of the tube. A microscopic examination showed it to be a typical intergranular stress

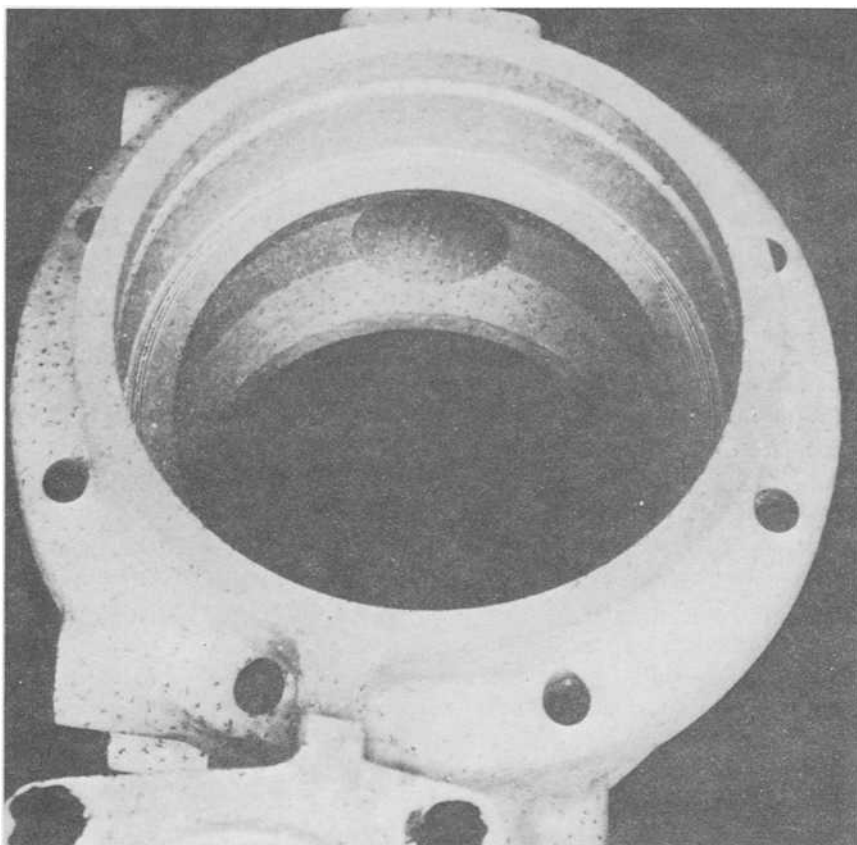


FIG. 21—Machined forging of 7075-T73 alloy similar to the 7075-T6 in Fig. 20 showed no evidence of cracking after an exposure of 30 days in the 3.5 percent NaCl solution by alternate immersion. Magnification approximately X1.

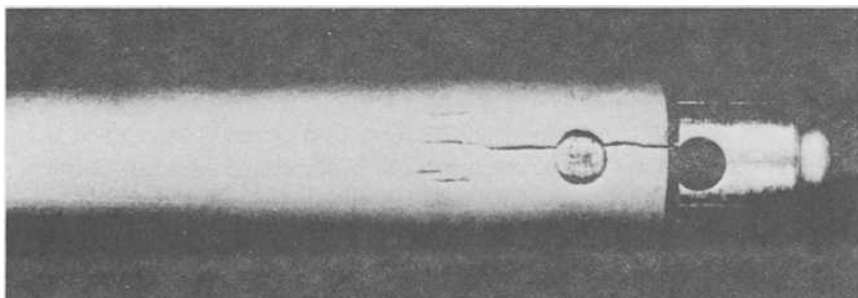


FIG. 22—Anodized 3/4 in. OD X 0.050 in. wall 7075-T6 drawn tube containing pressed-in plugs stress corrosion cracked in service. Photo shows plug partially withdrawn. (X1).

corrosion crack. The use of an alloy having a higher stress corrosion resistance in natural environments, such as 7075-T73 or 2024-T81, would have avoided the problem. In order to use 7075-T6 drawn tube, it was necessary to more carefully control the tolerances between the inside diameter of the tube and the outside of the plug in order that circumferential tensile stresses be held at a relatively low level.

Minimizing Stress Corrosion Cracking Difficulties

Stress corrosion cracking problems with aluminum alloys can be avoided by careful attention to the manufacturing methods employed, by the choice of alloys and tempers, and by the adherence to sound design and assembly practices that are based on an understanding of stress corrosion facts and mechanisms. The reliability of this statement is proven by the widespread use of the high strength aluminum alloy 2024 in the T3 and T4 tempers. Although certain products of this alloy, for example thick plate in these tempers, are known to have an appreciable susceptibility to stress corrosion cracking, they have been used for many years with only rare instances of stress corrosion problems. Those relatively few stress corrosion problems that have been encountered have resulted from a lack of appreciation of stress corrosion knowledge and experience.

Table 3, in outline form, lists the items that must be considered in stress corrosion cracking and the steps that can be taken to avoid this type of failure.

Stress Relieved Products

It is good practice to use stress relieved products wherever possible. As discussed previously, if the alloy and temper to be used are known to have an appreciable stress corrosion cracking susceptibility, manufacturing methods, such as the swaging operation previously discussed, should be avoided. Obviously the benefits of stress relieving will be lost if procedures, such as swaging, power bending, and installation of interference fitted parts are performed after the stress relief treatments. Products such as extrusions, rolled rod, rolled bar, tube, and plate are stretched (and hence straightened) in order to minimize residual stress gradients. Likewise, hand forgings and die forgings are cold pressed to minimize quenching stresses. Mild and less drastic quenches may be used under some circumstances to minimize residual quenching stresses, but such processes may introduce other problems and should not be used without very careful evaluation. Thermal stress relief treatments generally are not employed for heat treated aluminum alloys because they lower the mechanical properties.

Fabricating and Assembly

Jogging, swaging, or cold drawing will cause high residual tensile stresses.

TABLE 3—*Minimizing stress corrosion cracking.*

I.	Minimize the Magnitude of Residual Tension Stresses
(a)	Manufacturing Methods
(b)	Quenching
(c)	Design – Interference Fits
(d)	Assembly – Misfits
II.	Stress Relief
(a)	Thermal Treatments
(b)	Introduce Surface Compressive Stress – Peening
III.	Selection of Resistant Material
(a)	Composition
(b)	Product
(c)	Metallurgical Condition
IV.	Organic Coatings
V.	Cathodic Protection
(a)	Clad Alloys
(b)	Coatings – Hot Dip, Electroplate, Metallize

Such operations should be carried out prior to solution heat treatment. (The latter relaxes the residual stresses.) If because of certain metallurgical problems this approach is not feasible and the material must be processed in the solution heat treated condition, the product should be artificially aged to a more stress corrosion resistant temper, such as T81 or T73. Misfits, as when fastener holes in two mating parts do not match, or interference fits created by bushing components, can be a source of high sustained surface tensile stresses. If service conditions anticipate the need for a particular set of mechanical properties, and these can only be attained with an alloy of low stress corrosion resistance, better fitting up must be achieved (for instance, by reaming the fastener holes) or better control of tolerances in the interference fits.

Shot Peening

Machining of the external surface of heat treated parts that were not stress relieved will cause readjustment of the stress distribution, thereby risking the

product, for example, by using die forgings (especially precision die forgings) whereas machining the part from a hand forging or extrusion may require stressing normal to the grain flow direction. A guide for the selection of the most stress corrosion resistant alloys and tempers is given in Table 4.

An efficient method of preventing stress corrosion cracking is the use of alclad products. Since alclad products consist of a high strength aluminum alloy core metallurgically bonded to a surface layer of another aluminum alloy that will electrochemically protect the core, it is obvious that the surface layer should not be removed by machining. Most widely used alclad products are in the form of sheet and plate with cladding on one or both sides [4]. Other products of irregular contour, such as forgings, can have surface layers of a more anodic potential than that of the alloy applied by hot dipping, by electroplating, and by metallizing processes. Coatings, such as those applied by electroplating and metallizing, have proven to be the most beneficial and practical.

Summary

1. Stress corrosion cracking is defined in this paper as cracking that is initiated by directional chemical or electrochemical attack or both, synergized by sustained tensile stress at the surface.

2. Stress corrosion cracking results when the following four agents are present simultaneously:

- a. an enduring tensile stress at exposed surfaces,
- b. a specific composition,
- c. a unique microstructure, and
- d. a corrosive environment of a specific nature.

3. Service failures of aluminum alloys by stress corrosion cracking have been infrequent. These are generally caused by sustained surface tensile stresses introduced by certain fabrication or assembly procedures. Relief of surface stresses by peening or rolling may be effective. If it is not possible to avoid these stresses through control of fabrication and design practice, a change of alloy or temper is recommended.

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TABLE 4—Comparisons of the resistance to stress corrosion of various alloys and products.

Estimate of the Highest Sustained Tension Stress (ksi) at Which Test Specimens of Different Orientations To The Grain Structure Would Not Fail in the 3 1/2 Percent NaCl Alternate Immersion Test in 84 Days.^d

Alloy and Type of Temper	Test Direction	Plate 0.25 in.-3 in.	Rolled Rod and Bar	Extruded Shapes Section Thickness		Forgings
				0.25 in.-1 in.	1.25 in.-3 in.	
2011-T3	L	...	25	...	...	...
	T	...	10 ^b	...	...	...
-T8	L	...	>40	...	...	...
	T	...	>30 ^b	...	...	...
2014-T6	L	45	45	50	45	30
	LT	30	...	27	22	25
	ST	<8	15 ^b	...	<8	<8
2219-T8	L	>40	...	>35	>35	>38
	LT	>38	...	>35	>35	>38
	ST	>38	...	...	>35	>38
2021-T8	L	>48	...	>48	>46	>42
	LT	>46	...	>46	>45	>40
	ST	35	...	...	>45	35
2024-T3, -T4	L	35	30	>50	>50	...
	LT	20	...	37	18	...
	ST	<8	10 ^b	...	<8	...
-T8	L	>50	>50	>60	>60	>43
	LT	>50	...	50	50	43
	ST	30 ^c	>43	...	>45	15
7005-T53	L	...	>48, (>48) ^a	>48, (>48) ^a	>48, (>48) ^a	...
	LT	...	>48, (>45) ^a	>42, (35) ^a	>42, (35) ^a	...
	ST	...	...	15, (10) ^a	15, (10) ^a	...

7039-T63	L	>42, (>42) ^a	...	...	...	...
	LT	40, (35) ^a	...	...	...	...
	ST	10, (<8) ^a	...	...	...	...
7075-T6	L	50	50	60	60	35
	LT	45	...	50	32	25
	ST	<8	15 ^b	...	<8	<8
-T73	L	>50	>50	>54	>53	>50
	LT	>48	>48	>48	>48	>48
	ST	>43 ^c	>43 ^c	...	>43 ^c	>43 ^c
-T76	L	>49	...	>52	...	...
	LT	>49	...	>49	...	...
	ST	25	...	25	...	...
...	...	...	...	...	...	...
	...	...	...	...	...	...
	...	...	...	...	...	...
7178-T6	L	55	...	65	65	...
	LT	38	...	45	25	...
	ST	<8	...	...	<8	...
7178-T76	L	>52	...	>55	...	...
	LT	>52	...	>52	...	...
	ST	25	...	25	...	...
7079-T6	L	>55	...	>60	>60	>50
	LT	40	...	50	35	30
	ST	<8	...	...	<8	<8

^aSpecimens exposed in New Kensington Atmosphere which for these alloys provides more realistic values than alternate immersion in 3 1/2 percent NaCl.

^bRatings are for transverse specimens machined from round or square bar stock.

^cThese values will be lower for sections greater than 3 in. thick but will be at least equal to 75 percent of the guaranteed Y.S.

^dUpdated revision of table first presented in Ref 7.

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Overview of Corrosion Cracking of Titanium Alloys

REFERENCE: Feige, N.G. and Covington, L.C., "Overview of Corrosion Cracking of Titanium Alloys," *Stress Corrosion Cracking of Metals—A State of the Art*, ASTM STP 518, American Society for Testing and Materials, 1972, pp. 119-130.

ABSTRACT: Titanium depends upon the protective nature of a surface film, essentially an oxide, for its corrosion protection. Stress corrosion cracking results when the local breakdown of that film occurs causing a significant shift in the composition of the electrolyte and establishing electrochemical currents in the restrictive area which combine to prevent repassivation of the site.

Extensive testing has been conducted to define the threshold stress (K_{ISCC}) to sustain the electrochemical reaction. A large variation is seen between alloy, heat treatment, and mill conversion practice which can be related back to the notch and its strain conditions and the sensitivity of the alloy to the electrolyte present in the notch area. It has been demonstrated by rapid freezing of the reaction site that the electrolyte is a highly acidic reducing environment, and is in such a region of the Pourbaix diagram that the passive film will not reform. The electrochemist can further define the alloys susceptibility by evaluating the anodic current density in the pit area to sustain pitting and the cathodic current density to charge hydrogen. The pH of the electrolyte controls the hydrogen uptake efficiency at the cathodic site. Hydrides, formed at the local cell cathodic site under subsequent anodic control will react and pit at low anodic current density.

Stress corrosion cracking in the titanium alloys is the ability of the structure or test configuration to sustain by a moving crack front an actively corroding local site of a nonpassivating electrolyte. The classical argument as to whether the halogen or hydrogen are the cracking species is obscure, as both are interacting to sustain the reaction.

KEY WORDS: stress corrosion cracking, titanium alloys, cracking (fracturing), electrolytes, pitting, electrochemistry, corrosion protection, passivity, pH, fatigue (materials), environmental tests

Background History

Titanium is an inherently active metal which forms a thin passive film which is protective and self healing in many environments. The apparent stability and integrity of this film in the classic stress corrosion environment

¹Titanium Metals Corporation of America, West Caldwell, N.J.

which promptly failed the common structural materials, gave confidence to early corrosion investigators [1]. The first problem reported from the laboratory was anhydrous red fuming nitric acid. This was followed shortly by hot salt stress corrosion cracking of Ti-5Al-2.5Sn in the manufacture of welded titanium components [2]. Highly stressed, welded fabrications were cracking in the stress relief cycles. A simple thermal test treatment (1400 F zero time anneal) plus stringent controls on chloride contamination of parts eliminated the commercial problem. The industry failed to heed this warning and complacently held to the theory of the impregnability of the passive film.

In 1964 Dr. F. Brown of the Naval Research Laboratory burst the bubble when a candidate submarine hull material and a highly promising aircraft frame alloy were tested as a fatigue notched cantilever beamed specimen immersed in sea water and demonstrated a 66 percent drop-off in load carrying ability [3-4]. In early 1965 a slight change in the manufacture of nitrogen tetroxide caused a rash of failures of aerospace pressure bottles in the Ti-6Al-4V alloy [5]. The last remaining vestiges of its immunity were destroyed when in 1966 a Ti-6Al-4V alloy tank containing methanol failed catastrophically while under sustained load test with the resulting spectacular explosion destroying a significant quantity of expensive aerospace components [6].

By early 1967 the technical literature was filled with numerous reports characterizing the limits of these reactions, and the titanium industry was filling in the data on susceptible alloys and corrective manufacturing steps and heat treatments [7-12]. In the meantime, out in the field few failures could be located. This appeared to be based upon a combination of designer conservatism, and extensive laboratory testing of this late arriving industrial metal prior to any commercial application in the susceptible environments.

By late 1967 the characterization of commercial alloys was complete and the environmental limits and alloy limits were well documented [13-17], and the problem returned to the fundamental research laboratories for further probing into the specifics of the highly complex series of events which occur under the general term "stress corrosion cracking of titanium" [18].

The results of this fundamental laboratory work on aqueous stress corrosion are now becoming available in reports emulating from the ARPA Program [19], with a very good review of the status of the work presented in January 1971 in Atlanta, Ga. and reviews work done in organics and hot salt corrosion which have been published by V.C. Peterson [20] and A.J. Sedriks and J.A.S. Green [21]. Based upon this extensive effort a clear picture can be obtained delineating the limited threshold condition required to observe cracking in titanium base alloys.

The effect of six years of intensive effort has reestablished the confidence in the immunity of titanium to attack by unexpected stress corrosion cracking, and in the process has significantly modified alloy development research and mill conversion practices to minimize concern in industrial and aerospace usage of the material.

Environments of Concern

The environments which cause cracking can be categorized according to the different modes of failure thus:

1. The environment actively reacts with titanium and will dissolve the passive film. Cracking is occurring because the passivating agent (generally water) has passivated in excess of 95 percent, but less than 100 percent, of the exposed surface.

Hot molten salt

Dry chlorine gas, below 3 percent water content

Hydrochloric acid, 2 to 5 percent

Red fuming nitric acid

Sulfuric acid, 3 to 7 percent

Nitrogen tetroxide, below 1 percent water content

Methyl alcohol, below 1 percent water content

Ethyl alcohol, below 1 percent water content

Certain organic chlorides and bromides

Low melting point metals, above 750 F

2. The environment actively reacts with titanium but will only very slowly dissolve the passive film. Cracking occurring because the film is broached with time at a local upset on the surface or crevice which changes the environment locally to prevent repassivation of the film.

Hot salt crystal layer (above 525 F)

Hot brine solutions (above 200 F in commercially
pure titanium, as low as 140 F in high aluminum
content titanium-base alloys)

3. The environment actively reacts with titanium but will not dissolve the passive film. Cracking is occurring because the film is mechanically broached within a fine crack isolated from the bulk environment and has temporarily changed the local environment in the crack into the acid reducing active range. The crack is moving at a sufficient rate because of stress to prevent diffusion of the bulk electrolyte into the crack to extinguish the electrochemical reaction.

Chloride solutions at room temperature

Bromide solutions at room temperature

Iodide solutions at room temperature

Sea water

Liquid metals, below 750 F (titanium reacting
with the metal)

Low melting point metals, below 750 F (titanium
reacting with the metal)

In all of the above cases of stress sensitivity to the environment an active, highly local electrochemical reaction is occurring in an area where the passive

film has been broached. To mitigate attack one can alter the electrochemical reaction by surface films, alloy changes, or changes in the electrolyte. The rate controlling reaction, be it dissolution of titanium, ingress of hydrogen, or diffusion of electrolyte, determines the corrective action to be taken to stop the stress/chemical induced metal cracking.

The Electrochemical Aspects of Pitting Attack

In all environments, with the possible exception of liquid metals, an electrochemical reaction sustains the cracking. In the case of titanium the film is broached in a very limited area and an intense reaction occurs. The continuance of attack is dependent upon the ability of the film to repassivate in the environment or for the additional cracking to occur and extend the fresh surface exposed to the environment. A simple series of laboratory tests will record film cracking and repassivation in sea water in dynamically loaded, fatigue cracked specimens [22]. The second significant observation is that the pH in the pitting area is often greatly different from the pH in the bulk corrodent [7]. This difference is not surprising in view of the fact that the corrodent in filling the cavity has moved past the cracked walls which at some stage were active. Sophisticated laboratory techniques of freezing the electrolyte in place in liquid nitrogen during active pitting have demonstrated a chromatography column of varying pH and metal cations in which the extreme tip of the crack is in an active corroding region (Fig. 1) [23], (Fig. 2) [25]. In this caldron one can predict anodic dissolution and hydride formation occurring simultaneously in the tip region with only a small portion of the overall reaction occurring between the active pitting region and hydrogen reduction on the exposed passive surface film. To stop stress corrosion cracking one must extinguish this reaction.

There are at present a variety of techniques available to both the alloy developer and the designer which extinguish the reaction. Keeping in mind that selective anodic pitting and hydrogen embrittlement are occurring simultaneously within the crack, and that to stop the total reaction only one side of the electrochemical cell need be altered to modify the reaction.

Under class one the initial approach is to modify the corrodent to passivate the balance of the surface. In organic environments additional water and reduced halogens are suggested. The classic example is red to green N_2O_4 — increased water levels by less than 1 percent passivated the titanium surface and stopped the reaction.

Although a rare stress cracking failure, HCl and H_2SO_4 can readily be inhibited by additions of Fe^{+++} , Cu^{++} or Ni^{++} cations. Alloy modifications can be of some assistance such as the removal of phases with low anodic pitting resistance. Ti_3Al and its family of structures limits alloys to about 6 percent aluminum as an alloy addition. Iron and manganese alloy may also be troublesome in providing a surface which is not completely passivated.

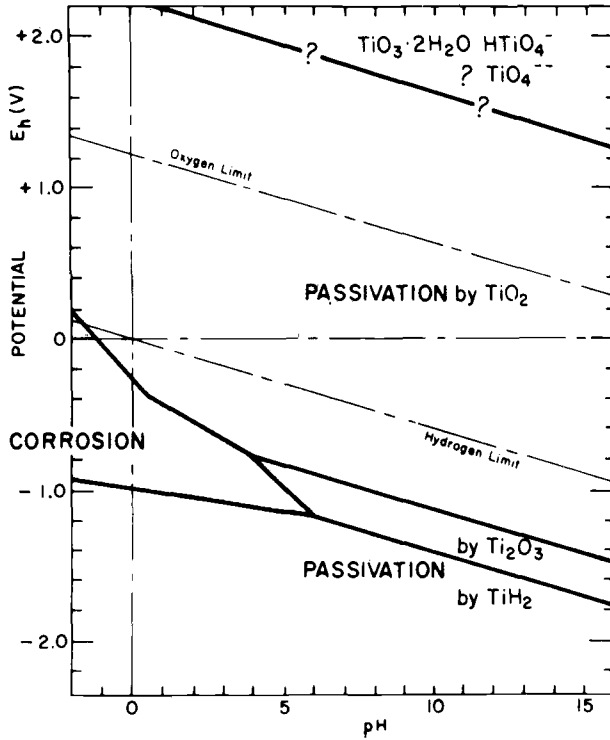


FIG. 1—Theoretical domains of passivation of titanium at 25 C (77 F) by the anhydrous oxides and by the hydride [24].

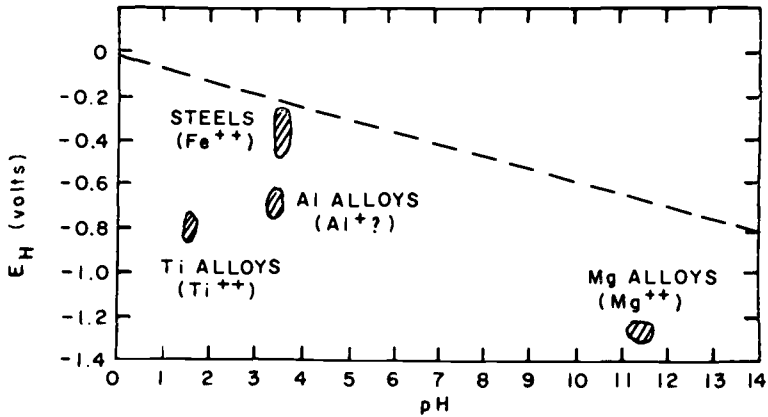
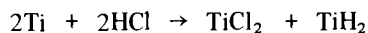
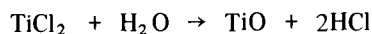
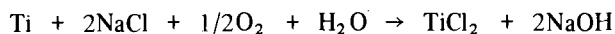


FIG. 2—Potential and pH data for the tips of growing stress corrosion cracks of four alloy systems in nearly neutral salt water—dashed line indicates the conditions below which hydrogen can be reduced from water [26].

Class two reactions present the problem of stopping very localized pitting attack. Hot salt stress corrosion cracking requires the combination of salt, oxygen, water vapor, and a stressed piece of titanium above 500 F. The most probable series of chemical reactions are as follows:



In a rather simplistic analysis, the moist salt crystal on the surface of the titanium above 500 F will pit or chemically attack the titanium and provide a creviced area where the reaction products of HCl vapor, hydrogen gas, and chlorine gas may collect along with an unstable, solid TiCl_2 . It can be demonstrated that gaseous HCl, H_2 and Cl_2 vapors at 500 F and above will react with titanium and cause cracking. The presence of TiCl_2 is an indication of an active pitting site generating the gaseous products which cause the cracking of the titanium alloy. X-ray diffraction techniques have identified the TiCl_2 under the salt crystal and followed its growth with time and temperature and plotted its decay with time as the temperature dropped below 500 F [9,18].

With a specific commercial alloy the various techniques of mill conversion practice and heat treatments can modify the time to failure and the probability of failure, but will not prevent surface pitting attack, change the threshold temperature, or the final endurance stress to assure completely its prevention. The rate of crack propagation can be significantly affected by alloying and thermal processing. However, the first tier properties in strength/density, high modulus, and ease of manufacture are a deterrent to the successful development of a titanium-base alloy designed specifically for hot salt stress corrosion cracking resistance.

The obvious answer to the problem is to deter pitting attack under the salt crystals. As only massive alloy additions appear satisfactory in developing pitting resistance, the most reasonable answer is to coat the part to stop the reaction at the surface and the obvious choice, based upon crevice corrosion work in hot brine, is a nickel cation addition to the coating [27]. Work conducted on hot salt had already shown the effectiveness of nickel plating, but further work had been deferred as the assumptions were that the nickel acted as a barrier coat and did not enter into the extinguishing of the electrochemical attack [9]. The second problem has been the inability to prevent deterioration of the fatigue properties of the plated part. Nickel based paint systems with good adherence at 1000 F have been developed and are commercially available [28]. The paint system overcomes the complexities of nickel plating and does not affect fatigue resistance.

In our third case, the dynamics of a moving crack front, a drop of highly acidic electrolyte, and diffusion of bulk electrolyte which will passivate the surface offers numerous opportunities to stop the reaction. The ARPA Program in all its complexity developed the Orwellian chant:

Lower the aluminum content,
Lower the oxygen level,
Increase the molybdenum content.

To extinguish the electrochemical reaction one must equate the forces sustaining the drop of acidic electrolyte in the crack. A small driving force is the potential between the passive surface/bulk electrolyte and the active crack/acidic electrolyte. Of greater interest is the observation that hydrogen is not taken up on the surface where the bulk electrolyte is 7 pH, but will be in the acidic brine at a pH of 1.5 [24]. If hydrides are present on the crack surface it can be demonstrated from anodic breakdown measurements that this phase is most susceptible to pitting attack providing an autocatalytic reaction of hydride formation and pitting in the pit area. The Ti_3Al compound or ordered phase has a very low pitting potential and favors a sustained pitting reaction. The oxygen plus aluminum levels determine the threshold for Ti_3Al compound formation. Trace Mo^{++} cations in the pit area drive the potential into the passive range.

The electrochemical approach continues to sustain the Orwellian chant: (lower the aluminum, lower the oxygen, increase the molybdenum).

In the electrochemist's view, aqueous stress corrosion cracking is the ability of the structure or test configuration to sustain by a moving crack front an actively corroding local site of a nonpassivating electrolyte. The classical argument as to whether the halogen or hydrogen are the cracking species is obscure as both reactions are required within the drop of electrolyte in the crack to sustain the reaction. Of significance is the chemical interaction of the acid electrolyte with the yielding plastic zone at the crack tip. Significant evidence has been obtained since the initial observation by Barrett [29] on an elastic aftereffect that mechanical properties can be altered in many materials by the removal of its passive oxide film. It would appear from evidence presented to date that insufficient time is available to dissolve the titanium with chlorides or diffuse the hydrogen to precipitate and crack massive hydrides. A surface reaction with emerging dislocations is at present a more reasonable explanation of the phenomena.

A major problem in data agreement on the loss of strength in an active electrolyte on the commercial titanium alloys is the complexity of the metallurgical phases which may or may not be present as controlled by mill processing. Further complication in processing is the texturing imposed by the processing by both the alpha and beta phases which give significant directionality to the metal in the distribution of phases. As these phases can accelerate

or extinguish the electrochemical reaction, the reported data has significant differences in the air and environmental numbers. Any attempt, therefore, to simply characterize susceptibility by chemical content has been beset immediately by contradiction. One must know the thermal process history, the phases present and their distribution as related to the chemistry to predict environmental sensitivity. General trends have been developed and those alloys where the $K_{I_{SCC}}$ value is reported less than 60 would be questionable in aqueous service.

Design Considerations for Aqueous Stress Corrosion Cracking

It becomes apparent that the main concern to the designer of parts in titanium alloys is the low cycle fatigue limit of titanium in the corrosive environment. Subcritical crack growth in air is gaining renewed interest with the fracture toughness technologists and with the imposing of the sea water environment as a design standard. These changes have significantly altered design values of high strength alloys, both in titanium and steel [30-31].

Initial data with the conventional fatigue tests gave titanium a very clean bill of health [32-34]. The smooth polished surface, with its passive film was immune. Machine notches in rotating beam fatigue tests confirmed the data as well as flat smooth plates in bending as the test values related more to the initiation of fatigue cracks rather than the rate of crack propagation. After Brown, renewed interest and additional testing clearly documented the problem in accelerated fatigue growth rates across the susceptible alloy [16].

The work of Lange and Crooker best illustrates this phenomena [31] (Figs. 3 and 4). In titanium because of its rapid environmental reaction rate, one cannot exceed the $K_{I_{SCC}}$ value for any great length of time or cycles prior to failure. At low stress intensity levels the titanium alloy is not affected by the environment. In the case of steel alloys, the reaction rate is lower (that is, the time to establish the minimum longer). The steel exhibits maximum environmental acceleration when cycled at low stress intensity levels. As one reviews the data critically it becomes apparent that in steel, given time, the stress intensity level to cause failure is less than 3 percent of the air stress intensity value. This is essentially confirmed by conventional fatigue testing by Gross who points out that notched ($K_t=6$) rotating beam, high cycle, fatigue specimens in steel fail at the 5 ksi stress level at 10^8 cycles [35]. Conversely, the steel alloys have better tolerance for the occasional cycles exceeding the $K_{I_{SCC}}$ value.

To place this whole discussion within the context of engineering data requirements, in a practical sense, a crack growth rate beyond $20 \mu\text{in./cycle}$ is unacceptable for a reasonable fatigue life. Beyond $20 \mu\text{in./cycle}$ the device had better be disposable after a few cycles. In this regard titanium is an ideal product in a corrosion fatigue application. The curves also point out the fallacy of going for high strength with a total disregard for the toughness and the $K_{I_{SCC}}$ value.

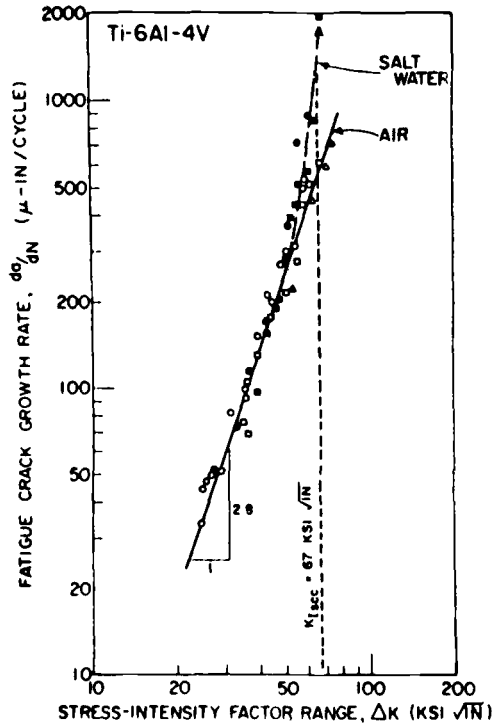


FIG. 3—Plot of da/dN versus K for a Ti-6Al-4V alloy in air and in salt water [23].

Conclusions

In titanium the stress corrosion characteristics in a practical design are not as serious as other metals as twelve years of industry application and numerous laboratory tests were to pass before the problem was even identified. In the more common environments, the requirement of rupture of the oxide film under plane strain conditions when submersed in the environment limits its probability of occurrence and makes it a problem primarily in corrosion fatigue. In certain limited environments where the oxide film is penetrated, the pitting range of the environment has been shown to be highly restrictive. Examples are the low water content in alcohols, chlorine gas, and nitrogen tetroxide to passivate the surface films.

At the time aqueous corrosion cracking was discovered, the alloys most susceptible to pitting attack in the environment were the new experimental alloys such as Ti-7Al-2Cb-1Ta and Ti-8Al-1Mo-1V or the early industry alloys which had fallen out of favor such as Ti-8Mn or Ti-4Al-4Mn. The common formulations such as Ti-50A and Ti-6Al-4V show relative immunity as do the

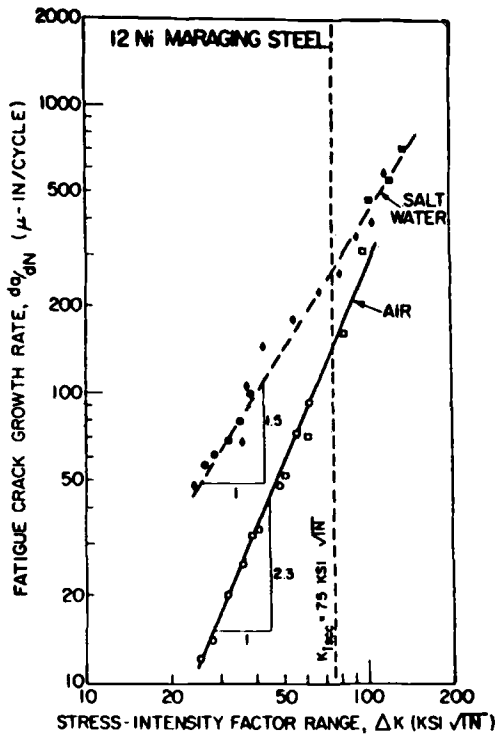


FIG. 4—Plot of da/dN versus K for high strength steel showing the effect of a salt water solution on fatigue crack growth. The threshold stress intensity level for stress corrosion cracking to occur (K_{Isc}) is indicated [23].

new generation of alloys in which pitting immunity has been introduced into the selective process of alloy development. Mill processing has been adjusted in a number of cases in commercial alloys to minimize the problem.

Today, the concept of access through the barrier film and the nature of the electrochemical reaction is sufficiently understood to predict the probability of attack if the environment is known. Simple laboratory tests will rapidly characterize both a new environment or new alloy.

The extensive engineering laboratory studies have characterized all alloys with many combinations of conversion practices. Based upon the review of this accumulated data, titanium rates high in its threshold immunity to stress corrosion attack, and in an engineering sense, its resistance to corrosion fatigue attack.

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Stress Corrosion Crack Protection from Coatings on High Strength H-11 Steel Aerospace Bolts

REFERENCE: Taylor, Edward, "Stress Corrosion Crack Protection from Coatings on High Strength H-11 Steel Aerospace Bolts," *Stress Corrosion Cracking of Metals—A State of the Art, ASTM STP 518*, American Society for Testing and Materials, 1972, pp. 131-138.

ABSTRACT: Stress corrosion cracking of high strength aerospace bolts is mostly limited to alloy steels, whose susceptibility to pitting corrosion is generally a secondary requirement compared to the outstanding tensile and fatigue properties needed. In order to provide environmental resistance for the bolt, a coating or plating is usually applied, which protects the underlying metal. In many cases, the coating chosen has proven to be inadequate. Therefore, a program was initiated to perfect a test method and gather reliable results from which predictable performance data could be obtained.

Many coatings were ultimately evaluated by a simple laboratory test method in which the coated bolt was statically stressed and exposed to a corrosive medium until failure occurred. The test is capable of evaluating a wide variety of coatings in periods from a few hundred to several thousand hours.

KEY WORDS: stress corrosion cracking, coatings, high strength steels, bolts, environmental tests, corrosion, plating, pitting

Stress corrosion cracking, as shown in Fig. 1, is the most common and frustrating catastrophic corrosion problem facing consumers and manufacturers of high strength aerospace bolts. While this phenomenon is not limited to steels, attention is usually focused on failures of ultra high strength steel bolts which command the major portion of the aerospace bolt market.

The steels require coatings to resist environmental attack which can result in general corrosion, pitting, or oxidation at elevated temperatures. Although many different elements, compounds, and alloys have been evaluated over the years, electroplated cadmium from a cyanide bath is still the most common coating. Prior underplating with nickel and subsequent diffusion produces an alloy of nickel and cadmium which is used at elevated temperatures and covered by the AMS 2416 Specification. Proprietary plating baths or vacuum

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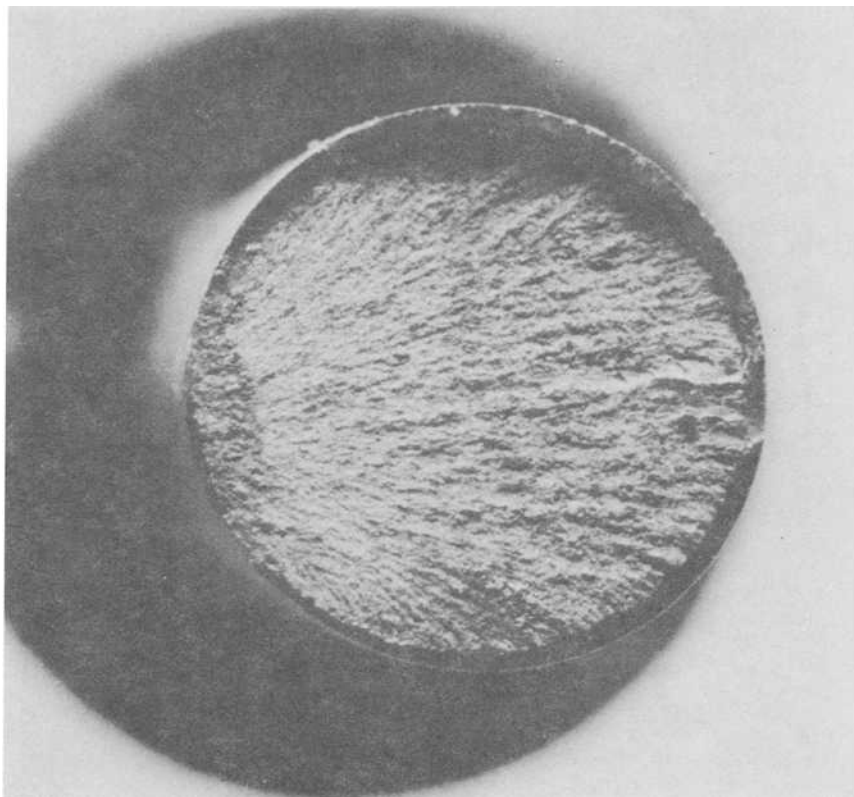


FIG. 1—Bolt fracture face after stress corrosion cracking.

deposition processes are employed to minimize hydrogen embrittlement, another high strength alloy problem.

Test methods for evaluating the stress corrosion protection afforded by coatings vary widely among users but generally involve a corrodent and a standard specimen. Any satisfactory method must be able to differentiate the effect of the coating from the basic material properties. One method, developed by Standard Pressed Steel Co. and reported previously,² uses production bolts and rigid fixtures to produce a “model” aircraft joint with an accelerated corrosion environment enveloping it. Results show that the test is capable of sorting or evaluating a wide variety of coatings on a qualitative basis.

² Lin, C.S., Laurilliard, J.J., and Hood, A.C. in *Stress Corrosion Testing*, ASTM STP 425, American Society for Testing and Materials, 1967, p. 84.

Test Method

The bolt specimens are accommodated by cylinders whose dimensions are shown in Fig. 2. The cylinders are made of the same material as the bolt and

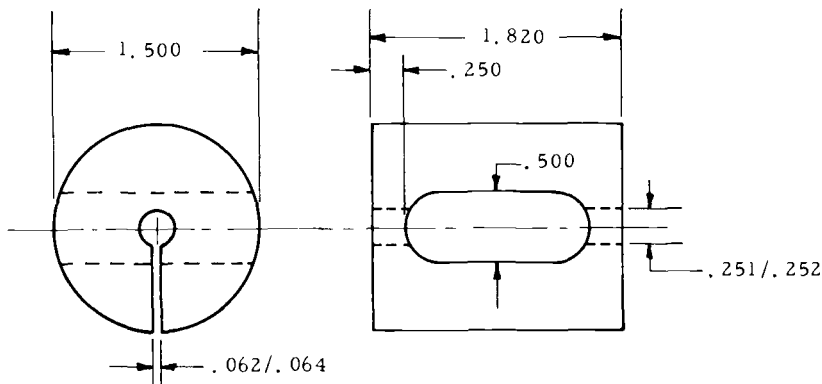


FIG. 2—Test cylinder dimensions, in.

in this study were H-11, heat treated to a 260 000 psi minimum strength level. The hole through which the bolt passes must be only slightly larger than the bolt diameter, as will be discussed later. The “window,” or opening, in the cylinder should be large enough to allow adequate air to flow, thus enabling the bolt shank to thoroughly dry off during each period of the test cycle. The slot is present to allow the corrodent unrestricted passage both to and from the entire exposed bolt shank.

The machined and heat treated test cylinders are cleaned by dry blasting with 120 grit alumina which will remove scale and dirt. A circle of tape is applied to both ends as a maskant. The cylinders are dipped in a vinyl solution and allowed to dry in air for about one hour. They are then baked in an oven at 150 F for 1 h. A second dipping, drying, and baking cycle completes the vinyl application whose sole purpose is to retard the corrosion of the cylinders during the long test exposure. The tape circles are removed, the pass through holes are scraped clean with a knife and then swabbed with methyl ethyl ketone to remove all excess vinyl. The test cylinders are now ready for loading.

The bolt used in this test program is an H-11 external wrenching bolt with a 260 000 psi strength level, a 1/4-in. diameter shank and a length which matches the cylinder.

Since the time to failure is a function of the applied stress, the latter must be known with a high degree of certainty. To accomplish this, a supermicrometer is used which easily measures to the nearest 0.0001 in. The bolts must be spot drilled on the ends to accommodate the hardened balls on the supermicrometer anvils. Three bolts of the same lot are loaded in a universal

testing machine with the aid of an extensometer to produce a stress elongation curve.

The point at which the elongation is no longer linear with respect to the applied stress is known as the Proportional Limit. The three values for the three curves are averaged and 90 percent of this value is selected for loading the bolts. The required elongation to achieve this stress is taken from the plot. For most of the H-11 bolts used in this study, the elongation required to produce a stress of 90 percent of the bolt's proportional limit was 0.011 in.

The bolt is inserted through a head washer (chamfered for the fillet radius), through the cylinder, through a flat washer, and finally threaded into a locknut lubricated with beeswax. The unloaded bolt length is measured on the supermicrometer, and the joint is then tightened until the bolt length reaches that which is required to achieve the desired applied stress level. The torsional component imparted to the bolt is virtually nil because the bolt is over-elongated slightly and then rotated in reverse a few degrees to counteract the induced torque. By using a lubricant, the residual torsional components for the bolts are practically identical, as measured in a test setup. The elongation is checked finally to insure against additional relaxation before the bolt head and nut ends are sealed.

The sealing is accomplished by brushing with the vinyl coating. They are allowed to dry for 1 h followed by a second application. This procedure protects the end drilled holes in the event that further length measurements are warranted. The vinyl coating also prevents the washers, nut, and bolt head from severely corroding.

The assembled specimens are suspended over a container of 3.5 percent NaCl solution, in which they are submerged for 10 min of each hour. For the remaining interval, they are dried by fan forced room air. The solution is changed daily, except for weekends, and no dissimilar assemblies are exposed in the same container. This cycle is repeated until failure by catastrophic cracking occurs, which is usually observed by the presence of broken bolts around or in the solution container.

Results

The cylinder hole diameter has been found to affect the duration of the test as shown in Fig. 3. The crevice produced between the bolt and the hole is very critical and significantly affects the corrosion rate. As the crevice becomes wider, the effect diminishes and the time to failure increases. In fact, when the entire crevice area is sealed up with vinyl and only the shank is exposed, the time to failure for a bare bolt increases to 1500 h.

If the cylinder bolt hole is cyanide cadmium plated instead of being left bare, the time to failure varies considerably in contrast to the close values obtained with bare holes, as seen in Fig. 3. The smallest possible clearance hole, specified in Fig. 2, was selected for all of the work presented here. This

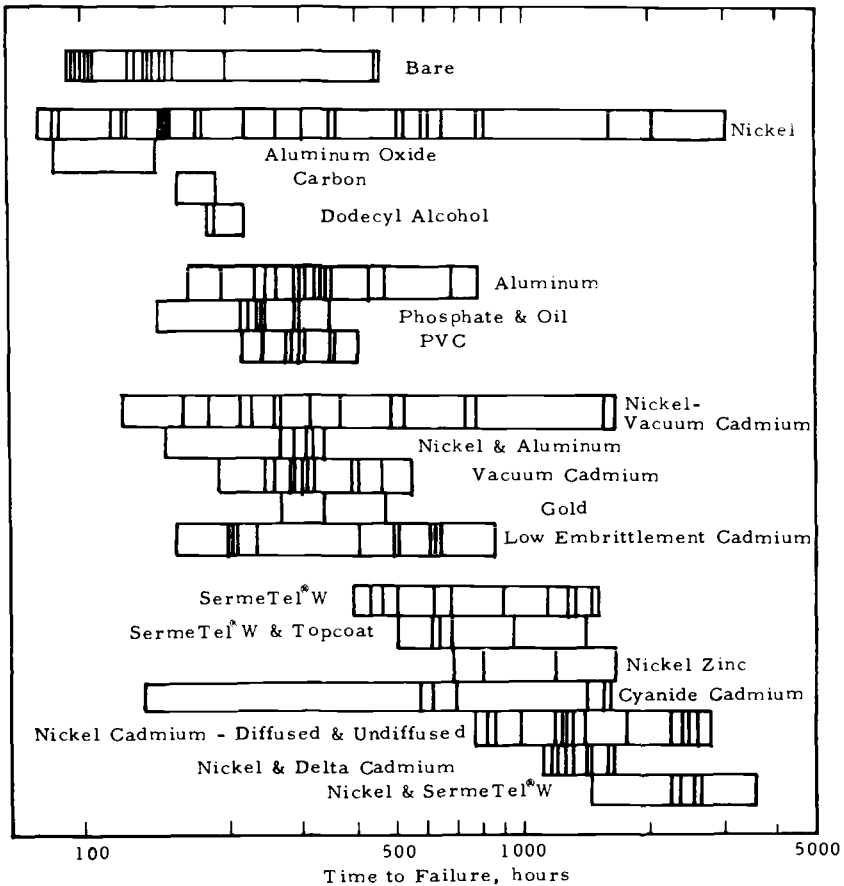


FIG. 4—Effect of coating on stress corrosion cracking resistance of H-11 bolts.

reason for this is not because of different thicknesses since all of the nickel data shown here is for thicknesses of 0.0003 to 0.0005 in. While nickel becomes much less porous above 0.0003 in., it is still susceptible to cracks, holes, chips, and scrapes. These can occur during installation and are almost impossible to detect or eliminate. Therefore, two bolts plated identically could yield substantially different behavior. For this reason, nickel is not advocated as a protective coating without subsequent protection where stress corrosion cracking is a threat.

Vacuum deposited cadmium has been the primary coating used for 260 000-psi bolts at temperatures below 450 F. In Fig. 4, we see that it is located near the middle. When nickel is plated under the vacuum cadmium, the scatter increases indicating the ambiguous nature of nickel. If the scatter band for pure aluminum coatings is now compared with that for nickel plus

aluminum, it is seen that the nickel has little or no effect on the results. This is apparently due to the rapid dissolution of the aluminum coating by the salt solution as well as by the influence of the 0.0001 to 0.0002-in. thick nickel cathode underneath.

Beyond the scatter band for low embrittlement cadmium, the time to failure significantly increases with the use of SermeTel³ W, a phosphate chromate bonded aluminum coating. In fact, beyond it, the other coatings protect well but must be thoroughly baked to prevent hydrogen embrittlement because of the cyanide cadmium. Limited data with nickel plus SermeTel W as an overcoat has shown it to surpass almost all of the other coatings in total performance. The reason for this is the protection period of up to 1000 h provided by the SermeTel W before the undercoat is exposed. The nickel then carries on with about another 500 h of protection.

Discussion and Conclusion

The work described here is concerned only with coatings on one type of bolt and does not take into account the protection afforded other alloy steel bolts of lower or higher strength levels. Tests have shown that different coatings exhibit varying degrees of protection to bolts susceptible to stress corrosion cracking at strength levels from 220 000 to 300 000 psi. Since the only measure is one of time to failure, it behooves the investigator to accelerate failure as much as possible. While this test method does not pretend to simulate any particular environment, it has been found to quickly produce failures which are usually generated only after significant lengths of service and are not reliably reported.

The failures observed in these tests and in actual service have fracture faces similar to that seen in Fig. 1, where a pit permitted intergranular stress cracking to occur, in turn causing a reduction in the load bearing area, resulting in the rapid cracking of the remaining section. The pits generally appear with cracks propagating normal to the direction of the applied stress.²

While general corrosion can usually be controlled by a number of methods, pitting is best avoided by changing the alloy to one more resistant. Although pitting can occur on any susceptible surface, crevice corrosion promotes this kind of attack according to several theories.⁴ Regardless of the exact mechanism which causes these test bolts to fail, crevices will always be present with bolted joints and it would be unrealistic to evaluate corrosion susceptibility without considering them.

³ SermeTel, a trademark of Teleflex, Inc.

⁴ Fontana, M.G. and Greene, N.D. in *Corrosion Engineering*, McGraw-Hill, New York, 1967, p. 41.

Since substitution of a surface is generally accepted as a means to retard corrosion, the choice of a suitable coating depends on the increased benefits it provides compared to the initial condition.

The diffused nickel-cadmium coating causes reduced fatigue life, ceases to be sacrificial to the H-11 bolt after elevated temperature exposure,⁵ and otherwise creates serious problems when the cadmium completely penetrates the nickel layer. If electroplating processes and cadmium are to be avoided because of hydrogen embrittlement and stress alloying, SermeTel W seems to provide an acceptable substitute, according to these tests. For extra longevity, a nickel undercoat looks promising.

Acknowledgments

I wish to thank the many people who contributed to this work: in particular, R.A. Hibbert for the experimental phase; A.C. Hood for helpful discussions; R.L. Sproat for technical support; C. Floros and G.J. Hansbarger for art and photographic services.

⁵ Taylor, E., "The Capabilities of SermeTel W Aluminum Coated Fasteners," SPS Report No. 1834, 1 Feb. 1970, p. 14.

Corrosion Fatigue at High Frequencies and High Hydrostatic Pressures

REFERENCE: Thiruvengadam, A., "Corrosion Fatigue at High Frequencies and High Hydrostatic Pressures," *Stress Corrosion Cracking of Metals—A State of the Art*, ASTM STP 518, American Society for Testing and Materials, 1972, pp. 139-154.

ABSTRACT: The high frequency fatigue technique originated independently by Mason and Neppiras was used to study the influence of corrosive environment on the fatigue of SAE 1020 steel. With this technique, uniaxial tensile and compressive stresses are produced at the node of a "tuned" test specimen vibrating at its resonant frequency. Tests were conducted at two frequencies, namely 14 000 and 20 000 Hz. At these frequencies the reduction in fatigue strength and fatigue life in corrosive environment was comparable to the value obtained in the more familiar low frequency fatigue tests. The fatigue strength is reduced by 50 percent in 5 h at high frequency, whereas the same reduction in strength requires about 300 h at low frequency. Furthermore, the corrosion fatigue life is reduced two orders of magnitude by the superposition of a hydrostatic pressure of 1000 psig. The high frequency fatigue data in noncorrosive environment support the two distribution interpretation of Swanson; however, the value of the Weibull shape parameter increases considerably in the corrosive environment and tends to become unique. This change in probability distribution of fatigue life is brought about in less than 5 min of exposure to the environment. The mean life is reduced from 2×10^8 cycles to 5×10^6 cycles in such a short exposure time. Internal friction is affected significantly in a relatively short exposure to corrosion fatigue. The frequency at which the maximum damping is produced also changes after exposure to corrosion fatigue. These results emphasize the importance of the microstructural aspects in the mechanism of corrosion fatigue.

KEY WORDS: corrosion, seawater corrosion, fatigue (materials), fatigue strength at N cycles, internal friction, relaxation (mechanics), stresses, hydrostatic pressure, grain boundaries, notch sensitivity, steels, fatigue tests, immersion tests (corrosion)

The importance of the phenomenon of corrosion fatigue need not be overemphasized. Modern requirements in engineering applications for long-life engineering systems (wire ropes, underwater cables, marine propellers, and offshore marine structures, to mention only a few) have called for a better

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understanding of the mechanism of corrosion fatigue. Failures due to corrosion fatigue cause great financial loss to many industries. In the oil industry alone the cost runs to millions of dollars annually [1].² One of the major causes of failure in underwater cables and wire ropes is corrosion fatigue [2]; it is this phenomenon that controls the cost and effectiveness of such ropes [3].

Over the last few years I have been using the high frequency fatigue technique originated by Mason [4] and Neppiras [5] to study the high cycle fatigue (in the range of 10^6 to 10^9 cycles) of engineering materials [6]. The frequencies used in the test ranged from 14 000 to 20 000 Hz. At such high frequencies, a million cycles are reached in a few minutes and a billion cycles may be accumulated in less than one day. The entire fatigue curve (stress versus number of cycles to failure curve) may be generated in less than a week. This technique was successfully used to test uranium oxide fuel elements [7] at 800 F in argon, 316 stainless steel at 1500 F in liquid sodium [8], and a titanium alloy (candidate skin material for supersonic transport) at 900 F in air [9].

Nevertheless, the time envelope in which the tests are conducted has greater significance in corrosion fatigue than when fatigue is not accompanied by corrosion [10]. This is mainly because corrosion is a function of time. When the high frequency fatigue technique was used to study the fatigue of steel in sodium chloride solution, a significant reduction in fatigue strength, as well as in fatigue life, was observed within a relatively short exposure time. For example, the fatigue strength was reduced by 50 percent after only 5 h of exposure. Such reductions are comparable to an exposure of 300 h in more conventional tests at lower frequencies [11]. Similarly, the fatigue life of SAE 1020 steel is reduced nearly two orders of magnitude when exposed to synthetic seawater at a hydrostatic pressure of 1000 psig. This result is a striking example of the importance of hydrostatic pressure on the performance of materials in environments such as deep oceans, nuclear reactors, and bearings.

Because of the short duration of each test, the high frequency fatigue technique is a convenient tool for studying the probability distribution of fatigue failures. Results presented in this paper support the two distribution interpretation of Swanson [12]. In a noncorrosive environment there are two values for the Weibull shape parameter; however, in a corrosive environment, the Weibull shape parameter increases significantly and tends to become unique. Such pronounced effects are noticeable in only 5 min. These observations emphasize the necessity to reexamine current thinking on the mechanism of corrosion fatigue. There is no doubt that the electrochemical aspects and dissolution processes are very important. Still, the observations at high frequencies (and hence short exposure times) tend to emphasize the importance of the microstructural aspects. To demonstrate this, internal friction measurements were made on SAE 1020 steel specimens after subjecting them

to fatigue in air and in synthetic seawater; the internal friction was changed significantly in a short time. Further evidence that these changes come from thermal relaxation phenomena at the grain boundaries is also included. Although the results presented in this paper are by no means complete, they emphasize the need for a systematic study of this phenomenon and a few promising avenues are indicated.

High Frequency Fatigue Technique

The earliest attempt to study fatigue at high frequencies was made by Jenkin [13, 14] in 1925. Since then several techniques have been developed to vibrate the fatigue specimen in different stress modes. One of them produces longitudinal vibrations in a properly designed test specimen at its resonant frequency and thus induces uniaxial alternating stresses at the node. In 1935, Gaines [15], who introduced the idea of using magnetostriction oscillators for cavitation erosion testing, also suggested the use of the same equipment for fatigue testing as well. He, in fact, carried out a few fatigue tests in his apparatus. However, this technique did not gain attention until Mason [4] and Neppiras [5] successfully used exponential and stepped velocity transformers, thereby making the technique more versatile, since high strains could be produced on any metal with moderate power. A detailed discussion of the various aspects involved in this method is given by Neppiras [5, 6].

In essence, the apparatus consists of a transducer and an associated power supply for driving the specimen. The measuring instruments include a high frequency power meter, a voice coil pickup, an oscilloscope, and a frequency counter, Fig. 1a. The frequency and amplitude of oscillations can be measured by a pickup located on the vibrating transducer. More recently, we have been using a commercially available piezoelectric transducer operating at 20 kHz, shown in Fig. 1b.

There are several types of fatigue specimens that can be used in this technique. The simplest is the notched fatigue specimen [6]. A notch of suitable size and shape is provided at the node to amplify the strains at the node. The notch sensitivity is a limitation for this type of specimen; to eliminate it, a dumbbell shaped fatigue specimen has been developed. Typical dimensions and shape of a steel specimen used at 20 kHz are shown in Fig. 2. The details of the design of the fatigue specimen are given in several references [7,9,17]. Another type of specimen has been used by Tanaka [18] and Kikukawa et al [19]; it consists of two cylinders of uniform radius with a fillet curve at the joint.

Influence of Corrosion on High Frequency Fatigue

During an earlier investigation on the mechanism of cavitation erosion in a

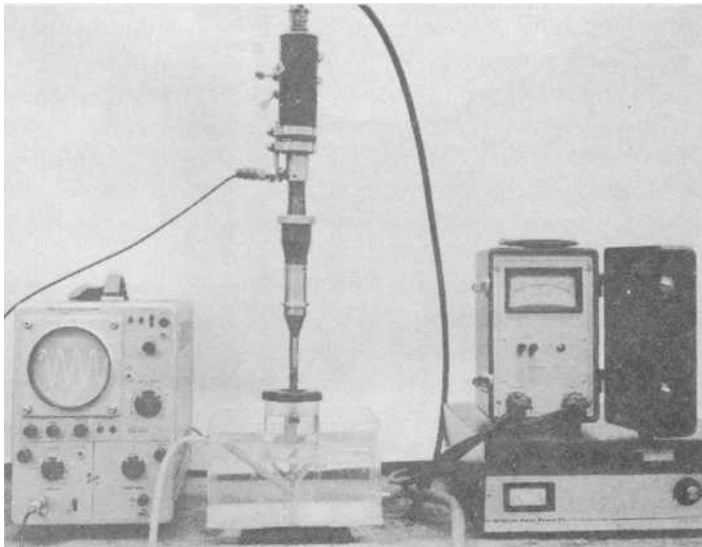
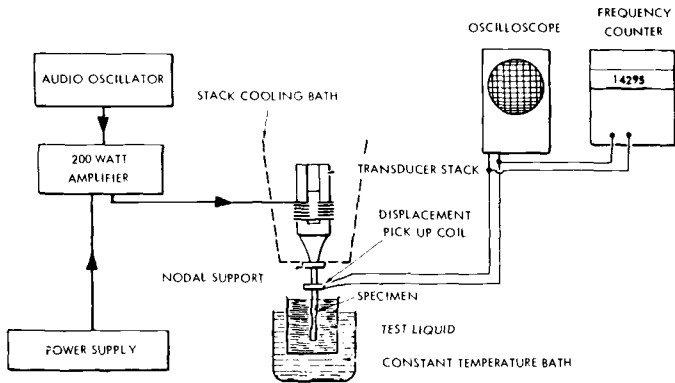


FIG. 1—(a) Block diagram of the apparatus used for the high frequency fatigue tests; (b) photograph of the high frequency fatigue testing apparatus (20 kHz).

corrosive environment [6], it was found that the fatigue strength of SAE 1020 steel can be reduced significantly even at these high frequencies (Fig. 3). In less than 10 h, the fatigue strength was reduced by a factor of two; conversely, the life corresponding to a stress amplitude of 45 000 psi was reduced by a factor of 100. This significant effect was produced in about 10 min of exposure to the corrosive environment.

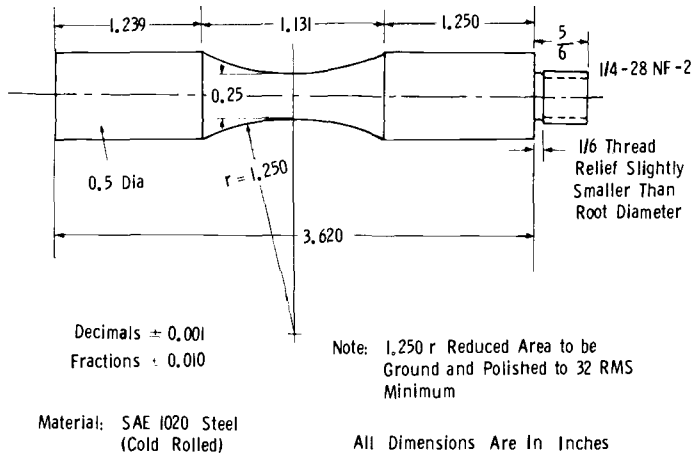


FIG. 2—Dumbbell shaped high frequency fatigue specimen.

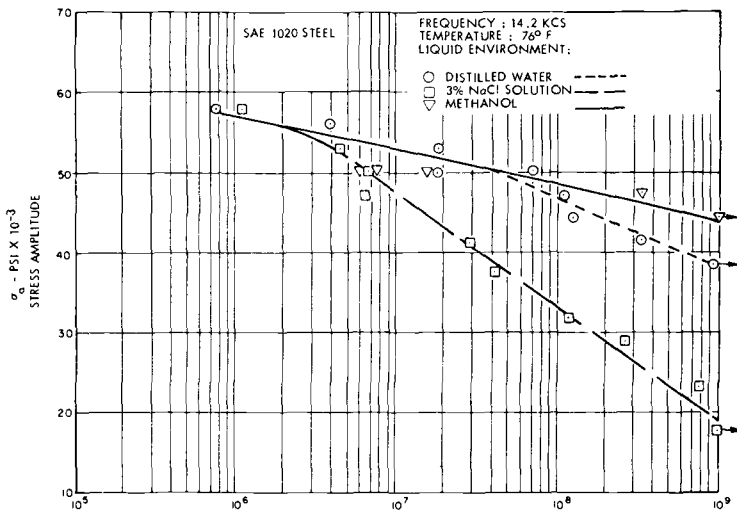


FIG. 3—High frequency corrosion fatigue of SAE 1020 steel.

The above result offers an interesting comparison with the data obtained by Hara [11] shown in Fig. 4. Hara tested a steel marine propeller shaft in repeated torsional fatigue at 1500 cpm (25 Hz) in three environments (air, water, and seawater). Our experiments were carried out at 14 200 Hz on SAE 1020 steel (hot-rolled) in methanol, water, and 3 percent NaCl solution.

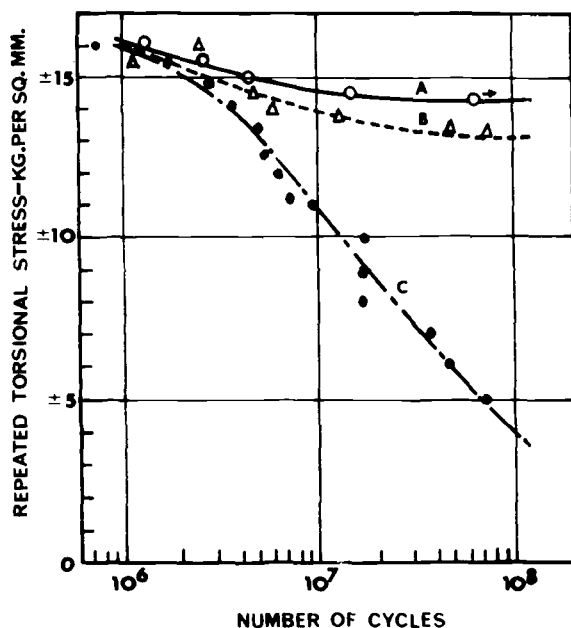


FIG. 4—S-N curves in air (A), fresh water (B), and seawater (C).

Despite the many differences in the frequency and the mode of stressing, the similarity between Figs. 3 and 4 is striking. The important point to be made is the reduction both in strength and in life due to corrosion in a relatively short time. To illustrate this point, the data in Fig. 3 and Hara's data are replotted in Fig. 5. The ordinate is the stress amplitude ratio, which is the stress amplitude at any number of cycles to failure divided by the stress amplitude corresponding to a million cycles. The abscissa is the time to failure. According to Fig. 5, the endurance strength is reduced by 50 percent in about 300 h at the low frequency. The same reduction in strength takes place in only 5 h at high frequency in a corrosive environment. This interesting result raises several questions about the mechanisms of corrosion fatigue.

The fatigue specimens were completely immersed in the test liquid, which was maintained at a constant temperature. There was no appreciable increase in the temperature of the fatigue specimen. Our own calculations, as well as those of Kikukawa et al [19], show that the temperature gradients are also negligible when the specimen is completely immersed in the liquid at a constant temperature.

The fact that substantial reduction in fatigue strength may occur in a relatively short time at high frequencies is highly significant. The commonly

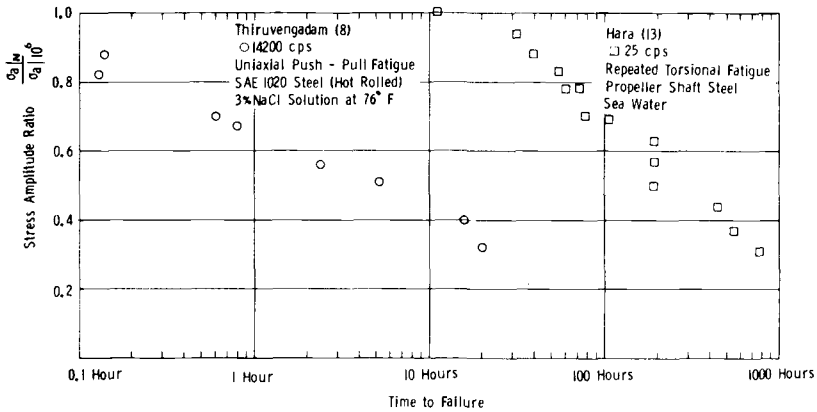


FIG. 5—Comparison between corrosion fatigue at high frequency and that at low frequency.

advanced mechanism for the corrosion fatigue assumes that the corrosive environment produces local pits which act as stress raisers. The relatively short exposure time at high frequencies excludes this possibility.

According to Uhlig [1], the metal is more susceptible to corrosion at clusters of slipbands under alternating strains. The clean metal produced at the slipband “extrusions” and “intrusions” acts as an anode with a marked tendency for dissolution. Anodic polarization is also decreased under dynamic strain. Such conjoint actions of alternating strains and corrosive environment seem to be greatly accelerated in high frequency fatigue.

The production of transgranular slipbands leads to changes in the internal friction of the material (Mason [4], Mason and Wood [20], and Zener [21]). That the corrosive environment affects the energy dissipation process in the material is further evidenced by the observation of an active medium changing the hysteresis loop [22]. Figure 6 shows the relationship between the damping coefficient and the number of fatigue cycles (as well as the time) both in air and in synthetic seawater (for SAE 1020 hot-rolled steel). These tests were made on a flat strip (6 by 1 by 1/16 in.) vibrated at its natural frequency, clamping it at one end (as a vibrating cantilever beam). The internal friction was determined by periodically interrupting the fatigue test. The procedure for the determination of the internal friction consisted of observing the amplitude decay in elastic vibration, which is fully described in Ref 23.

As shown in Fig. 6, the internal friction is very significantly affected by the phenomenon of corrosion fatigue. This lends support to Evan's contention that a corrosive environment destroys the interlocking material which would otherwise “hold up gliding” [24]. I previously [23] hypothesized that surface active media interact with polycrystalline material, giving rise to significant

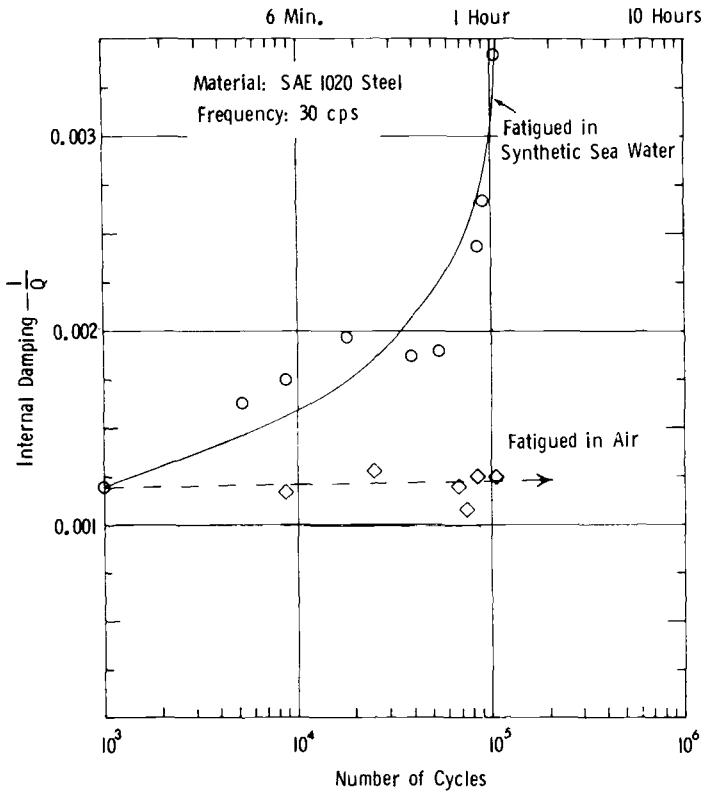


FIG. 6—Dependence of internal damping of SAE 1020 steel (hot-rolled) on the number of cycles of fatigue in corrosive environment.

changes in the thermal relaxation of the metal. If this were to be true, then the changes in internal friction would be pronounced in the range of frequencies predicted by Zener's [21] theory for thermal relaxation. The optimum frequency at which the internal friction maximized is about 55 Hz for SAE 1020 cold-rolled steel. This optimum frequency increases in dry air fatigue whereas it decreases in corrosion fatigue as shown in Fig. 7. The results in Fig. 7 were obtained on SAE 1020 cold-rolled steel (6 by 1 by 1/16-in. sheets) after subjecting them to fatigue in air and in salt spray. The fatigue stresses were produced by vibrating the specimens at their natural frequency (75 Hz) at the cantilever mode for 2 h. The lower frequencies for the damping tests were obtained by adding weights to the test specimens.

This line of reasoning would lead one to the systematic investigation of the effects of pressure and temperature on the mechanism of fatigue. For example, it is well known that the pressure in the environment affects the energies associated with reactions. This scientific interest, combined with

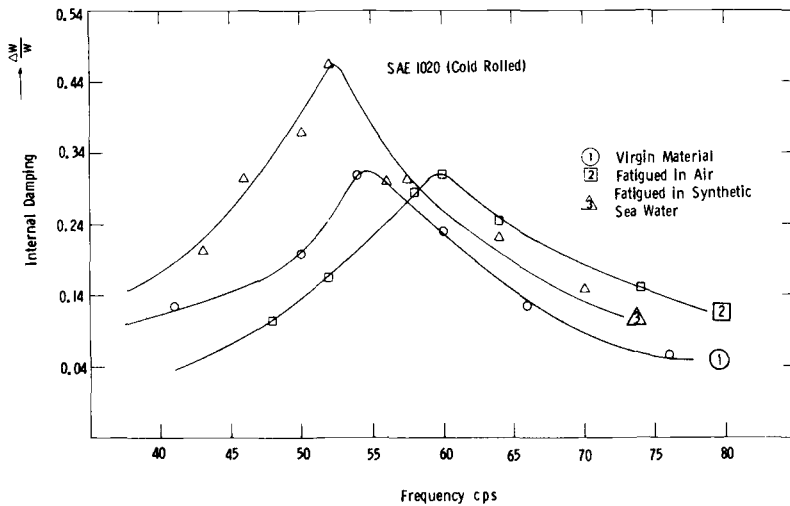


FIG. 7—Effect of corrosion fatigue on the relaxation frequency.

several practical applications, led to an investigation of the effect of hydrostatic pressure on corrosion fatigue life.

Effect on Hydrostatic Pressure

The influence of hydrostatic pressure on the performance of materials is becoming increasingly important in several applications such as ocean engineering, nuclear engineering, and petroleum engineering. Recently Johnson, Lewenstein, and Imembo [25] investigated the effect of pressure on mechanical properties such as yield strength, ultimate strength, and impact strength. They observed marginal effects on these properties at a pressure of 25 000 psi. Their results were in agreement with the classical studies of Bridgman [26]. Unfortunately, there are no systematic investigations of the effect of hydrostatic pressure on corrosion fatigue of metals. Crossland [27] made some studies of the influence of large hydrostatic pressure on the torsional fatigue strength of an alloy steel. He found that certain lubricants affected the fatigue life quite significantly under hydrostatic pressure and attributed this effect to the interaction of hydrostatic pressure on the corrosion fatigue of the material.

In order to evaluate this effect, high frequency fatigue tests were performed in a high pressure chamber. The velocity transformer was rigidly attached at the node to the top cover of the chamber, permitting the fatigue specimen to be completely immersed in the test liquid, and high pressure was applied with compressed air, argon, or nitrogen. The experimental setup is shown in Fig. 8.

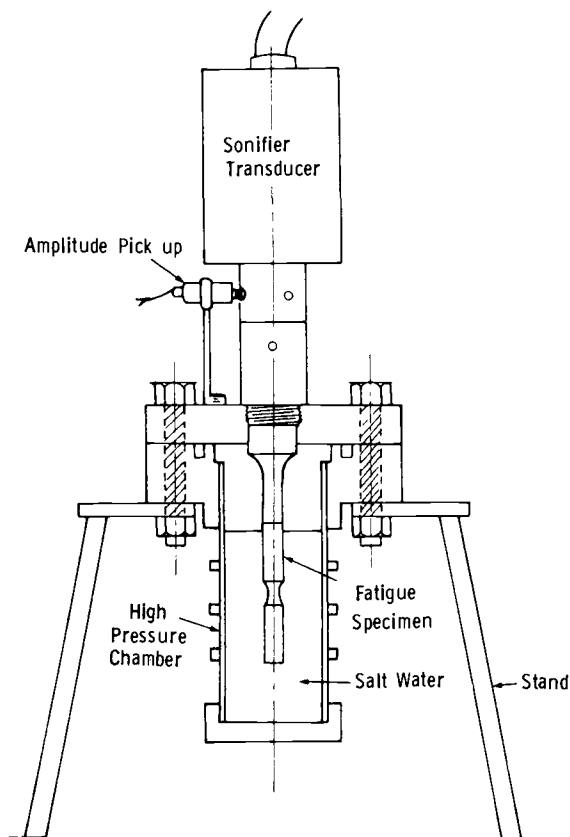


FIG. 8—High pressure corrosion apparatus.

Fatigue specimens made of SAE 1020 hot-rolled steel were tested at a frequency of 14 kHz first in methanol at a stress level of $\pm 22\,000$ psi; they failed after 2×10^8 cycles. Three more specimens of the same material, submerged in salt water at atmospheric pressure (Fig. 9) were tested; at a stress level of $\pm 22\,000$ psi, the fatigue life was reduced to about 4×10^6 cycles. Then the static pressure in the salt water was increased 1000 psig by using compressed air. At an alternating stress of $\pm 16\,000$ psi, the fatigue life under hydrostatic pressure was about 10^6 cycles, whereas, at the same stress level, the life was about 5×10^7 cycles at atmospheric pressure. In other words, the fatigue life was reduced from 5×10^7 cycles to 10^6 cycles by applying a hydrostatic pressure of 1000 psig. To see if this effect had anything to do with the increase of dissolved oxygen from the compressed air or with the superimposed mean compressive stress of 1000 psi on the fatigue specimen, we replaced air with compressed nitrogen and with a methanol-argon

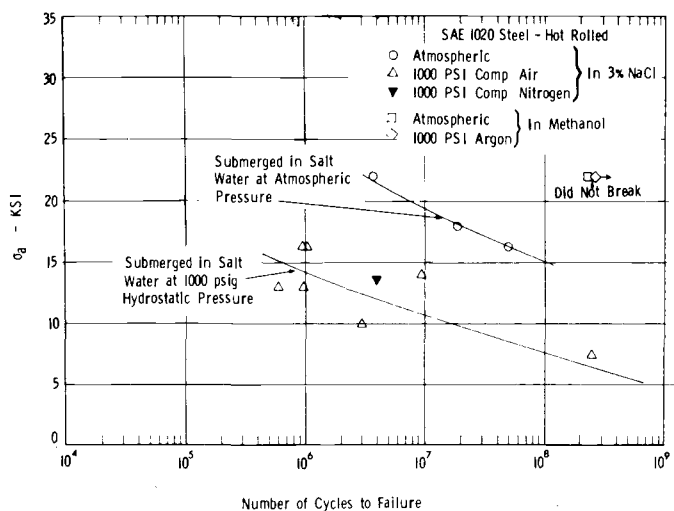


FIG. 9—Effect of hydrostatic pressure on corrosion fatigue of SAE hot-rolled 1020 steel.

combination. As shown in Fig. 9, the result at atmospheric pressure in methanol coincided with that at 1000 psig compressed with argon. However, under compression with nitrogen to 1000 psig in 3 percent NaCl solution, the result agreed with those obtained by compressing the NaCl solution with air. These two tests demonstrated the negligibility of the effects of mean stress and increased oxygen content in these experiments.

At the suggestion of Horton [28], we repeated these experiments in sodium hydroxide solution at 1000 psig using a test specimen of 316 stainless steel. This problem has some relevance in the development of liquid metal fast breeder reactors. At 22 500 psi alternating stress, the specimen did not break after 7.5×10^8 cycles at atmospheric pressure in 3 percent NaOH solution. However, the life reduced to less than 10^8 cycles when the pressure was increased to 1000 psig (two specimens were tested and they failed at 2×10^7 cycles and 7×10^7 cycles).

The above experiments raise very interesting scientific questions apart from their practical implications. The mechanisms of the action of hydrostatic pressure on corrosion fatigue are little understood at the present time. It is well known that the hydrostatic pressure affects the energies associated with chemical reactions. The electrochemical reaction at the microscopic and macroscopic crack tips depends greatly on the pressure and temperature of the surrounding medium. Recently, Schatzberg [29] presented data on the kinetics of electrochemical reactions at the crack tips and on how pressure interacts with these reactions. Much more effort is needed before the detailed mechanism of the effect of hydrostatic pressure is fully understood.

Statistical Distribution of Corrosion Fatigue Life

During recent studies on cavitation erosion [30] and liquid impact erosion [31], I became interested in the statistical distribution of fatigue life. At high cycles of fatigue life (mean life being on the order of 10^7 cycles), the Weibull distribution has two slopes as shown in Fig. 10. This is very similar to the two

Material: Titanium 6AL - 4V Annealed	Stress Level: 52,800 psi (AXIAL PUSH PULL)
Number of Specimens Tested: 30	Temperature: 70° F
Frequency of Test: 14,000 kcs	Environment: Water Cooling Bath

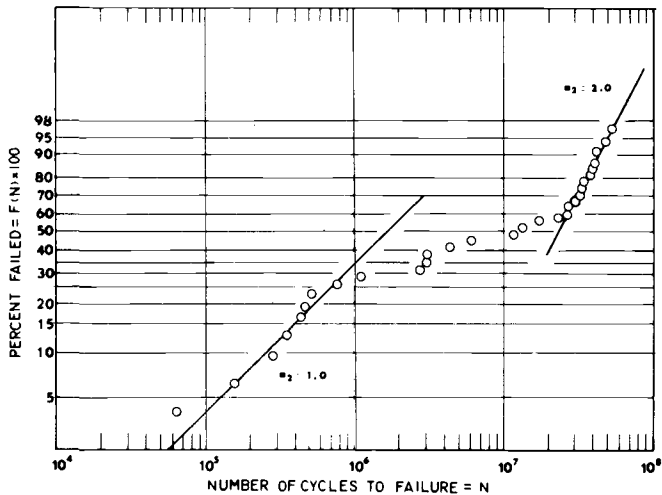


FIG. 10—Weibull distribution for high frequency fatigue of annealed Ti-6Al-4V.

distributions observed by Swanson [12]. More recently, Bily and Williams [32] reviewed the work of various investigators including Weibull, Wood, Shabalin, and Ivanova and discussed the importance and significance of the discontinuities in the life distribution. According to some of these investigators, the probability functions determining the scatter in fatigue life resemble the data in Fig. 10. Swanson [33] suggested to me that it would be interesting to see how corrosive environment would affect the fatigue life distribution. He also mentioned that there were some indications to show that the scatter becomes smaller when a specimen is exposed to corrosion. In order to learn more about these effects, the fatigue life distribution for cold-rolled SAE 1020 steel was experimentally determined at a frequency of 20 kHz both in methanol and in synthetic seawater. Twenty-nine specimens were studied in each case. The test data were reduced as outlined in Ref 34. Figure 11 shows the plot of the results on Weibull probability paper. In methanol the Weibull

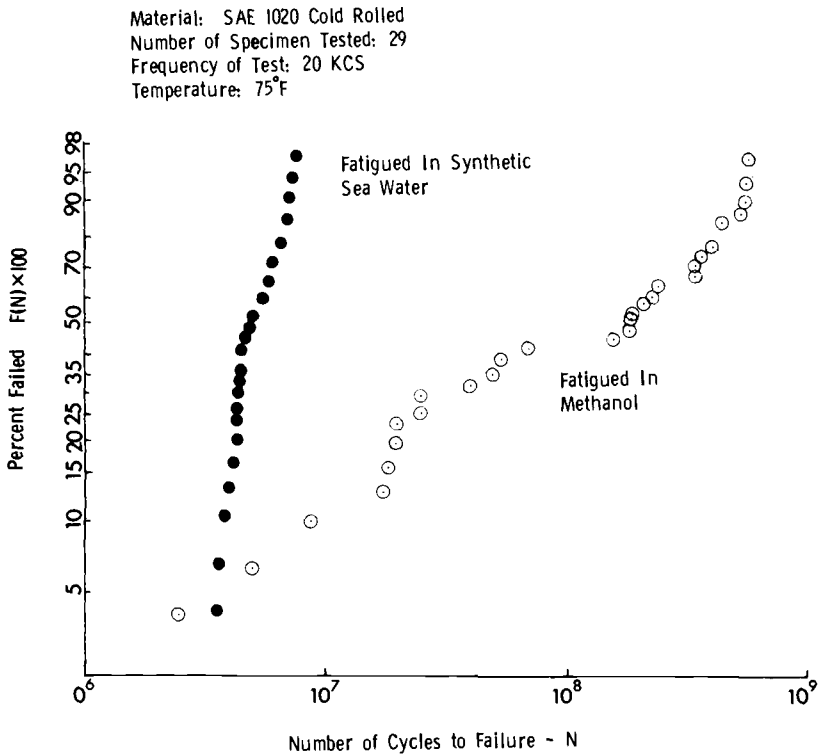


FIG. 11—Weibull distribution of high-frequency (20 kHz) fatigue failure of cold-rolled SAE 1020 steel.

slope is small and the scatter is large, whereas in synthetic seawater the slope increases considerably with a significant reduction in the scatter.

This may be explained *a priori* as follows. It is known that the shape parameter tends to become higher and unique at relatively shorter mean life ranges [31,35]. In a corrosive environment, the mean life reduces greatly (Fig. 11) and, consequently, the Weibull slope increases, approaching a unique value. However, a more basic explanation may be forthcoming if we pursue the work of Wood [36], who attributes these effects to microstructural changes in the material. Deeper understanding of the fatigue life distribution in corrosive environment is essential in practical applications such as ocean engineering structures and vehicles that may have to withstand wave forces [37].

Summary and Conclusions

Current ideas are inadequate to explain some of the observations made of fatigue at high frequencies; for example, the reduction of fatigue strength of

steel by 50 percent in 5 h of exposure. Such reductions are comparable to an exposure of 300 h in more conventional tests at lower frequencies [11]. The relatively short exposure time at high frequencies reduces the possibility of formation of corrosion pits which may act as stress raisers. However, internal damping measurements support Uhlig's [1] view that the clean metal produced at the slipband extrusions and intrusions acts as an anode with a marked tendency for dissolution. The internal damping is affected significantly in relatively short exposures to corrosion fatigue. This also lends support to Evan's [24] contention that corrosive environment destroys the "interlocking material which would otherwise hold up gliding."

The corrosion fatigue life of SAE 1020 steel was reduced from 5×10^7 cycles to 10^6 cycles by the application of a hydrostatic pressure of 1000 psig in 3 percent NaCl solution. Similarly, the fatigue life of 316 stainless steel decreases by an order of magnitude in 3 percent NaOH solution at a hydrostatic pressure of 1000 psig. These observations have important practical implications in ocean, nuclear, and petroleum engineering fields. In addition, the scientific aspects of this effect remain to be explored in full detail.

In noncorrosive environments a plot in Weibull coordinates of the probability of failure of fatigue specimens tends to have two slopes and the Weibull shape parameter is of the order of one, corresponding to mean life ranges above 10^7 cycles. This observation agrees with those of earlier investigators such as Swanson [12] and Weibull [23]. However, when corrosive environment was superimposed, the Weibull shape parameter increased considerably and tended to reach a unique value. The scatter in fatigue life was reduced considerably. At high frequencies these significant results may be observed in less than 5 min of exposure to corrosion fatigue. Such observations bring forth the necessity to investigate the interaction of corrosive environment on microstructural changes, which presently are being studied carefully by Wood [36]. These observations demonstrate the necessity for continued efforts toward an overall understanding of the mechanism of corrosion fatigue.

Acknowledgments

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The recent experiments at 20 kHz were performed at the dynamics laboratory of the Catholic University of America. Several of my colleagues participated in these experiments: Sophia White, Lee Rudy and Gunasekaran of Hydronautics Incorporated, and Sung Tung, Frank Matanzo, and Ambrose Hochrein, graduate students at Catholic University, deserve special mention.

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Resistance of High Strength Structural Steel to Environmental Stress Corrosion Cracking

REFERENCE: Townsend, H.E., Jr., "Resistance of High Strength Structural Steel to Environmental Stress Corrosion Cracking," *Stress Corrosion Cracking of Metals—A State of the Art, ASTM STP 518*, American Society for Testing and Materials, 1972, pp. 155-166.

ABSTRACT: High strength structural steel, ASTM A 514/517, Type J, was evaluated for susceptibility to environmental stress corrosion cracking. Precracked cantilever beam specimens, prepared from 1-in. plate and loaded up to 90 percent of the air determined critical stress intensity, withstood 1000 h exposure to 3.5 w/o NaCl without failure. At loads greater than 90 percent of the load required to cause failure in air, fracture occurs without evidence of stress corrosion cracking. Additional specimens prepared from butt-welded plate and subjected to sustained loads beyond yielding in 4 point bending were alternately immersed in 3.5 w/o NaCl solution and dried in air for 10 000 h without cracking. These results indicate virtual immunity to environmental stress corrosion cracking for both base plate and weldments of this quenched and tempered steel.

KEY WORDS: stress corrosion cracking, corrosion, cracking (fracturing), evaluation, high strength steels, immersion tests (corrosion), salt water, steels, stress corrosion, tests, weldments

As indicated on Fig. 1, structural steels with yield strengths greater than 40 000 psi (2.76×10^8 N/m²) are generally termed high strength, while steels with yield strengths greater than 140 000 psi (9.65×10^8 N/m²) are called ultra high strength [1]. This study deals with quenched and tempered steels included within ASTM designation for High-Yield-Strength, Quenched and Tempered Alloy Steel Plate, Suitable for Welding (A 514-69) and for High-Strength Alloy Steel Plates, Quenched and Tempered, for Pressure Vessels (A 517-69a) having minimum yield strengths of 100 000 psi (6.90×10^8 N/m²) and ultimate tensile strengths of up to 135 000 psi (9.31×10^8 N/m²).

Stress corrosion cracking is a low energy (brittle) failure which can result from a combination of stress and exposure to a corrosive milieu. Generally, steels at the lower end of the strength spectrum are affected only when

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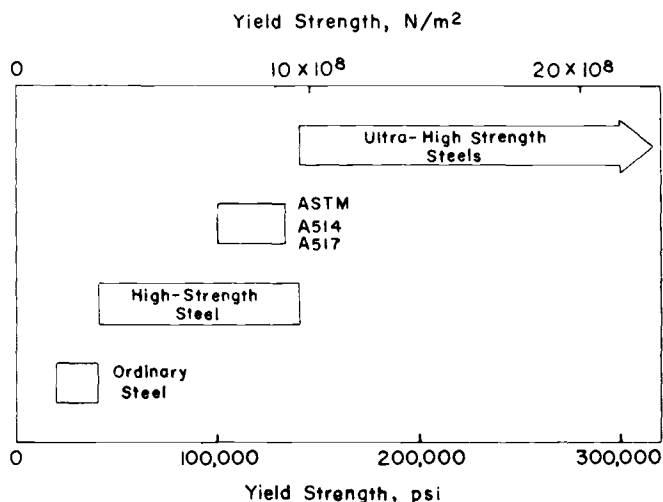


FIG. 1—Classification of steels according to yield strength.

exposed to one of a limited number of specific environments such as hot caustics, hot nitrates, and anhydrous ammonia [2]. As the strength of steel is increased, however, the requirement for the presence of a specific environment becomes less important. In the case of ultra high strength steels, cracking can occur in virtually any environment which contains water or other solvents capable of autoprotolysis. Since stress corrosion cracking of ultra high strength steels can occur in naturally occurring environments such as seawater and the atmosphere, it is often termed environmental stress corrosion cracking, or EC for brevity.

Stress corrosion cracking of ultra high strength steels has been the subject of several recent reviews [3-6]. All work indicates that susceptibility to EC increases with increasing strength level. A critical strength or hardness value, below which EC is unlikely, has yet to be determined.

Only limited EC data are available for steel in the strength range of ASTM A 514/517. Phelps reported testing steels in this strength range by exposure to a severe marine environment of beams bent to 75 percent of the yield stress [6]. Horikawa et al have reported atmospheric tests of similar steels stressed as bent beams to 90 percent of the yield value in both welded and unwelded conditions [7]. However, it is known that alloys which appear resistant to EC when tested as smooth specimens can actually be quite susceptible if a small crack is initially present [8]. Thus, in order to establish complete confidence in a particular material, it is necessary to test in the precracked condition.

The data for precracked specimens of steel in the ASTM A 514/517 strength range are few also. Leckie and Loginow report that the load bearing capacity of 89 000 psi (6.14×10^8 N/m²) yield strength steel is unaffected by exposure to salt water, while that of 135 000 psi (9.31×10^8 N/m²) yield

strength steel is reduced by more than 25 percent in tests of precracked specimens [9]. Colangelo and Ferguson report that the load bearing capacity of a 142 000 psi (9.79×10^8 N/m²) yield strength steel is unaffected when exposed to distilled water in the precracked condition [10]. Wacker reported that the load bearing capacity of a 139 000 psi (9.58×10^8 N/m²) yield strength steel was reduced by roughly 12 percent when exposed in the precracked condition to seawater for times up to six months [11]. Peterson et al noted that the load sustaining ability of AISI 4340 heat treated to 125 000 psi (8.62×10^8 N/m²) yield strength was reduced by approximately 20 percent when exposed to sea water [12].

The purpose of this study was to determine the degree of susceptibility of the ASTM A 514/517 grade to environmental stress corrosion cracking. In order to make the test as severe as possible, material at the high end of the allowed strength range, that is, at 126 000 psi (8.69×10^8 N/m²) yield strength, was tested in the precracked condition. Further, since practical use of this steel often involves fabrication by welding, additional tests of welded material were also conducted.

Experimental Procedure

Materials

All tests were performed with material taken from the same 1-in. (2.54-cm) thick plate of commercial ASTM A 514/517, Type J steel. The chemical composition of this plate was determined to be as follows:

Percent by Weight

<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>B</u>
0.22	0.66	0.004	0.024	0.27	0.02	0.02	0.66	0.005

Tension tests results for 0.505-in. (1.28-cm) diameter specimens machined from the plate are given below:

Direction of Specimen Axis Relative to Rolling Direction	0.2% Yield Stress	Ultimate Tensile Stress	% Reduction in Area	% Elongation in 2 Inches
Parallel	125 000 psi (8.62×10^8 N/m ²)	131 000 psi (9.03×10^8 N/m ²)	58	20
Perpendicular	126 000 psi (8.69×10^8 N/m ²)	131 000 psi (9.03×10^8 N/m ²)	50	18

Cantilever Beam Tests of Precracked Specimens—The test technique employed in this study is based on that described by Brown [8, 13]. By this method one determines: (a) the stress intensity factor, K_{IX} , required to cause rapid fracture of a precracked cantilever-loaded specimen in air, and (b) the stress intensity factor, K_{ISCC} , required to cause stress corrosion cracking during prolonged exposure of similar precracked cantilever beams to a corrodent. The ratio of K_{ISCC} to K_{IX} provides a quantitative measure of resistance to stress corrosion cracking.

The specimen used in this investigation is shown at the top of Fig. 2 and is similar to one previously described [14]. The specimens are oriented in relation to the plate rolling direction in one of two ways, either longitudinal or transverse, as shown at the bottom of Fig. 2.

The stress intensity factor, K_I , is calculated from Eq 1, the Kies equation as given by Brown [8, 13] and modified to account for side grooves:

$$K_I = \frac{4.12 M \left(\frac{1}{\alpha^3} - \alpha^3 \right)^{1/2}}{(B B_n)^{1/2} W^{3/2}} \quad (1)$$

In Eq 1, M is the applied moment, W is the overall specimen height, B is the overall specimen width, B_n is the net specimen width at the side grooves, and α is defined:

$$\alpha = 1 - \frac{a}{w}$$

where a is the overall crack length, notch depth included.

In order to insure valid plane strain conditions according to the tentative ASTM method for fracture toughness testing [15], the minimum specimen dimension should exceed the value given by:

$$2.5 \left(\frac{K_{Ic}}{\sigma_{ys}} \right)^2$$

where σ_{ys} is the yield stress, and K_{Ic} is the plane strain fracture toughness which is approximately equal to K_{IX} . For the material considered here, the minimum allowable dimension calculated from the above is 1.6 in. (4.1 cm). Accordingly, the values of K_{IX} and K_{ISCC} calculated from Eq 1 for the results of this investigation are not valid plane strain parameters. Nevertheless, these quantities are significant in that they represent critical values of load

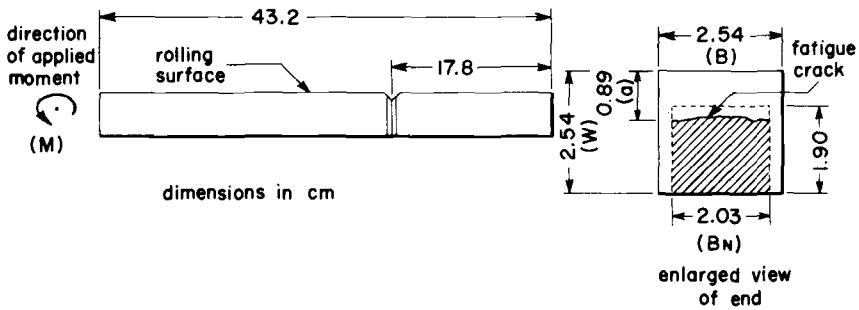


FIG. 2—Cantilever beam stress corrosion specimens showing orientation in the plate. Terms in parentheses defined in Eq 1.

normalized to account for the effect of crack length, and the ratio $K_{I_X}/K_{I_{SCC}}$ can be used to quantitatively assess the EC resistance of material of a particular size. For purposes of this paper, the subscript I on the stress intensity factor is used to indicate the type of loading (opening mode I as opposed to shear modes II and III) and it is not intended to denote plane strain. From a practical point of view, tests of specimens sufficiently large to meet the ASTM plane strain requirement would not be very useful in that the ASTM A 514/517, Type J grade is available only in thicknesses of up to 1 1/4 in. (3.18 cm).

Precracking of the specimens was accomplished by fatigue cycling in 3 point bending across a 9-in. (22.9 cm) span under a maximum load of 1300 lb (5.78×10^3 N) and a minimum load of 130 lb (5.78×10^2 N) at 26.5 Hz. Anywhere from 60 000 to 500 000 cycles were required to produce a fatigue crack roughly 0.35 in. (0.89 cm) in length. The corresponding maximum stress intensity applied to the specimens during the precracking procedure is 25 ksi $\cdot$ in.^{1/2} (2.7×10^7 N/m^{3/2}).

Tests to determine the critical stress intensity in air, K_{I_X} , were conducted in 23 C (73 F) laboratory air at 55 percent relative humidity by adding weights in small increments until instability and fracture occurred.

Tests to determine $K_{I_{SCC}}$, the threshold value of stress intensity for EC, were conducted in solutions consisting of 3.5 w/o technical grade NaCl in distilled water contained within 1 liter plastic containers cemented about the specimen. After addition of the solution, weights were added sufficient to apply a predetermined fraction of K_{I_X} for periods of time ranging up to 1000 h. Sandoz has reported that 100 h is adequate for evaluating the stress corrosion cracking resistance of low alloy (for example, AISI 4340) steels in salt water by use of the precracked cantilever beam test [16]. Steigerwald has shown that the time required to produce failure of precracked specimens of steels with varying composition generally increases with total alloy content [17]. Accordingly, the 1000-h exposure period of this investigation should provide sufficient time for the occurrence of stress corrosion in the very low alloy ASTM 514/517, Type J steel, thus insuring a conservative evaluation of this material.

During the exposure period, test conditions were observed to vary within the following limits:

Temperature	22 to 24 C (72 to 75 F)
pH	6.5 to 4.7 (decreasing with exposure time)
Potential of specimen relative to a saturated calomel electrode, V	-0.62 to -0.70 (decreasing with increasing exposure time)

Bent-Beam Tests of Welded Material—Welded material was prepared by manually butt welding together sections of plate using AWS E 12018M electrodes with a heat input of 3.3×10^6 J/m. Test specimens were prepared by cutting 2 x 12-in. (5.08 x 30.5-cm) strips containing the welded region centrally located in one of two ways as shown in Fig. 3. The weld reinforcement was left intact and the strips were loaded in 4 point bending in jigs which are similar to the type previously described by ASTM [18] and are shown in Fig. 3. Four strips were loaded with the direction of stress normal to the direction of the weld bead as shown at the top of Fig. 3, and four strips were loaded with the direction of stress parallel to the direction of the weld bead as shown at the bottom of Fig. 3. All parts of the jig, including nuts and bolts, were machined from material taken from the same plate as the test specimens in order to avoid galvanic problems. Loading was effected by compressing the ends of the beams together in a hydraulic press well beyond yielding and then tightening the bolts in order to hold in this position and maintain the load. The end portions containing the bolts were protected from corrosion by a microcrystalline wax coating.

The bent-beam weld specimens were subjected to an alternate immersion cycle of 5 min in 3 w/o NaCl solution followed by 55 min in air for a total exposure time of 10 000 h.

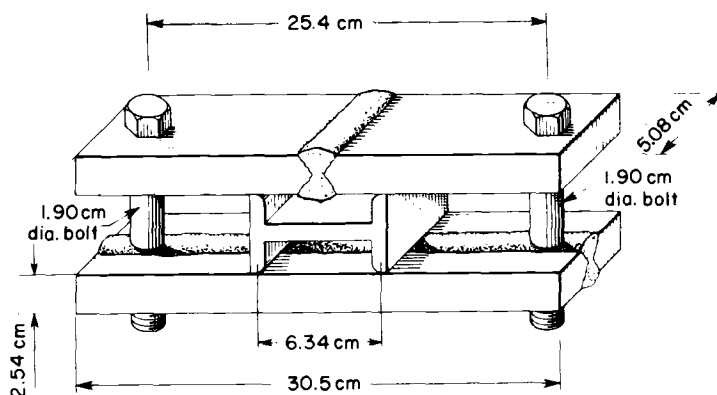


FIG. 3—Welded specimens and method of loading in 4 point bending. Direction of bending stress is perpendicular to the weld bead for the upper specimen and parallel to the weld bead for the lower specimen.

Results and Discussion

Precracked Cantilever Beam Tests in Air—For each of the two plate directions, longitudinal and transverse as defined in Fig. 2, four measurements were made of K_{I_X} , the critical stress intensity factor for rapid fracture in air. These results are shown plotted at the far left of Figs. 4 and 5. The uppermost horizontal dashed line in these figures is drawn through the average of the four measurements.

The average K_{I_X} values are given in Table 1 along with the associated standard deviations. A T test [21] of these data indicates that the difference between longitudinal and transverse toughnesses, although small, is statistically significant ($P < 0.01$). Thus, in comparing $K_{I_{SCC}}$ to K_{I_X} as a measure of EC susceptibility, it is important to maintain the distinction between properties in each direction.

Also shown in Table 1 are values of air determined toughness that have been observed for similar materials, but with differing test techniques. It is clear from a comparison of the data that the results are largely dependent upon the type of test or size of specimen. A size dependence is expected [22] for specimens which are smaller than the minimum size required for valid plane strain conditions [15]; all specimens in Table 1 fail to meet this requirement. Thus, in comparing $K_{I_{SCC}}$ to K_{I_X} as a measure of EC susceptibility, it is important that each of the two values be obtained by use of identical test techniques and specimen sizes.

Precracked Cantilever Beam Tests in Salt Water—The results of sustained load tests of precracked cantilever beam specimens in salt water are shown in Figs. 4 and 5. The line labeled $K_{I_{SCC}}$ was drawn by inspection as the

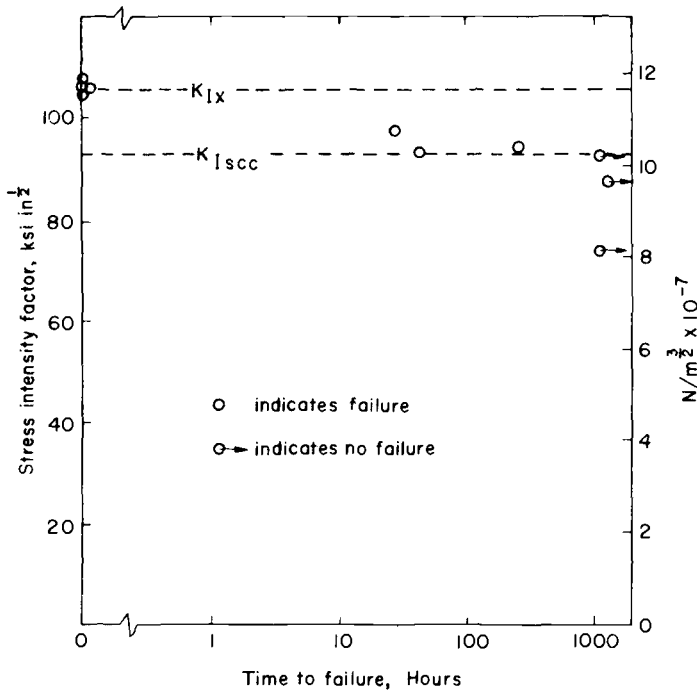


FIG. 4—Results of precracked cantilever beam tests in salt water for longitudinal specimens.

boundary between values of stress intensity that either will or will not produce failure within 1000 h. The ratio of K_{Isc} to K_{Ix} is very nearly 0.9 for both of the two principal rolling directions, thus indicating that the resistance of this material to crack propagation is only slightly reduced by long term exposure to salt water under sustained load.

Following completion of the 1000-h exposure period, those specimens which endured without breaking were loaded to failure without removing the solution from the cell. The values of K_{Ix} thus determined after 1000-h exposure were not significantly different ($P \approx 0.5$ in a statistical T test) from those measured for specimens without prior exposure. This result lends additional support to the conclusion that the load bearing capacity of this material is not substantially altered by long term exposure to salt water.

No evidence of stress corrosion crack growth could be detected in the macroscopic appearance of the fracture surfaces of those specimens which failed at loads above $0.9 K_{Ix}$. The fracture faces were identical to those produced in air and contained only regions identifiable as either fatigue precracking or rapid fracture. In addition, microscopic examination of polished sections normal to the plane of the crack failed to uncover any sign of stress corrosion such as branching or intergranular cracking. Accordingly,

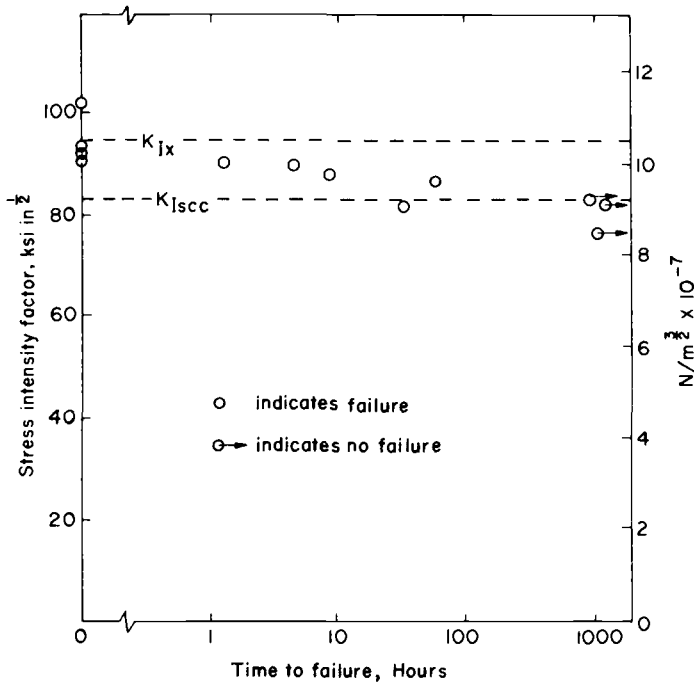


FIG. 5—Results of precracked cantilever beam tests in salt water for transverse specimens.

the failures observed at high loads ($K_I > 0.9 K_{Ix}$) should be characterized as mechanical or corrosion-assisted-mechanical rather than stress corrosion cracking failures. Indeed, in the case of ultra high strength steel, slow crack extension is reported to occur even in dry argon at very high stress intensities by a mechanism distinct from that of stress corrosion cracking [23]. It is concluded that the base plate of this grade is virtually immune to EC failure.

Alternate Immersion Tests of Welded Specimens—Eight butt-welded specimens loaded as shown in Fig. 3 were subjected to alternate immersion exposure for 10 000 h. Following removal from test at the end of the exposure the specimens were unloaded and the amount of elastic springback was recorded. In all cases, the amount of springback was greater than the deflection calculated for an elastic beam [24] which is loaded so that the outermost fibers are at the yield point. This result verifies that the outer fibers were plastically deformed during the initial loading and subsequently maintained at greater-than-yield-point loads throughout the test as intended.

Following springback measurements, the welded specimens were sectioned and pickled in 50 percent hydrochloric acid to remove the heavy layer of surface rust and also to decorate any cracks that might have been present. The

TABLE 1—Comparison of critical values of air-determined stress intensity factor for ASTM A 514/517 steels.

ASTM A 514/517 Designation	Plate Direction	Yield Strength, N/m ²	Specimen Size, m	Type of Test	Critical Stress Intensity in Air $\pm$ Standard Deviation, N/m ^{3/2}	Reference
Type J	longitudinal	8.61×10^8	2.54×10^{-2}	cantilever beam	$1.15 \pm .01 \times 10^8$	this study
Type J	transverse	8.69×10^8	2.54×10^{-2}	cantilever beam	$1.04 \pm .06 \times 10^8$	this study
Type F	...	7.59×10^8	2.54×10^{-2}	cantilever beam	1.15×10^8	[19]
Type J	longitudinal	8.61×10^8	1.27×10^{-2}	center cracked tensile	1.31×10^8	[20]
Type J	transverse	8.69×10^8	1.27×10^{-2}	center cracked tensile	1.25×10^8	[20]
Type F	...	7.59×10^8	5.08×10^{-2}	4 point bending	1.86×10^8	[19]

acid pickling also etches the steel, delineating the regions of weld metal, heat affected zone, and unaffected base plate. Each of these regions was examined by use of a stereo microscope at magnifications ranging up to 200. No evidence of cracking was found anywhere in the welded specimens. This result agrees with that of the work with precracked cantilever beams, namely, that the base plate is resistant to EC. It further indicates that: (a) the weld material is also resistant, and (b) susceptibility is not induced in the heat affected zone of the base plate by the welding process.

Conclusion

Two types of laboratory tests were employed in order to evaluate the resistance of high strength quenched and tempered steel, ASTM A 514/517, to environmental stress corrosion cracking. These were: (a) tests in salt water of cantilever-beam-loaded specimens which contained precracks as a test of the base plate under the most severe conditions, and (b) tests involving alternate immersion in salt water of specimens subjected to sustained greater-than-yield loading as a practical test of this material in the welded condition. No evidence of environmental stress corrosion cracking was observed in either test, thus indicating excellent resistance of this type of failure for this steel.

Acknowledgments

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