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ARPA Coupling Program on Stress-Corrosion Cracking

Final Technical Report: Second Edition

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ABSTRACT

The technical background, organization, and *modus operandi* of the ARPA coupling program on stress-corrosion cracking are summarized. The problem of interpreting the data from smooth stress-corrosion cracking specimens is discussed. This is followed by a summary of technical achievement highlights in narrative form treating specimen types, titanium alloys, high-strength steels, aluminum alloys, and surface sciences. An Abstracts of Achievements section (abstracts arranged by organization) is the most important part of this report, for it gives not only indications of technical contributions but also the literature citations where the interested reader can examine the detailed account of a given topical area. The Abstracts of Achievements section includes a subject index.

The program was one of multiple goals, including experimentation involving coupling NRL with academic personnel and amplifying NRL's capabilities by the addition of an industrial contractor. Since the present report is a purely technical one, it does not treat these non-technical goals. The present report represents an updating of NRL Report 7168 to include material published during the phase-out year of the program.

PROBLEM STATUS

This is a final technical report.

AUTHORIZATION

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ARPA COUPLING PROGRAM ON STRESS-CORROSION CRACKING

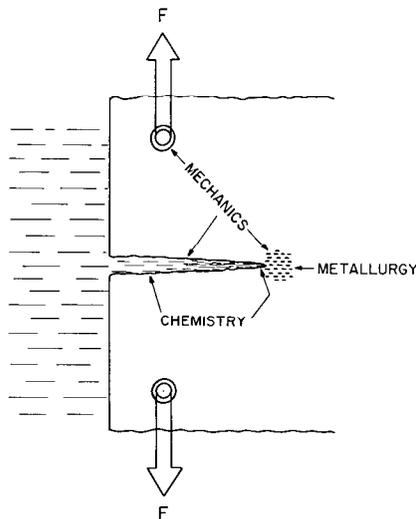
Final Technical Report

INTRODUCTION

History

By 1966 the phenomenon of SCC had affected all the military services (and NASA); had caused serious surprises to the designers of aircraft, submersibles, and rockets; and had involved all three major families of high strength structural alloys—titanium, steels, and aluminum. The Advanced Research Projects Agency (ARPA) of the Department of Defense recognized both the military importance of the problem and its technical complexity, compounding as it does the difficulties of the brittle fracture problem with chemical reactions occurring inside inaccessible cracks (Fig. 1). ARPA also was aware of new developments in surface physics and surface chemistry, some of which might be expected ultimately to afford advances in the science of metallic corrosion. ARPA therefore asked the Naval Research Laboratory to organize an intensive attack on the problem of the SCC of high-strength structural alloys with provision for coupling science to technology and also for coupling academic laboratories with an industrial laboratory and a government laboratory.

Fig. 1 - The three scientific elements of stress-corrosion cracking. Progress requires attention to all three.



Organization

The principal member institutions were NRL, The Boeing Company, Lehigh University, and Carnegie-Mellon University, to which was added Georgia Institute of Technology because of special capabilities in surface physics.

Two other universities had supplementary roles for special purposes: At a time when graduate students specializing in the electrochemistry of corrosion were almost

nil, both in the program and nationally, such students became enrolled at American University under well-qualified thesis supervision; hence, American University became a supplementary member of the program to ensure the involvement of at least a few electrochemistry graduate students, in this case studying the role of anions in corrosion reactions. At the University of Florida, Professor M. Pourbaix became available as a visiting professor and consultant to the program, and for this reason the University became a supplementary member, concentrating on experimental methods to apply Pourbaix' potential-pH method for analyzing the corrosion behavior of complex alloys (commencing with chromium steels).

There were no exclusive charters at any of the institutions, but in general the emphasis at Lehigh was on surface chemistry, that at Carnegie-Mellon was on physical metallurgy, and that at Georgia Tech was on surface physics. NRL contributed to both basic and applied research, and Boeing's role was to amplify the capabilities of NRL. Boeing and NRL filled an additional role by providing opportunities for graduate students to observe and/or participate in applied research in the course of their graduate careers.

SCC, which is caused by the conjoint action of a corrodent and a stress which may be constant, represents one of the limiting cases of corrosion fatigue (as R-1), which differs from SCC in that in corrosion fatigue the stress is necessarily fluctuating. For this reason corrosion fatigue in a limited sense was considered an appropriate subject to be included in the program, and particularly appropriate for a DoD program, since corrosion fatigue is said to be the major cause of failures in vehicles and in moving machinery. Analysis shows that there is no such thing as a simple method of generating the general engineering corrosion-fatigue characteristics of a given alloy, however, and accordingly from midprogram onward the corrosion-fatigue studies were restricted to academic research on mechanisms. Research on corrosion-fatigue mechanisms was also conducted at NRL with Navy funds but associated with the program.

The alloy families of interest were titanium, high-strength steels, and aluminum, and the relative emphasis on the three systems was set at 3:2:1. The reason for this relative emphasis was not alone the relative importance of the problem to DoD, but also the relative amount of accumulated knowledge in the three systems and the activity of producers on the problem in the area of their own products.

Modus Operandi

The program was conducted as a national one in the sense that it was fully integrated into the national technical community. Reports from the program were given unlimited distribution, and attendance at the quarterly meetings (described briefly below) was open to personnel from outside the program, subject only to the limitations of manageability. It was found that keeping the agenda of the quarterly meetings to a single narrow topic (e. g., titanium alloys) accomplished several ends: It permitted an in-depth review of the subject matter, it eased the problem of limiting outside participants, and it promoted interchange between persons working in different disciplines such as surface physics, electrochemistry, metallurgy, crystallography, and mechanics. The program profited immensely by the regular participation of outsiders.

The program was integrated into the national technological community in another manner, namely, by sharing costs. For example, in studies in which, to have technological significance, portions of large heats (batches) of alloys were required, these alloy heats were sometimes procured by other DoD interests, and the small amounts required for SCC studies were traded to the ARPA project in return for the stress-corrosion information generated. Mixed support of another type was practiced in which students whose stipends were paid from one source had the costs of their laboratory supplies and services paid by the ARPA program. These jointly supported activities

provided not only breadth of contact but also economies which in the case of large alloy heats were of important magnitude.

Also as part of the design of the program to serve the national technological community, personnel in the program were encouraged to present the output of their research at various types of technical meetings. The effectiveness of this policy is evident in the Presentations section of the Abstracts of Achievements.

Documentation

This report is primarily technical, but a brief background account is given here for the interested reader.

As another part of the final reporting sequence, there is in preparation a monograph on the state of the art of stress-corrosion cracking (SCC) of titanium alloys, high-strength steels, and aluminum alloys. That monograph is designed to be not only a summary of what has been contributed to the subject by the ARPA program, but a state-of-the-art summary without restriction as to source of contributions. The monograph will therefore be the most useful technical summary of the program for most purposes, for in it the pertinent output of the program is integrated into the entire literature on the subject.

The present report is limited to contributions from the ARPA program. Such contributions from a program as large and as productive as this one cannot be *detailed* in a manageable fashion in a single document such as the present report, but the key contributions are given herein in a consolidated narrative form. In addition, Abstracts of Achievements, modeled after the Interdisciplinary Laboratory reports, are given, together with references to the literature, so that the reader has a key directly to the technical literature of interest to him. The present report was written at the end of the program, and by the nature of the publication machinery of the technical societies many of the manuscripts generated by the program have not yet been printed. In such cases the journal or society is noted so that the interested reader can monitor the appropriate literature for the appearance of a paper of special interest. Requests for reprints should be directed to the individual authors. Qualified recipients may request from the Defense Documentation Center those reports for which accession numbers are given.

In the present report the author uses the term *stress-corrosion cracking* (SCC) to designate a cracking process caused by the conjoint action of a stress (which need not be fluctuating), and a corrodent. The term *corrosion fatigue* is used to designate a cracking process caused by the conjoint action of a fluctuating stress and a corrodent. The terms are thus based upon macrophenomenology rather than mechanisms, and the introduction of new terms such as *corrosion-assisted crack growth* and *subcritical cracking* becomes unnecessary.

The emphasis on reporting was to get contributions presented expeditiously at standard technical society meetings and published expeditiously in their journals, and the function of the quarterly reports was most importantly to notice the writing and the publication of such manuscripts in the standard literature.

THE PROBLEM OF THE MACROSCOPIC TEST

Regardless of how small the scale of events which may cause SCC, ultimately it is the macroscopic phenomenon which must be controlled. The traditional method for

characterizing SCC was to stress a specimen in a corrosive environment and report time to failure, usually meaning time for complete separation of the specimen. Although this parameter has afforded progress, particularly in the low-strength alloys, it is a defective parameter because it represents the undifferentiated *sum* of the effects of three processes, (a) incubation (usually film breakdown plus corrosion pitting), (b) SCC, and (c) terminal mechanical overload fracturing (Fig. 2). If an alloy is not susceptible to pitting, then a (smooth) specimen may give an indication of an infinite time to failure, i. e., the alloy may appear to be immune to SCC, whereas in fact it may be highly susceptible to stress-corrosion crack *propagation*. (Titanium alloys in water exemplify this behavior.) Alloys with different fracture toughness characteristics require different lengths of stress-corrosion cracks (and hence different exposure times) before the onset of overload fracturing; thus time-to-failure data could lead to grossly erroneous inferences regarding the relative SCC characteristics of these alloys. Some materials are so brittle that if they are stressed and a corrosion pit forms, the pit can initiate "brittle fracture," and an indication of high susceptibility to SCC might be inferred from a test in which in fact no SCC has occurred at all. (The 5% Cr die steel heat treated to maximum strength tends to behave in that fashion.)

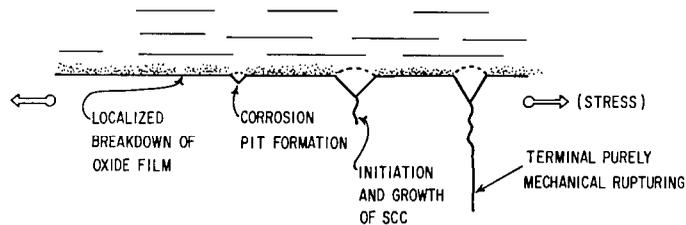


Fig. 2 - Sequence of events (left to right) by which a metal under stress with an originally smooth surface undergoes successively localized film breakdown, corrosion pitting, stress-corrosion cracking, and finally mechanical rupture

The foregoing complications are illustrated in Fig. 3, which is a plot of depth of pitting plus SCC plus mechanical fracturing on the ordinate vs time on the abscissa.

At the beginning of the program, the great bulk of data in the literature and most of that being inserted into the literature were of the undifferentiated time-to-failure type, and as has been shown above, this sort of data can be very misleading about stress-corrosion characteristics. One of the tasks of the program, therefore, was to establish the true SCC characteristics of the structural alloys of most current importance to military designers.

To do this characterization, as well as to conduct other studies both basic and applied, one or more specimen types were used containing pre-existing cracks. This tactic has three advantages: (a) It obviates waiting for a corrosion pit to grow, saving time. (b) It enables one to avoid an erroneous conclusion of immunity to SCC because of a nonpitting combination of alloy and environment. (c) It enables one to get a conservative evaluation by evaluating the material in the presence of the ultimate flaw, namely a sharp crack. There is a fourth advantage, for if the specimen meets certain criteria, the methods of fracture mechanics can be used to predict from the behavior observed in one geometry of specimen and crack what will happen in other geometries.

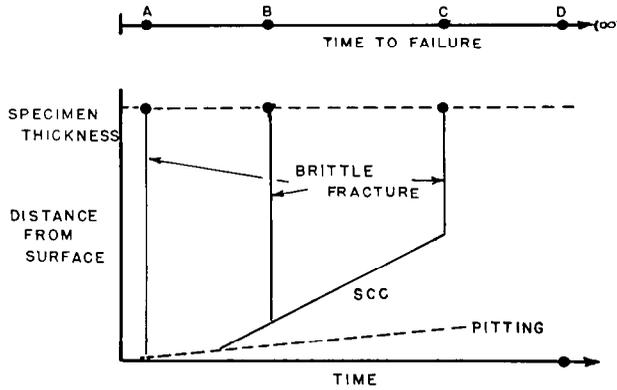


Fig. 3 - The time-to-failure information from stress-corrosion cracking tests of smooth specimens, as plotted in the line at the top, indicates an ascending order of merit with respect to stress-corrosion cracking from A through B and C to D. In point of fact, as shown schematically in the lower portion of the figure, B and C may have the same SCC characteristics but different fracture toughnesses. The SCC characteristics of A and D have not really been measured at all.

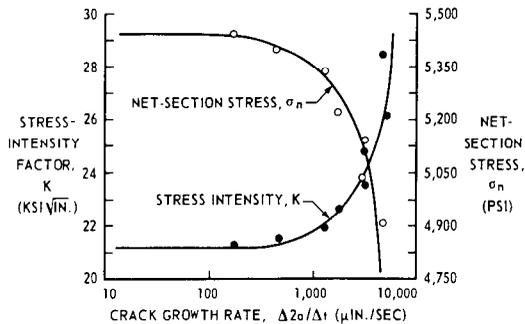
Fortunately for the program, the high level of activity in the fracture mechanics field during the decade preceding the program had produced technological information on various specimen geometries which become useful to the problem of SCC, as will be noted later in this report.

HIGHLIGHTS OF PROGRAM ACHIEVEMENTS

Specimens and Macroscopic Test Methods

During the course of the program the methods of fracture mechanics were demonstrated to afford predictability of stress-corrosion behavior from one geometry of specimen and stress configuration to another, whereas nominal stress was shown to be misleading (Fig. 4). The stress-intensity factor K thus was shown to be the most useful

Fig. 4 - Stress-corrosion cracking data for Ti-8Al-1Mo-1V in salt water. Specimen is stressed at the crack line and the crack growth rate is measured. (Chronologically the experiment proceeds from right to left in this figure.) Experiment shows that as K decreases (because of crack growth), the crack growth rate decreases, but meanwhile the nominal stress (net section stress) increases. This is an illustration of the inability of net section stress to correlate with cracking behavior. Extrapolation of data indicates a K_{ISCC} of about 21 ksi $\sqrt{in.}$.



way to quantify stress in the presence of a stress-corrosion crack. Evidence was found that for titanium alloys there is a threshold value of K below which SCC is not expected (for a given combination of alloy and corrodent), and this threshold was designated $K_{I_{SCC}}$. In the absence of positive knowledge that a true threshold exists, an arbitrarily defined $K_{I_{SCC}}$ (such as "nil crack growth in 1,000 hours") does indeed convey more information than an index of the patience of the experimenter or his skill with instrumentation; for at slightly higher K levels, one can make the positive statement that SCC will occur.

To fully characterize the SCC of a given alloy in a given K corrodent, one would like to have cracking kinetics as a function of K all the way from a threshold ($K_{I_{SCC}}$) if one exists to K_{I_C} , the stress intensity at which brittle fracture occurs. Even if one has only the value $K_{I_{SCC}}$, and even though in a given system this may not be known to be a true threshold but may represent, for example, the minimum K at which SCC is observed in 1,000 hours, the $K_{I_{SCC}}$ numbers can be plotted as a function of yield strength to produce an interesting analysis of the relative merits of various compositions or heat treatments in a given alloy family. In such a plot (Fig. 5), one can simplify the Irwin equation for a surface crack by assuming yield-strength stresses, and assuming that any surface flaw will be long compared with its depth and will lie perpendicular to the stress field, he can then draw a series of straight lines as shown in Fig. 5. Any one of these represents conditions for a given flaw depth, and the line simply means that if one may have a given flaw size as represented by the line, he must have a material with a $K_{I_{SCC}}$ lying above that line to avoid SCC.

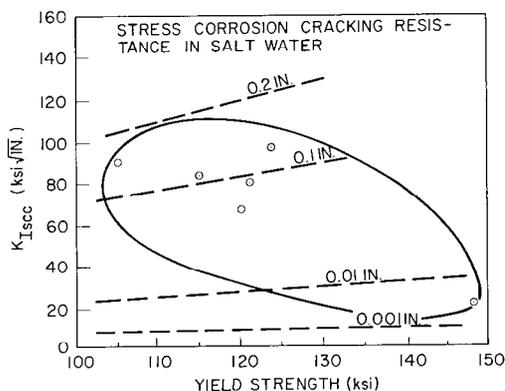


Fig. 5 - $K_{I_{SCC}}$ data in salt water for six commercial heats of Ti-6Al-4V rolled to plates 1-in. thick. All $K_{I_{SCC}}$ data for commercial heats of this alloy have been found to lie within the oval. The broken lines indicate $K_{I_{SCC}}$ values which an alloy must have (or exceed) in order to avoid SCC initiating at a long flaw of the depth shown on the line, assuming yield stresses. (Data show that no commercial alloy can tolerate a flaw as deep as 0.2 in. if the operative stress equals the yield strength.) The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

$K_{I_{SCC}}$ can be determined by a number of specimens, some set at K levels above and others below the $K_{I_{SCC}}$ level. The program showed that there are alternative ways to determine a threshold. For example, one can use the "wedge-loaded" (crack-line-loaded) sheet tensile specimen and await arrest of the stress-corrosion crack, or one can use a load-relaxing system such as an elastic ring to stress a specimen which experiences relaxation as the stress-corrosion crack advances (Fig. 6). It was shown elsewhere during the program that a specimen similar to the one of Fig. 6 can be self-stressed with a bolt and used as a stress-corrosion specimen. During the program the specimen of Fig. 6, self-stressed with a bolt instead of the elastic ring, has been shown to be extremely useful for characterizing the SCC behavior of high-strength aluminum alloys by determining the rate of crack growth as a function of K (Figs. 7, 8). Such a test has been found far more rapid and more discriminating than the traditional methods.

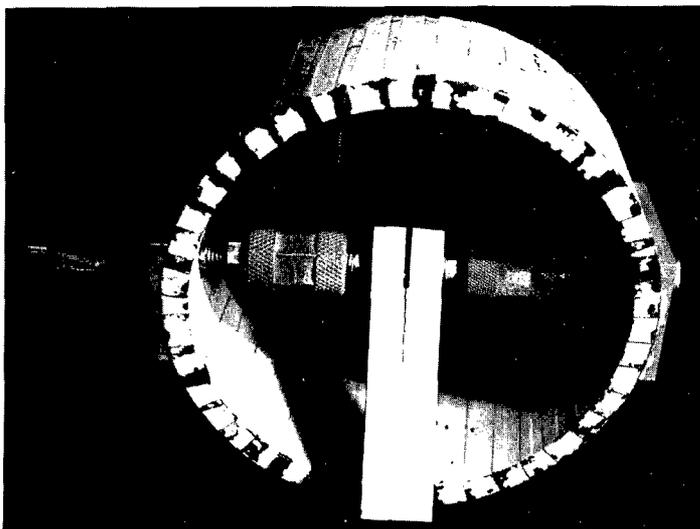


Fig. 6 - DCB aluminum alloy specimen ($1 \times 1 \times 3.5$ in.) stressed by an elastic ring which relaxes as the crack propagates. (Ring is made of high-strength steel wrapped with tape to prevent stress-corrosion cracking.) Load on ring is monitored by strain gage (not shown).

Since K has been shown to be the proper way to quantify stress around a stress-corrosion crack, and since SCC kinetics have been found to be K -dependent, specimens having the property of constant- K conditions regardless of crack length would be of obvious interest. Two such constant- K specimens were studied in the program. One of these, designated the tapered, double-cantilever beam (DCB) specimen, has given experimenters problems with the arms breaking off, and that was found to be true using the specimen for SCC, even though the experimenters were expert with that particular specimen. It was found possible, however, in using this specimen at a number of K levels, to extrapolate the crack rate to zero, which was found to correspond to K_{Isc} for the same steel as determined by a beam specimen. The other constant- K specimen, sometimes designated the double-torsion specimen and sometimes the Outwater specimen (after its inventor), is of additional interest because of its simplicity—it can be satisfactorily prepared from a sheet of metal using a bandsaw. For constant- K conditions the specimen can be satisfactorily stressed by a dead-weight-lever system, and it appears to be well behaved in stress-corrosion tests, at least for high-strength steel.

A small inexpensive self-stressed specimen was developed for possible use as a quality-control specimen for sheet materials.

The newcomer seeing all the various specimens for measuring SCC characteristics might reasonably ask which one he ought to use. It might be helpful to the metallurgist or engineer to regard this selection question somewhat like the question of which *hardness* test one should use. In both cases the answer to the question depends partly on the geometry of the material of interest and partly on the answer one ultimately gets.

Titanium

The resistance to SCC of all the commercial titanium alloys and many developmental and research alloys has been determined using precracked specimens. Electrochemical

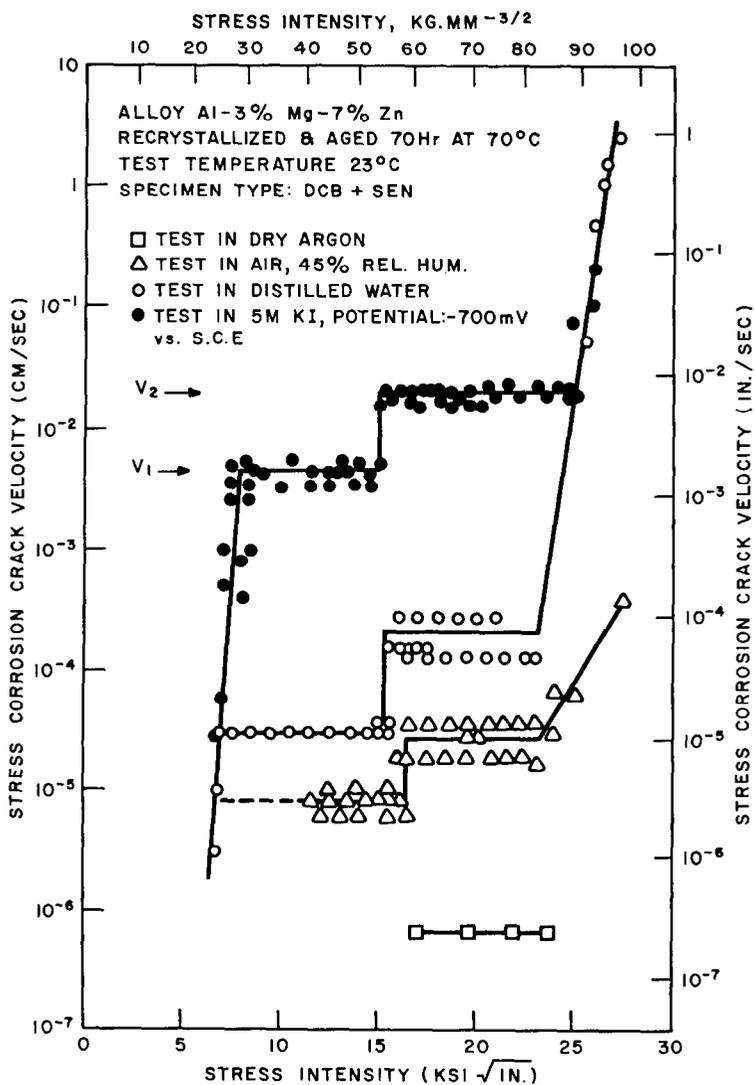


Fig. 7 - Crack-growth rate as a function of K for an aluminum alloy in several environments, illustrating the three stages of the V-K behavior

evidence was interpreted to indicate that for titanium alloys in salt water there is a genuine stress-intensity threshold below which stress-corrosion cracks do not propagate.

The resistance to SCC was found to be strongly dependent upon microstructure and dislocation substructure (Fig. 9). Alpha and alpha-beta alloys that exhibited planar slip in the alpha phase had low resistance to SCC. Beta grains in alpha-beta alloys tended to act as obstructions to the SCC fractures in the alpha phase, but with complications noted below (Fig. 10).

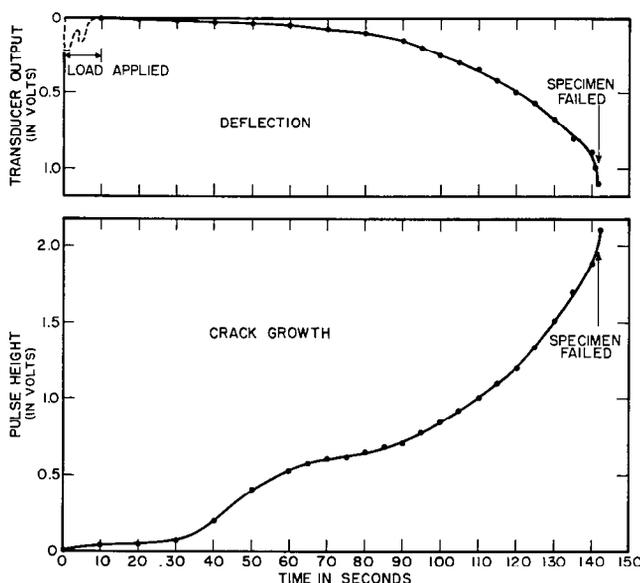


Fig. 8 - Crack-growth rate measurement continues to challenge the experimentalist. An alternative to the clip-gage technique is to monitor the reflection from an ultrasonic pulse (data shown above for a dead-weight-loaded, cantilever-bend specimen of titanium alloy).

Planar slip was found to be characteristic of alloys containing

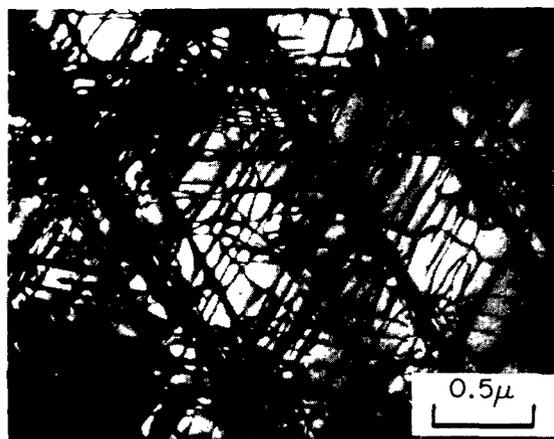
- High oxygen, or
- Aluminum in excess of about 6%, or
- Aluminum in excess of about 5% and tin content of 2.5% or more.

The formation of ordered domains of Ti_3Al or $Ti_3(Al, Sn)$ in the alpha phase further restricted slip and decreased SCC resistance.

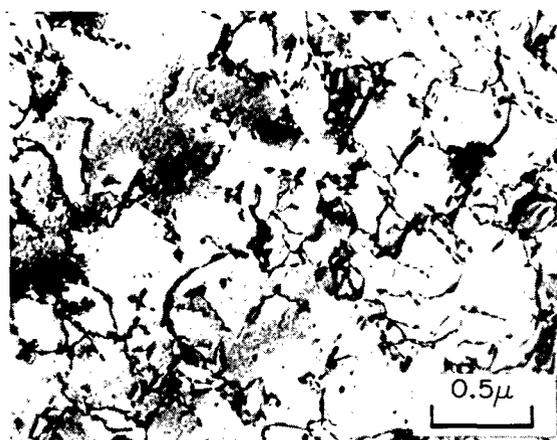
In an alpha-beta alloy, increasing the proportion of beta by increasing the amount of alloying elements such as Mo or V increased SCC resistance, perhaps by the crack-obstructing mechanism mentioned above (Fig. 11). But decomposition of the beta phase (to form omega, Ti_2Cu , or Ti_5Si_3) may embrittle the alloy and markedly lower its SCC resistance.

Of the common commercial alloys, Ti-8Al-1Mo-1V was found to be the least resistant to SCC, Ti-4Al-3Mo-1V was found to be highly resistant, and Ti-6Al-4V was found to have intermediate resistance. These observations were again observed to be correlative to the type of dislocation substructure.

In the all-beta alloy Ti-13V-11Cr-3Al, SCC fractures were observed to occur on or near the (001) plane. The crystallography of twinning of another all-beta alloy (Ti-11.5Mo-6Zr-5Sn) was found to be different from that of most other bcc metals. Mechanical fracture occurs macroscopically parallel to (001), but microscopically the fracture mechanism is not cleavage but microvoid coalescence. Unfortunately, aging this alloy to optimum strength (153 ksi yield) and toughness ($K_{Ic} = 66 \text{ ksi} \sqrt{\text{in.}}$) produced minimum resistance to SCC in halide solutions. The SCC fracture path in this alloy is intercrystalline, in contrast to the transcrystalline fracture path seen in most titanium



(a)



(b)

Fig. 9 - Coplanar dislocation arrays (above, associated with SCC-prone titanium alloys) and tangled dislocations (below, associated with SCC-resistant alloys)

alloys. The formation of omega phase during aging was observed to be an important factor reducing the ductility of the aged alloy; this phase is distributed as small particles (100 to 1,000 Å), but even so may constitute a high volume fraction of the alloy.

The SCC fractures in the alpha phase of alloys lie $15^\circ \pm 2^\circ$ from the basal plane of the hexagonal lattice. This relatively good consistency in crystallographic habit plane has led the resulting flat fracture facets to be termed cleavage (Figs. 12 & 13). The entire SCC fracture surface, however, is not cleavage, but cleavage areas are interspersed with rupture dimples (microvoids) which resemble the dimples of a purely mechanical fracture (Fig. 14). Thus, a stress-corrosion crack appears to be formed by two mechanisms, one (cleavage) involving stress plus an environmental reaction, and the other (dimples) wholly or largely of mechanical origin. The proportion of the dimple areas increases as K increases from $K_{I_{SCC}}$ to K_{I_C} , at which stress intensity the remaining ligament separates entirely by dimple rupture.

Methanol and several other organic fluid environments, including hydrocarbons, were observed to cause the SCC of titanium alloys. Carbon tetrachloride also caused

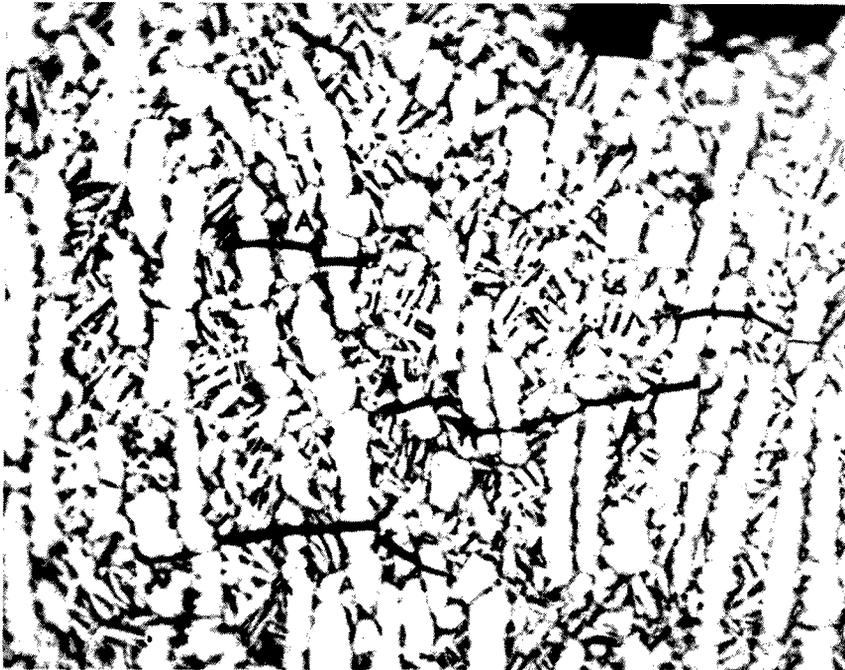
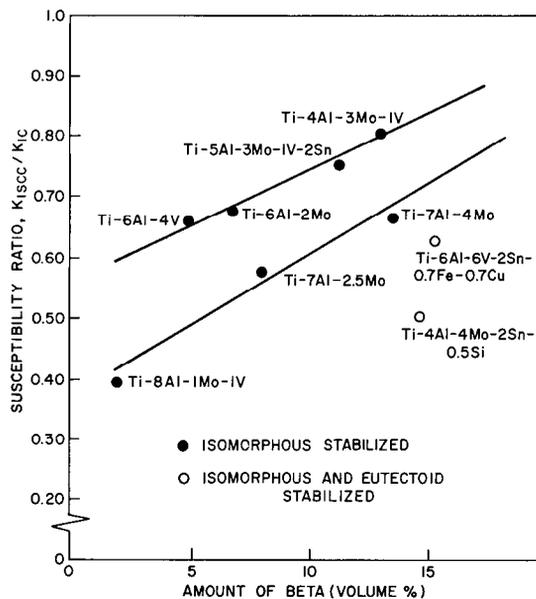


Fig. 10 - Partial stress-corrosion cracks in alpha-beta titanium alloy showing cracks in the alpha phase arrested by the beta phase. 1,000X magnification.

Fig. 11 - Increasing proportion of beta in alpha-beta titanium alloys tends to increase the ratio K_{Isc}/K_{Ic}



severe cracking. These findings have practical implications in the selection of paints and of cleaning and degreasing fluids. Except for liquid metals, carbon tetrachloride is the only environment not containing hydrogen (assuming the CCl_4 was free from HCl), which cracks titanium.

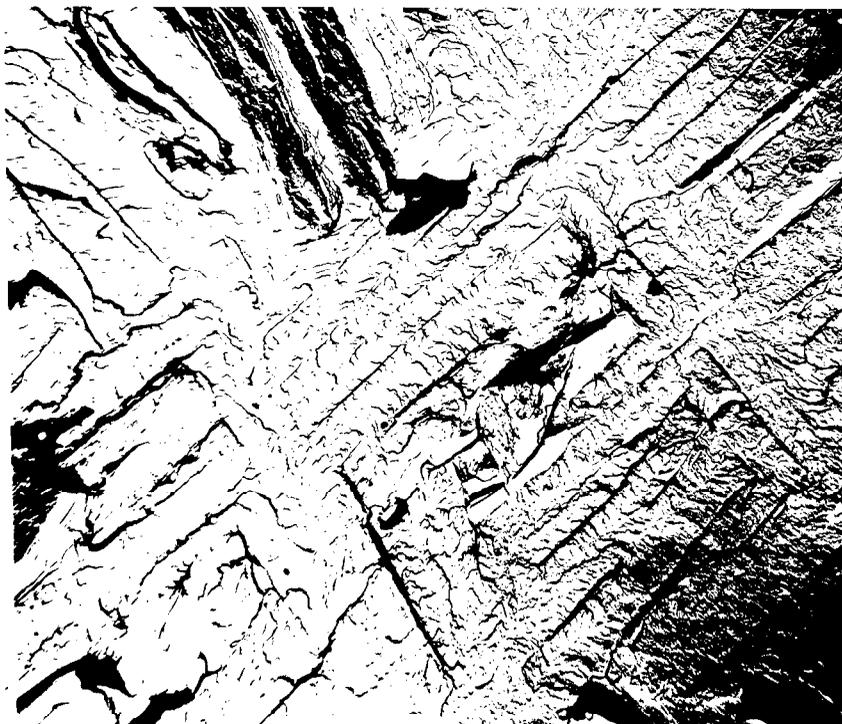


Fig. 12 - Fractograph showing cleavage surface typical of stress-corrosion cracking in titanium alloys in water at a low K level. 6,000X magnification.

Slow crack propagation was observed in titanium alloys in the absence of atmospheric moisture and also in a hard vacuum somewhat better than 10^{-7} torr. In these specimens as in those cracked in organics and in aqueous liquids, the fracture was cleavage interspersed with dimples. Heat treatment which reduced the hydrogen content of the titanium reduced its tendency to slow crack growth in vacuum (Fig. 15).

Methods were developed and applied to elucidate the nature of the corrodent near the advancing crack tip. With neutral salt water as the corrodent, the pH at the advancing crack tip was highly acid (about 1.6). The pH and the potential place the crack tip in a thermodynamic regime in which the hydride may be stable, but not an equilibrium oxide. The addition of FeCl_3 to the salt water increased the SCC resistance of the titanium, perhaps by substituting the reduction of copper for the reduction of hydrogen as the cathodic reaction.

One model which has been proposed for SCC of titanium, in accord with the observations noted above, is the hydrogen model. The reaction of a clean titanium surface with any of the hydrogen-bearing environments studied would release hydrogen which would be expected to react with or dissolve in the titanium. In aqueous salt solutions, the pH at the growing crack tip remains sufficiently acid (because of the occluding action of the SCC path) that repassivation is not possible at the crack tip, which continuously provides clean surfaces for reaction to remove more hydrogen from the corrodent. Thus the function of the precrack in specimens tested in salt water is to provide a little local straining plus the restriction to diffusion which will permit the acidity to remain high locally, whereas smooth specimens tested in salt water would repassivate because of the inability of the geometry to keep the acidity high locally. In methanol, however, the situation is different because the product of the reaction of titanium and methanol is soluble in methanol, i. e., the reaction product does not form a protective film in the

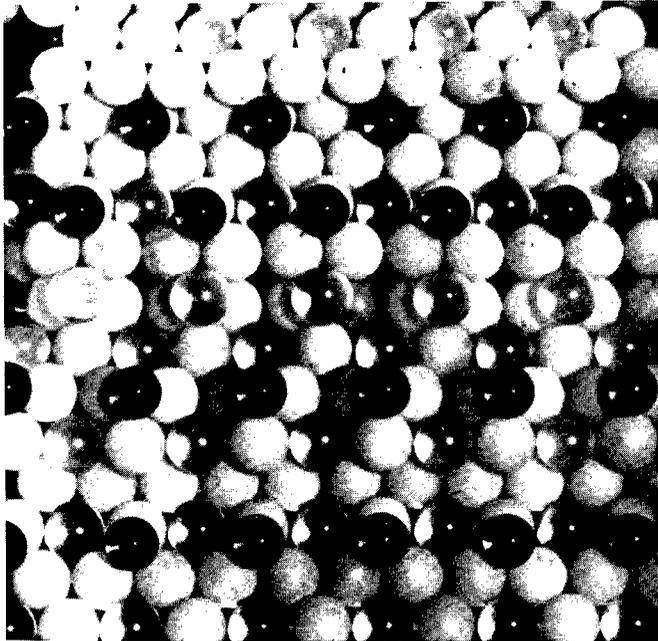


Fig. 13 - Ball model of simulated SCC fracture surface in Ti-Al alloy. Aluminum atoms on base surface are designated by clear balls and on the matching plane by dark balls. The fracture plane occurs where there is the highest concentration of Ti-Al bonds in ordered alpha.

bulk environment. This has been concluded to be the reason *smooth* specimens will initiate SCC in methanol.

Straining Ti-Al alloys in salt water was observed to cause large increases of the active range during anodic polarization, and this too is consistent with the picture of reactions occurring near the crack tip. A computer program has been developed for solving the complex electrochemical transport equations involved in SCC. The aspect ratio was found to dominate all else.

Ti-Al alloys were found to show the same precipitation of hydride at coplanar dislocations in SCC specimens as in slow strain-rate hydrogen-embrittlement specimens, again suggesting the hydrogen model.

Acceptance of the hydrogen model would require a resolution of two apparent anomalies: a) the observation of SCC in reasonably pure CCl_4 (containing traces of water), and b) the observation that increasing $[\text{Cl}^-]$ increases SCC crack-growth rates at a given K level.

Steels

The SCC characteristics of a large number of commercial and near-commercial steels were determined using salt water and natural seawater (Fig. 16). The use of pre-cracked specimens to determine SCC characteristics of alloy steels in seawater can save half a year to a year, which otherwise may be required to generate the pits which in turn initiate SCC. (A precracked specimen may, however, give erroneous data if it is



Fig. 14 - Fractograph showing flat cleavage areas plus dimpled (mechanical rupture) areas typical of SCC in titanium alloys in water at a K level much higher than that of Fig. 12

stressed to a high level before being placed in an SCC test at a lower stress level.) From the data of Fig. 16 it is apparent that the maraging steels and at least some of the precipitation-hardening steels were clearly superior to the conventional martensitic steels at the same strength level.

The following observations were made on low-alloy martensitic steels: Silicon content had no effect on $K_{I_{SCC}}$, but above about 1.5% the increased silicon greatly retarded the cracking kinetics at a given K level. Reducing the grain size also decreased the cracking kinetics, but did not affect $K_{I_{SCC}}$. Increasing the manganese or carbon content caused markedly reduced $K_{I_{SCC}}$ values (Figs. 17, 18). None of the following metallic alloying elements was observed to have a significant effect on $K_{I_{SCC}}$: nickel, cobalt, chromium, and molybdenum.

Fig. 15 - Effect of hydrogen content (varied by vacuum treatment) on fracturing of a commercial titanium alloy in various modes. The line designated K_{IH} represents the stress intensity above which a crack propagates in an inert environment, presumably due to internal hydrogen.

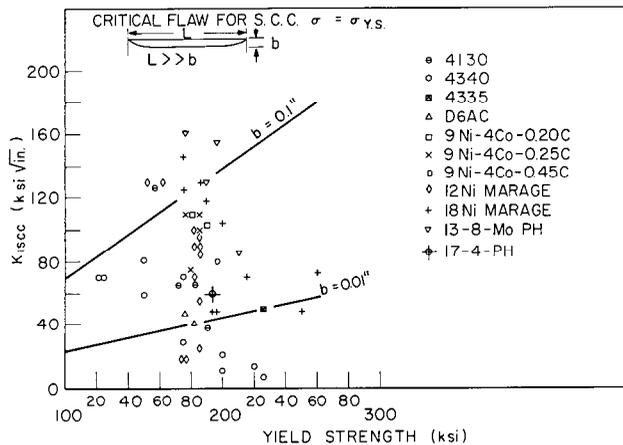
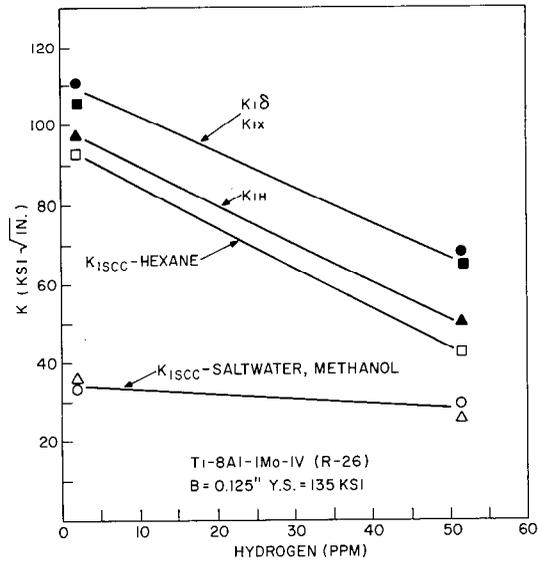


Fig. 16 - $K_{I SCC}$ data in salt water for a number of commercial alloy steels made in production-size heats. The strength range covers strengths of interest to deep-diving submersibles, rockets, and manned aircraft. Flaws of the depth shown in a given steel would propagate stress-corrosion cracks at yield-strength stress unless the $K_{I SCC}$ of that steel lies above the line. The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

The purity of maraging steels with respect to sulfur and phosphorus was not found to have an important effect on SCC characteristics. The same was observed in low-alloy martensitic steels of the 4340 type.

Among the maraging steels, thermal history appears to have an effect above and beyond its effect on strength. Underaging the 350-grade maraging steel was found to be bad for SCC, whereas overaging was helpful. Overaging of 18%-Ni maraging steel

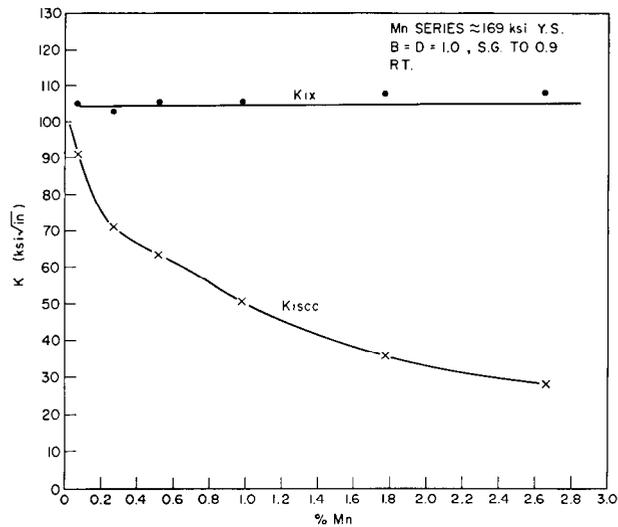


Fig. 17 - Effect of manganese content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

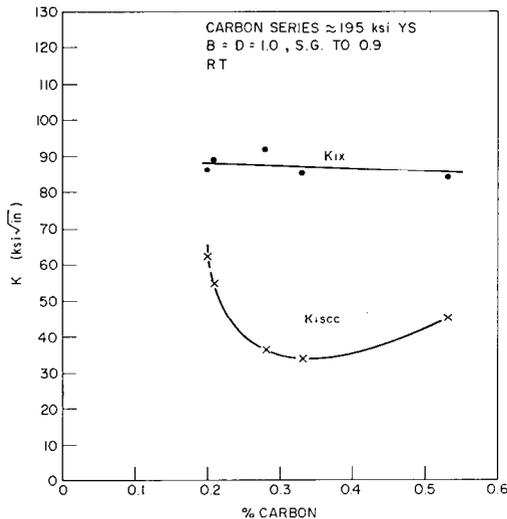


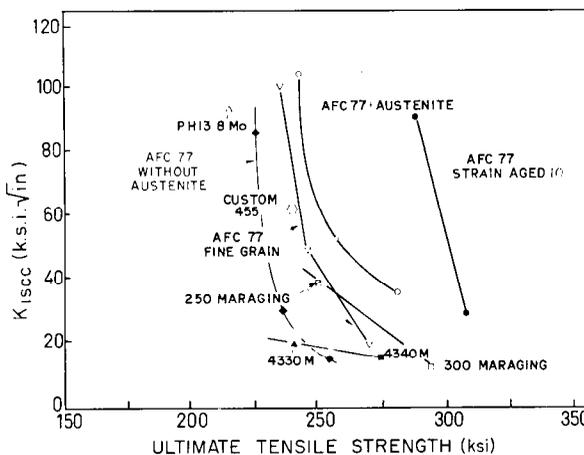
Fig. 18 - Effect of carbon content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

produces reverted austenite, the primary site for which appears to be the compound $Ni_3 Mo$.

$K_{I_{SCC}}$ has a complex curvilinear dependence on strength level, but for a given martensitic steel in the 175- to 185-ksi yield-strength range, a 7% increase in yield strength (by differences in tempering treatment) caused a 20% loss in $K_{I_{SCC}}$, which is linearly proportional to the load-carrying capability of a component containing a standard flaw. The program demonstrated, however, that strengthening by strain aging (in a precipitation-hardening steel) entails a smaller penalty in SCC than the strengthening of martensitic steel by choosing the tempering temperatures, thus providing a possibly useful avenue for further advances for special needs (Fig. 19).

Stress-corrosion cracks are commonly thought to be characteristically multiply branched, because SCC was first observed in cold-worked products, which have complex

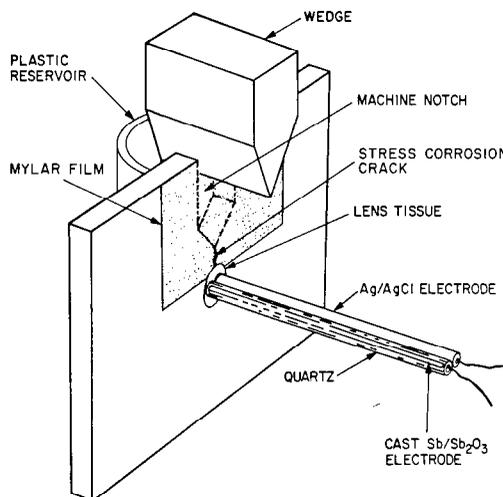
Fig. 19 - K_{Isc} for several commercial steels and one developmental steel (AFC 77) in salt water. Note, for AFC 77 in any given condition, the rapid decrease in K_{Isc} with rising ultimate tensile strength. Note also that by increasing the strength by strain aging, the strength can be increased over that of regular AFC 77 by more than 50 ksi while maintaining the same K_{Isc} .



residual stress patterns that change continuously as the article cracks. In the present program it has been found with many materials that the crack-growth rate rises sharply with increasing K until a point (K_{In}) of apparent process saturation is reached, beyond which the rate is more or less independent of K . If the material is reasonably isotropic, then at a K level of about $2K_{In}$ the crack will tend to divide or branch. This finding is useful in understanding tests in which the crack divides and thereby terminates the utility of the experiment.

During the course of the program, methods were developed which for the first time were successful in measuring the pH near the tips of growing stress-corrosion cracks in steel (Fig. 20). These methods employed successively color-change pH indicators,

Fig. 20 - One method for determining the pH at the tip of a stress-corrosion crack. The potential and pH probes rest against a small paper disk (thin to minimize the solution required to moisten it), and are connected to high-resistance recorders. They do not register a reading until the crack propagates to the disk and moistens it. (The disk does not contain solutes which affect pH.) A glass electrode designed for surface measurements can be used in place of the antimony oxide electrode.



the antimony electrode, and finally the glass electrode, and all three methods gave the same result. This work on crack-tip chemistry gave new insight on SCC (and eventually on most forms of localized corrosion, as will be discussed in a later section). It was found that regardless of the pH of the bulk solution (external to the crack) or the potential impressed upon the steel, the combination of potential and pH at the crack tip are such as to be favorable for the reduction of hydrogen (Fig. 21). This finding makes it unnecessary to postulate any mechanism for SCC in (high-strength) steel other than that commonly termed *hydrogen embrittlement*. The mechanism of hydrogen embrittlement has

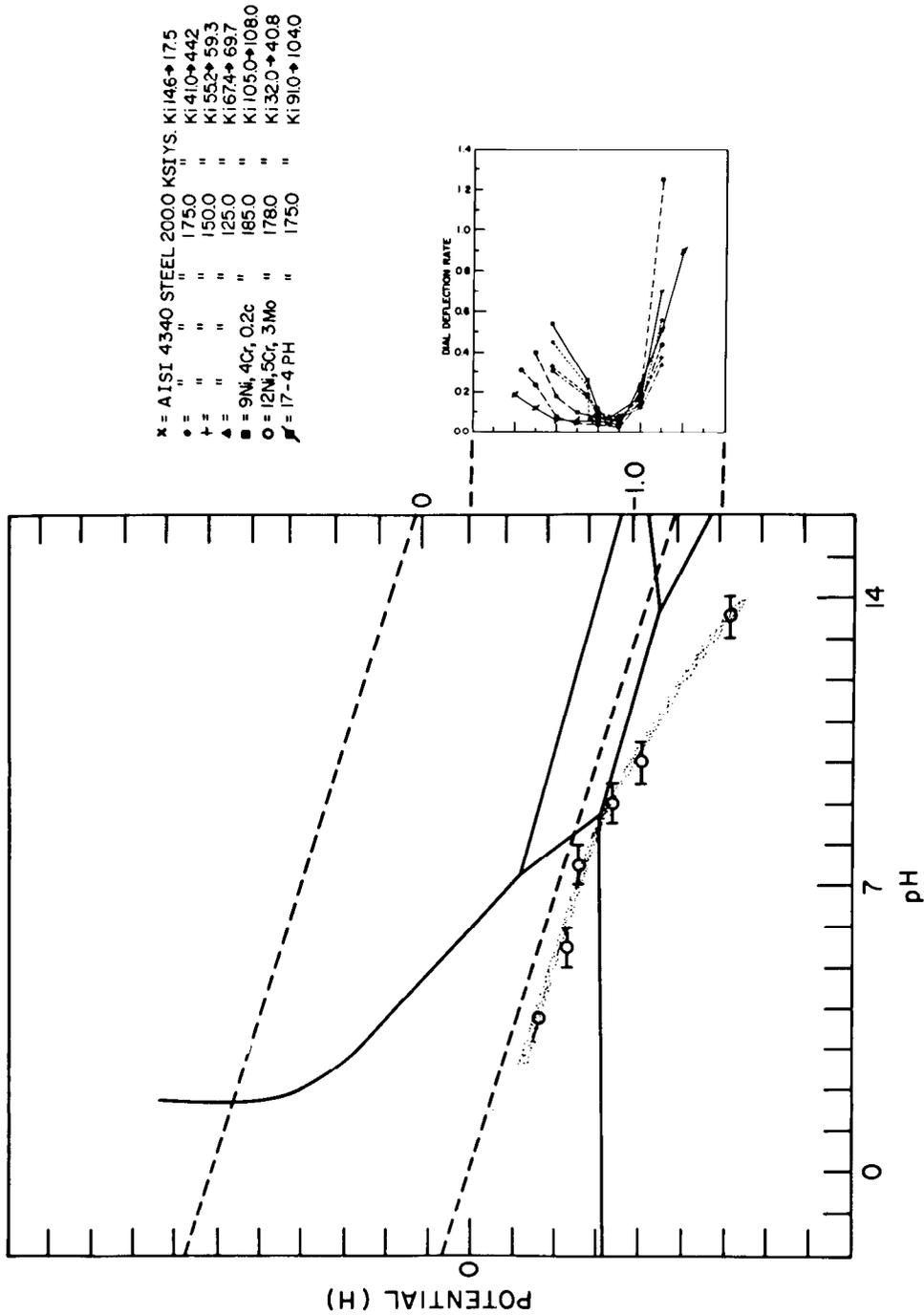


Fig. 21 - pH at the tips of growing cracks in neutral 3.5% NaCl solution, specimens potentiostatted to various levels. Curves at right indicate a function of crack-growth rate (dial deflection rate) at approximately constant K for a given steel (but different K's for different steels). These data were taken by color-change pH indicator technique but have since been confirmed by the glass electrode. Stress-corrosion cracking in steels occurs only under conditions of local pH and potential which place the crack tip under the hydrogen reduction line (lower sloping broken line).

been postulated to involve the formation of an iron hydride, thought to have been prepared and partially characterized, but work during the program has shown that the alleged iron hydride (prepared by a Grignard method) was really an organic compound of iron.

The work on crack-tip chemistry forms the basis for postulating a new role for either a corrosion pit or a pre-existing crack in initiating SCC: Formerly the pit and crack were viewed as stress concentrators, but it is now concluded that their *essential* role is to produce the local acidity which helps establish the conditions for hydrogen reduction. In the corrosion pit the acidity caused by hydrolytic reactions is retained locally by the porous cap of corrosion products, and in the stress-corrosion crack the local acidity is retained because of the long narrow diffusion path between the crack tip and the external corrodent. These observations are consistent with current findings in the program on the nature of pitting of Fe-Cr alloys (Fig. 22).

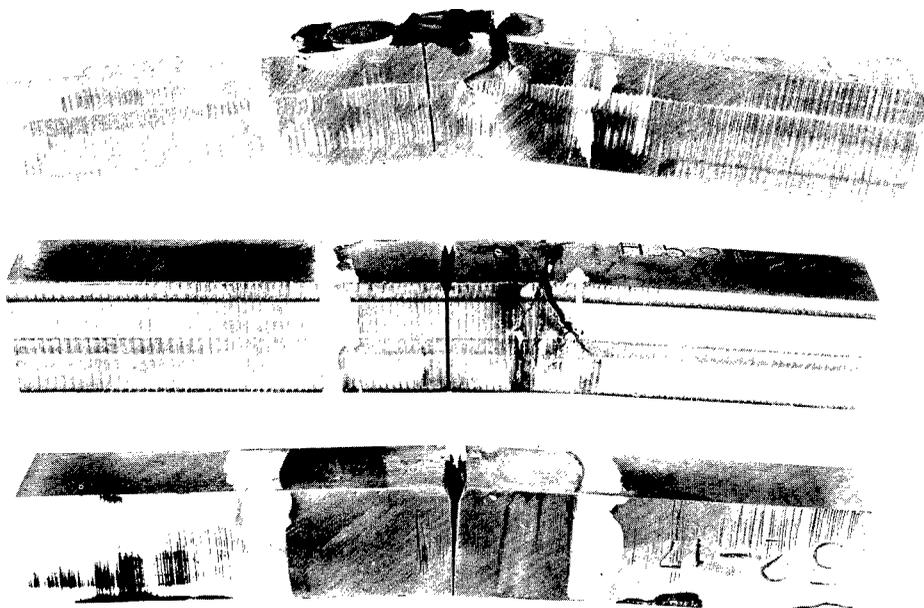


Fig. 22 - Three specimens of a 13-8Mo precipitation-hardening steel whose stress-corrosion cracking characteristics, at first puzzling, become comprehensible in the light of the experiment of Fig. 21. The lower specimen, stressed at a high K , commenced cracking at the notch. At a lower K (center specimen) there was no cracking at the notch but, after a delay of 1300 hours, there was rapid cracking under the wall of the corrodent cell. This was attributed to lowering of pH in the crevice under the wall by crevice corrosion so as to cross the hydrogen reduction curve. The upper specimen also cracked immediately at an unnotched area on which a crystal of ferric chloride had been laid to lower the pH locally.

The acidity role of the corrosion pit suggested that inhibitors and buffers which prevent the formation of the corrosion pit would be effective in preventing SCC of a smooth specimen, and this inference was confirmed experimentally. A specimen containing a precrack, however, responds only to a limited degree to inhibitors and buffers: K_{Isc} cannot be raised to K_{Ic} by such additives, doubtless because not enough of such additives are present inside the crack at the crack tip to fully control the local pH.

Cathodic protection can readily effect changes in pH deep within growing stress-corrosion cracks (contrary to a commonly held rule of cathodic protection technology to the effect that cathodic protection cannot function deeper down a crack than about eight times the crack opening dimension). [Partly because of the foregoing discrepancy, an NRL study in another program showed that the factor of 8 cited above was too pessimistic by at least a factor of 10^3 .] Cathodic protection has not appeared to be a solution to the problem of SCC in high-strength steel because, although the local hydrolytic acidification can be prevented by cathodic polarization, the conditions are still met for hydrogen evolution and cracking does continue to occur. The rate of stress-corrosion crack growth is highly dependent on potential and goes through a minimum at about -0.85 to -0.9 V (SCE) for all alloy steels which have been studied; this minimum in kinetics corresponds approximately to the potential at which iron becomes thermodynamically stable in water, suggesting that the reason for the minimum may be caused by the transfer of the anodic reaction from within the crack (when electropositive to the minimum) to outside the crack (when electronegative to the minimum). As a practical application of this information, one should be able to achieve approximately the minimum in cracking kinetics by plating with cadmium.

If one studies the details on the fracture surfaces using high-resolution replication electron fractography, one finds that regardless of potential, the fracture surface is one of smooth facets (prior austenite grain boundaries) upon which are superimposed plastic tear ridges. The tear ridges increase in number with increasing stress intensity K , until at K_{Ic} the fracture is totally tear ridges surrounding craters (purely mechanical microvoid coalescence, or dimple rupture, fracture). This identical nature of fracture details regardless of which side of the potential minimum one is on is consistent with the conclusion that only one model (hydrogen cracking) is required to account for SCC in high-strength steels.

Consistent with the hydrogen model of SCC in steels, the presence of sulfide in the corrodent (which would tend to promote the entry of hydrogen into the steel) has a strikingly adverse effect on SCC.

One can change the oxide film on the exterior of the specimen from one which is conductive (Fe_3O_4) to one which is poorly conductive ($MnFe_2O_4$), but this change does not appear to have any significant effect on SCC behavior.

The crack tip chemistry studies on *steels* in salt water or in ordinary distilled water showed that the corrodent is concentrated with respect to iron. Thus the newly formed crack surfaces do not behave like pure iron in superpure water, in which environment the iron has been shown to be as inert as platinum.

Large changes in pH locally compared with that of the bulk environment are characteristic of the corrodent in stress-corrosion cracks in all alloy families studied (Fig. 23).

One practical *caveat* appears to be provided by the finding that the behavior of pre-cracked specimens of the stainless steel designated 17-4 PH in (nearly neutral) salt water does not correlate with the poor resistance of this alloy to SCC in service. A possible explanation for this apparent discrepancy is that in service, localized hydrolytic reactions (in crevices, for example) may provide such high local acidity as to create a fundamentally different environment, perhaps also contaminated with sulfur compounds, with a different (and lower) K_{Isc} from that measured in neutral salt water.

Aluminum

The work on aluminum alloys in this program, although by design receiving the least emphasis of the three alloy families, became particularly productive in the more

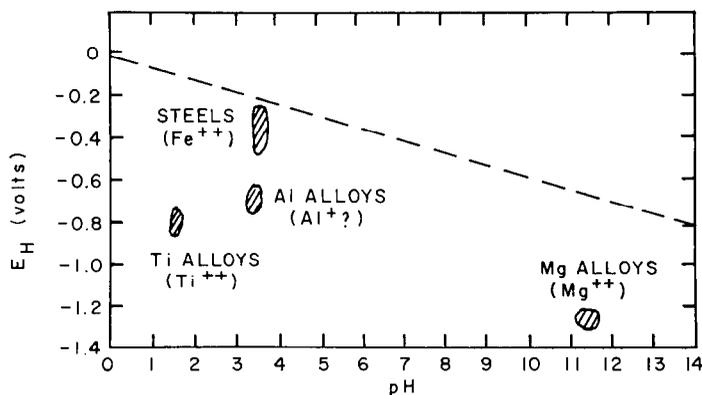


Fig. 23 - Potential and pH data for the tips of growing stress-corrosion cracks in four alloy systems in nearly neutral salt water. Data taken by color-change pH indicator paper technique. Illustrates the large differences between pH of the bulk solution and that at the occluded reaction site. (Hydrogen can be reduced from water below the broken line.)

practical aspects of the problem because of the adoption of the precracked specimen technique (Fig. 24). Wrought products of the Al-Zn-Mg group of alloys which have strengths of special interest to the DoD are highly textured, and SCC is a problem primarily only parallel to this texture. Ordinary bent-beam or tensile specimens cannot be cut in such a fashion as to test this maximum vulnerability direction unless either the plate is very thick or extensions can be welded or otherwise firmly attached to the plate material, which has never been an attractive approach.

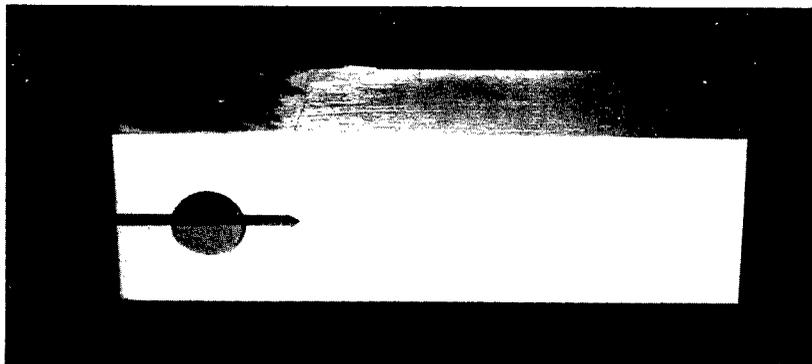


Fig. 24 - Aluminum specimen of Fig. 6 self-stressed (after the method of Novak and Rolfe) by a setscrew. Dark region is paraffin used to insulate the steel setscrew from the crack area. A stress-corrosion crack is seen emanating from the machined notch. This type of specimen was used for most of the characterization data on aluminum alloys in the program.

Early work with the specimen of Fig. 6 suggested that there was a stress intensity below which SCC stopped, but later work has indicated that, although the rate of crack growth diminishes with decreasing K at low levels of K , there does not appear to be any true threshold below which the cracking absolutely stops. Events have shown that the

best way to characterize the SCC behavior of a given alloy is to report the kinetics of crack growth as a function of K, which will be referred to here as V-K characterization.

A contribution from outside the program has been highly beneficial in using the DCB specimen of Fig. 6. This contribution was the demonstration that one could use a bolt to spread apart the two arms of the DCB specimen to stress it without the need for the proving ring, and that stressing in such fashion still permitted quantification of the stress intensity at the root of the crack. This specimen can then be described as a self-stressed DCB specimen, and it has become a most productive research tool, with demonstrated usefulness for sheet material at least as thin as 0.05 in. Among its other advantages, the self-stressed specimen has that of being suitable for wide distribution for readily assessing, say, the effect on SCC of the environment of an airport runway, or of a deep-diving submersible, or of a noxious chemical.

V-K studies have been completed on a large number of commercial and experimental alloys in various tempers (Fig. 25). These studies have shown that at low values of K, log V rises rapidly and linearly with increasing K (Stage I) until a saturation level (Stage II) is reached, after which V is nearly independent of K. In some alloys there is a third stage, near K_{Ic} , in which V is again dependent upon K. Curves of $K \log V$ yield

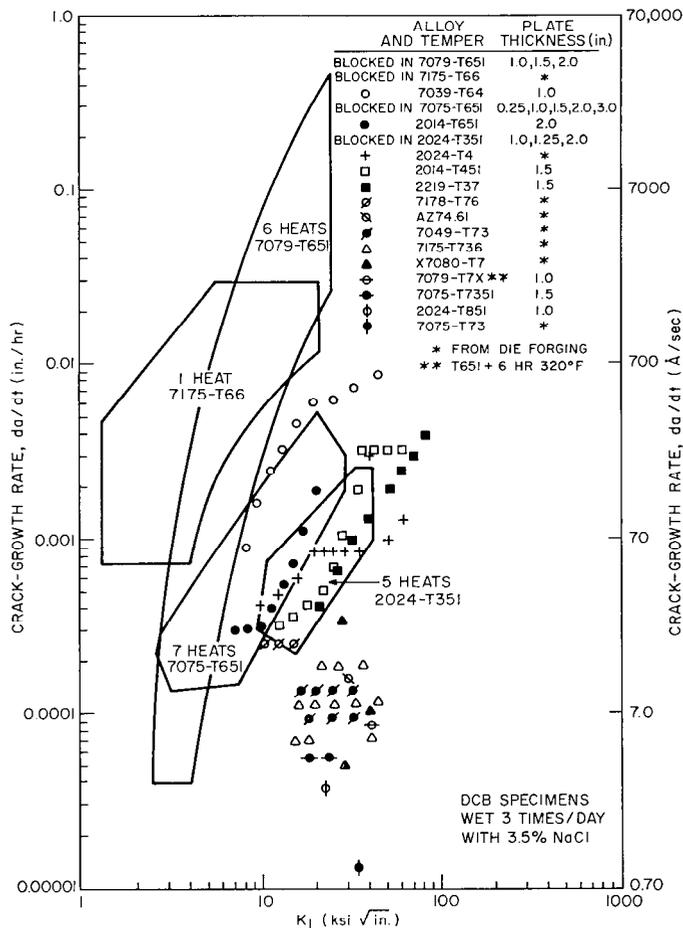


Fig. 25 - Comparison of several commercial and experimental aluminum alloys using the self-stressed DCB specimen and the crack-growth rate method

rangings which agree with established rankings using smooth specimens with two differences: The K-log V rankings are enormously more rapidly obtained, and they are more discriminating than the smooth-specimen rankings when applied to alloys having approximately the same SCC characteristics.

The DCB specimens demonstrated in a very graphic way the magnitude of the effect which quenching stresses can produce in the SCC of aluminum alloys.

The evidence to date is that in Stages I and III the rate of crack growth is little influenced by halide-ion concentration, but the velocity of Stage II apparently can be strongly affected by anion concentration.

Commercial alloys do not experience SCC except when water is present, and only the anions Cl^- , Br^- , and I^- accelerate V (in Stage II) appreciably.

New information was developed on the effects of microstructure on SCC (Fig. 26). It was shown, for example, that the microstructure controlled the cracking process through its effect on the deformation process: Specimens which were strengthened by large Guinier-Preston (G-P) zones exhibited coarse slip characteristics and proved to crack readily, while specimens hardened by small G-P zones exhibited fine slip and cracked slowly. Work on bicrystals revealed that when slip could be transferred across the grain boundary, cracking was slow, but when slip transfer was impeded by the boundary, cracking was rapid.

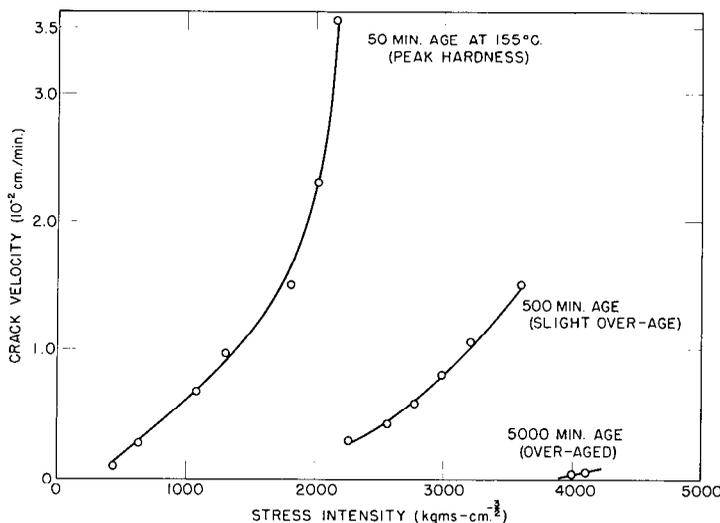


Fig. 26 - Effect of heat treatment on the stress-corrosion cracking kinetics of Al-15%Zn. Transmission electron microscopy shows that the increasing aging time at 155°C causes a progressive decrease in the volume fraction of Guinier-Preston zones.

Neither the presence nor the width of the precipitate-free zone was observed to have any effect on the stress-corrosion susceptibility of a ternary Al-Zn-Mg alloy (Fig. 27). This finding has been explained in terms of slip-band behavior.

Methods have been developed to measure the pH at the tips of growing cracks using both color-change pH indicators and the glass electrode, and in the case of 7000-series

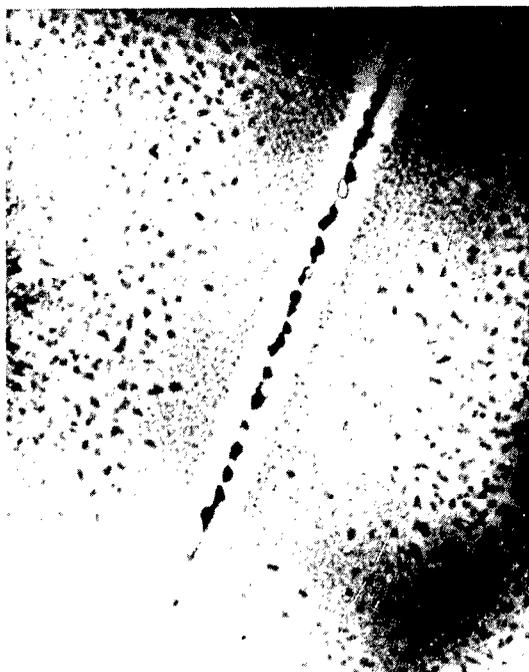


Fig. 27 - The precipitate-free zone adjoining a grain boundary in an Al-6.8% Zn-2.3% Mg alloy. There has been much controversy over the role that this zone plays in stress-corrosion cracking behavior. Studies on high-purity alloys have led to the conclusion that it is primarily the matrix precipitates, and not the grain boundary precipitate, that determine susceptibility to SCC.

aluminum alloys undergoing cracking from nearly neutral salt water, the pH at the crack tip was found to be 3.2 to 3.5. A macroscopic model was also devised to simulate the sides and the base of a stress-corrosion crack, with the simulated base electrically isolated from the simulated walls. This model has given interesting results to date and gives promise of more to come.

In addition to other basic contributions to aluminum corrosion, two reviews were written by program personnel. One of these was concerned with the aluminum-hydrogen system. A second review treated chemical effects in the corrosion of aluminum and aluminum alloys.

An academic study of the corrosion fatigue of an aluminum alloy demonstrated that hydrogen diffusion is not rate controlling (Fig. 28).

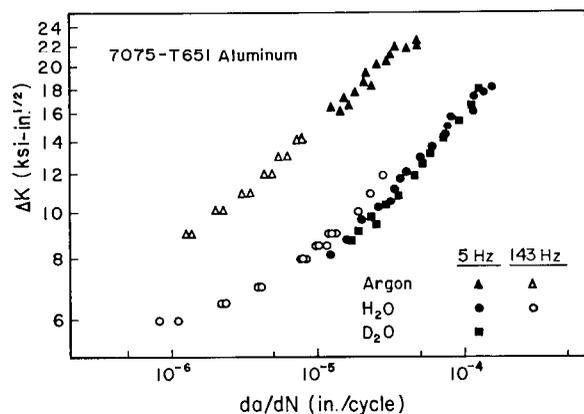


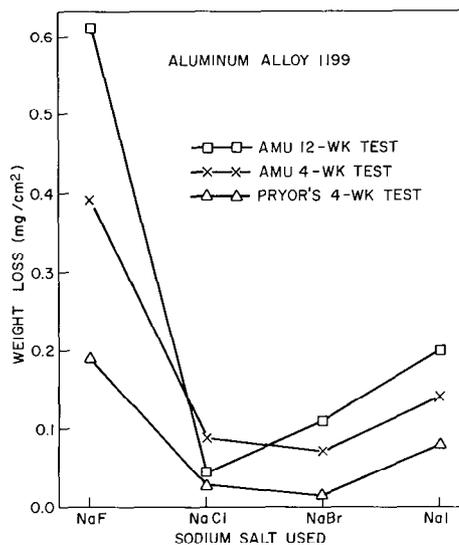
Fig. 28 - Fatigue (in argon) and corrosion fatigue (in water) crack-growth rates in an aluminum alloy. Deuterium studies indicate that hydrogen diffusion is not rate-determining.

Surface Sciences

Various entries in the Abstracts of Achievements identify contributions of some of the subdisciplines which are sometimes called collectively *surface science*. For example, techniques of Low-Energy Electron Diffraction (LEED) have been advanced by the program to enable the experimenter to study the initial reaction of any chosen gas (however corrosive) with a clean metal surface. An international conference was held in which the status of field ion microscopy and field emission microscopy were reviewed by internationally recognized experts, and the proceedings have now been published. Electron spin resonance studies were made on oxide surfaces exposed to various gaseous species.

As indicated by the foregoing, the program was instrumental in drawing to the attention of surface scientists the existence of a challenging technological problem. As a consequence many basic studies were made using various ones of the newer surface science techniques, much new and interesting information was developed, and more techniques were added to those available to the surface scientist (Figs. 29 to 31). The technique of LEED in particular made significant advances because of the program. The experimental and theoretical difficulties of the program area are such, however, that much more work is required before these newer approaches can make their contributions to corrosion technology.

Fig. 29 - Basic study of the role of the chloride ion in the corrosion of aluminum. Kinetic data show that although there are some quantitative differences between the behavior of the various halide ions, there are no qualitative differences, and the role played by chloride is due to its ubiquity rather than any uniqueness.



The electrochemical techniques and concepts, especially those developed and applied by Evans, Hoar, Pourbaix, and their students, have been shown to be of immediate value both in advancing the theory of stress-corrosion cracking and in guiding technological experimentation. Since electrochemistry is generically a surface science, the tenet that surface science would be useful to the stress-corrosion problem at an early date has thus been vindicated. As one example, it has been postulated elsewhere that hydrogen can only be reduced from aqueous solutions at a cathode, that by making a piece of steel an anode one establishes conditions incompatible with hydrogen reduction and that any SCC occurring under such conditions cannot be attributed to hydrogen. A more sophisticated analysis of the situation is as follows: A given site (electrode) can serve as an anode for the dissolution of iron and at the same time function as a cathode for the reduction of hydrogen, if the potential and pH are favorable.



Fig. 30 - Field ion micrograph Ni₄Mo. This is one of several modern techniques in surface physics which are useful to study the ultrafine-scale nature of clean metal surfaces.

The experience of the program, in summary, is that there are numerous new areas of surface science capable of yielding important scientific knowledge about metal surfaces and their reaction with environment. The more mature discipline of electrochemistry has been demonstrated to have immediate utility in the understanding of the processes of aqueous corrosion, including stress-corrosion cracking, and in the guidance of future technological advances.

ABSTRACTS OF ACHIEVEMENTS

Explanatory Notes

These abstracts were prepared by the organization performing the research as a means both of summarizing progress and giving the reader a key to the literature generated by the program. They were modeled after annual reports of Interdisciplinary Laboratories, listing task title, personnel, objective, usually the approach, the achievements, and publications and presentations.

It will be noted that a given task, represented by a single task title, may differ greatly from another in scope, staffing, and productivity. This is due in considerable measure to the broad technical nature of the program and to the fact that each organization grouped its work under a given task title as seemed most effective for conveying the output to the imagined readers.

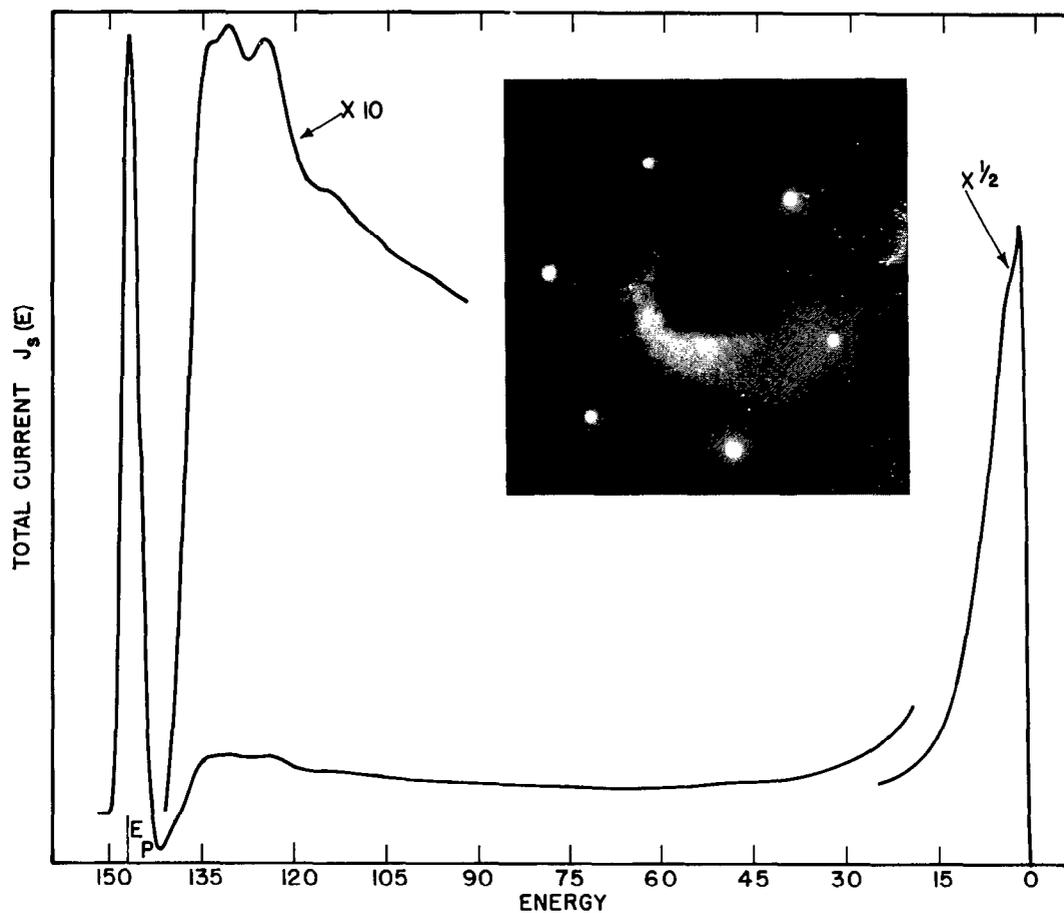


Fig. 31 - Low energy electron diffraction pattern and secondary electron energy distribution curve for an aluminum (111) surface. The curve includes a peak indicating that the elaborate steps used to prepare an entirely clean surface were not quite successful. This observation illustrates one of the many challenges of state-of-the-art surface physics and surface chemistry.

The abstracts are arranged in the following pages by institutions, commencing with The Boeing Company, followed by the universities (alphabetically), and finally the Naval Research Laboratory.

The Boeing Company

USE OF PRECRACKED SPECIMENS IN STRESS-CORROSION TESTING OF HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for several high strength commercial aluminum alloys, and to compare the rating of the alloys based on this data with the ratings established from smooth specimen time to failure data.

Approach

The V-K curves were obtained using bolt-loaded, double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Alloys and tempers tested were 7079-T651, 7079-T651 + 6 hr/325°F, 7075-T651, 7075-T7351, 7175-T66, 7175-T736, 7178-T76, AZ74.61, X7080-T7, 7039-T64, 7049-T7, 2024-T351, 2024-T4, 2024-T851, 2014-T451, 2014-T651, 2219-T37.

Achievements

The V-K curves showed a double slope behavior. At lower crack tip stress intensities the crack velocities were highly dependent on K_I , whereas at the higher K_I levels crack velocities were nearly independent of the applied crack tip stress intensity. Maximum crack velocities ranged from 4×10^{-5} in./hr for the highly susceptible 7079-T651 to 1×10^{-5} in./hr for the highly resistant 7075-T73. Although crack velocities often continued to decrease with decreasing K_I level, true K_{Isc} values (K_I levels below which growth ceases) were not observed for any alloy tested. Rankings of the various alloys based on the V-K curves agreed with established rankings based on smooth specimen time to failure data. In many cases the V-K curves provided more discriminating data than is available from smooth specimen time to failure tests. For example, at the higher K_I levels stress-corrosion crack growth rates in 7079-T651 were one to two orders of magnitude faster than in 7075-T651 even though both alloys show similar behavior in the standard smooth specimen, alternate immersion test.

A relationship between the smooth specimen stress-corrosion threshold stress from time to failure data and the V-K curves is presented.

Publications

"Use of Precracked Specimens in Stress-Corrosion Testing of High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24466, November 1969; submitted to Corrosion

The Boeing Company

USE OF PRECRACKED SPECIMENS IN SELECTING HEAT TREATMENTS FOR STRESS-CORROSION RESISTANCE IN HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for the alloy 7075 after various overaging heat treatments between T6 and T73.

Approach

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Three different techniques were employed. Two techniques used single DCB specimens containing aging gradients along their lengths. The third technique used multiple DCB specimens, each one having a different heat treatment.

Achievements

Results from each technique showed that for the 7075 alloy, overaging to an electrical conductivity of at least 38% IACS is necessary before stress-corrosion crack growth rates approach those of 7075-T73. Stress-corrosion performance was established most rapidly using multiple DCB specimens. After only a few hundred hours the crack growth characteristics were sufficiently established using this technique that the different heat treatments could be rated against the known performance of 7075 in the T6 and T73 tempers.

Publications

"Use of Precracked Specimens in Selecting Heat Treatments for Stress-Corrosion Resistance in High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-2447, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF RESIDUAL STRESSES ON STRESS-CORROSION CRACK GROWTH RATES
IN ALUMINUM ALLOYS

M. V. Hyatt

Objective

To determine the effects of quenched-in residual stresses on the behavior of pre-cracked double cantilever beam (DCB) stress-corrosion specimens of high strength aluminum alloys 7075, 7175, and 7079.

Approach

The V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were obtained using bolt loaded DCB specimens intermittently wetted with an aqueous 3.5% NaCl solution. Tests were conducted on specimens containing quenched-in residual stresses and on specimens which had been stress relieved after quenching by stretching or explosive shocking.

Achievements

Large differences in crack front profiles were observed between specimens with and without residual quenching stresses. Severe crack front bowing occurred in non-stress relieved specimens. In addition the crack opening displacement in the non-stress relieved specimens was effectively increased at the crack tip by the bowing apart of the two DCB specimen arms as the stress-corrosion crack propagated through the material. These effects result primarily from the residual compressive stresses on the surfaces of the non-stress relieved specimens. Both the crack front bowing and the bowing apart of the DCB specimen arms cause errors in the calculated K_I levels. These problems were eliminated by stress relieving DCB specimens after quenching. This work underlines the fact that residual quenching stresses in actual parts susceptible to stress-corrosion cracking not only increase chances of initiating stress-corrosion cracks, but also play an important role in increasing average growth rates. This can result from the increased crack opening displacement (and therefore K_I level) at the crack tip due to deflections caused by the residual stresses.

Publications

"Effect of Residual Stresses on Stress Corrosion Crack Growth Rates in Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24469, November 1969; submitted to Corrosion

The Boeing Company

EFFECTS OF SPECIMEN GEOMETRY AND GRAIN STRUCTURE ON STRESS-CORROSION CRACKING BEHAVIOR OF ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for aluminum alloy double cantilever beam (DCB) specimens with various side grooves, grain structures, and thicknesses.

Approach

DCB specimens with various side grooves, grain structures, and thicknesses were tested in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Branch cracking and arm breakoff may occur during testing of DCB specimens of aluminum alloy materials with equiaxed grain structures. Side grooves on DCB specimens had a negligible effect on crack growth rate data. Double cantilever beam specimens from materials as thin as 0.050 in. can be successfully tested.

Publications

"Effects of Specimen Geometry and Grain Structure on Stress Corrosion Cracking Behavior of Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24470, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF QUENCHING RATE ON STRESS-CORROSION CRACK GROWTH RATES
IN 2024-T4 ALUMINUM

M. V. Hyatt

Objective

To determine the effect of quenching rate on the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for 2024-T4.

Approach

Specimens of 2024 were resolution treated, quenched at two different rates, and naturally aged to the T4 temper.

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution.

Achievements

Actual stress-corrosion crack growth rates were higher in the more slowly quenched 2024-T4 alloy. This behavior agrees with trends observed by others based on percent loss in tensile strengths of pre-exposed specimens which have been quenched at different rates.

Publications

"Effect of Quenching Rate on Stress-Corrosion Crack Growth Rates in 2024-T4 Aluminum," M. V. Hyatt, Boeing Document No. D6-24471, November 1969; submitted to Corrosion

The Boeing Company

DEVELOPMENT OF A HIGH STRENGTH, STRESS-CORROSION RESISTANT ALUMINUM ALLOY FOR USE IN THICK SECTIONS

M. V. Hyatt and H. W. Schimmelbusch

Objective

To develop a new high strength Al-Zn-Mg-Cu alloy with a smooth specimen stress-corrosion threshold stress of 25 ksi, good toughness and fatigue properties, and a quench sensitivity such that the properties can be maintained at a high level in thick plate and forgings.

Approach

To meet the strength goals an alloy with zinc and magnesium contents intermediate between those of 7075 and 7178 was selected. To reduce quench sensitivity the copper content was reduced to about 1.0%, and zirconium and manganese were added in place of chromium which is the normal recrystallization retardant in 7075 and 7178 alloys. The amount of overaging required to meet the stress-corrosion goal was determined using both smooth specimens and precracked double cantilever beam (DCB) specimens. Finally, hand and die forgings, plate, and extrusions of the new alloy were given the selected heat treatment and evaluated to determine mechanical, fracture, fatigue, and stress-corrosion properties.

Achievements

Mechanical, fracture, and stress-corrosion properties for die forgings of the new alloy (alloy 21) and several other forging alloys are compared in the following table.

Alloy	Thickness (in.)	Minimum longitudinal properties		Longitudinal K_{Ic} range (ksi $\sqrt{\text{in.}}$)	Short-transverse stress-corrosion threshold (ksi)	
		F_{tu} (ksi)	0.2% F_{ty} (ksi)		3.5% NaCl alternate immersion	Industrial atmosphere
Alloy 21	6.75	69*	60*	30-38*	> 25*	> 25*
7049-T73	5.0	70	60	30-38*	45	?
X7080-T7	6.0	65	57	27-30	25	15
7075-T73	3.0	66	56	27-38	> 47	> 47
7075-T73	6.0	61	51	27-38	> 47	> 47
7175-T736	3.0 max	76	66	27-38	~ 35	?
7075-T6	3.0 max	75	65	25-32	7	14
7079-T6	6.0	72	62	25-32	7	6

*Estimated values

The mechanical properties of alloy 21 are comparable to those of 7049-T73. The fracture toughness of alloy 21 is as good as or better than that of the other alloys listed. The smooth-specimen short-transverse stress-corrosion threshold appears to be greater than 25 ksi. Test data also indicate that the smooth and notched axial (tension-tension) fatigue properties of alloy 21 are comparable to those of 7075-T6 and 7075-T73.

Publications

"Development of a High-Strength, Stress-Corrosion Resistant Aluminum Alloy for Use in Thick Sections," M. V. Hyatt and H. W. Schimmelbusch, Technical Report AFML-TR-70-109, May 1970, Boeing Document No. D6-60122

The Boeing Company

EFFECT OF EXPOSURE TIME AT 250°F ON STRESS-CORROSION CRACK GROWTH RATES IN 2024-T351 ALUMINUM

M. V. Hyatt and W. E. Quist

Objective

To determine the degree of sensitization to stress-corrosion cracking of 2024-T351 after exposure at 250°F (a temperature commonly used during curing of adhesively bonded assemblies).

Approach

Double cantilever beam (DCB) specimens of 2024-T351 were exposed at 250°F for times up to 300 hours. V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were then obtained in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Stress-corrosion crack velocities were observed to increase in specimens which had been exposed for only 2-5 hours at 250°F. Maximum crack velocity increases of about 60% occurred on specimens which had been exposed from 15 to 100 hours.

The Boeing Company

FUNDAMENTAL ASPECTS OF STRESS-CORROSION CRACKING OF HIGH STRENGTH ALUMINUM ALLOYS

Markus O. Speidel

Objective

At the Boeing Scientific Research Laboratories experimental and theoretical studies of stress-corrosion cracking in high strength aluminum alloys have three aims: (1) to identify the major influential parameters, that is, the conditions under which stress-corrosion cracks can grow; (2) to compare such conditions with those that cause stress-corrosion cracking in other alloy systems, polymers, and glasses, in an attempt to define their limits of applicability; and (3) to increase our understanding of the basic mechanisms of stress-corrosion crack propagation.

Approach

With complementary fractography and metallurgical examination, the main effort was concentrated on the measurement of stress-corrosion crack tip velocity as a function of the following parameters.

1. Mechanical parameters
 - a) applied crack tip stress intensity
 - b) specimen geometry
2. Environmental parameters
 - a) concentration of halide ions
 - b) concentration of other inorganic anions
 - c) concentration of water in the environment
 - d) presence of various gases
 - e) concentration of organic liquids
 - f) concentration of protons
 - g) presence of other cations
 - h) presence of liquid metal in the crack
 - i) temperature
 - j) viscosity of electrolyte
 - k) electrochemical potential
3. Metallurgical parameters
 - a) aging time
 - b) aging temperature
 - c) alloy concentration
 - d) recrystallization

Achievements

Crack propagation was shown to be affected by almost all the parameters listed. The first step in each case was to measure the effect of the variation of just one parameter on the velocity while keeping all the other parameters constant at some "reasonable" value. Our data showed that this can lead to quite different results,

depending on the actual value chosen for those parameters that were kept constant. The interdependence of the effects of various parameters on stress-corrosion crack velocity is illustrated in Figs. 1, 2, and 3.

Effect of Stress on Crack Tip Velocity—Crack tip stress intensity has a decisive effect on stress-corrosion crack velocity. It can cause the velocity to vary from less than 5×10^{-9} cm/sec to more than 2 cm/sec, a range that exceeds by far the lowest and the highest subcritical crack velocity ever before directly observed in aluminum alloys. Although the slowest cracks took a year to become visible, a movie camera had to be used to record the fastest cracks. Generally, there are three regions of the crack velocity versus stress intensity curve: region I at low stress intensities where the crack velocity is strongly stress dependent; region II at intermediate stress intensities where the crack velocity is independent of stress and which subsequently may show one or two plateaus; and region III at stress

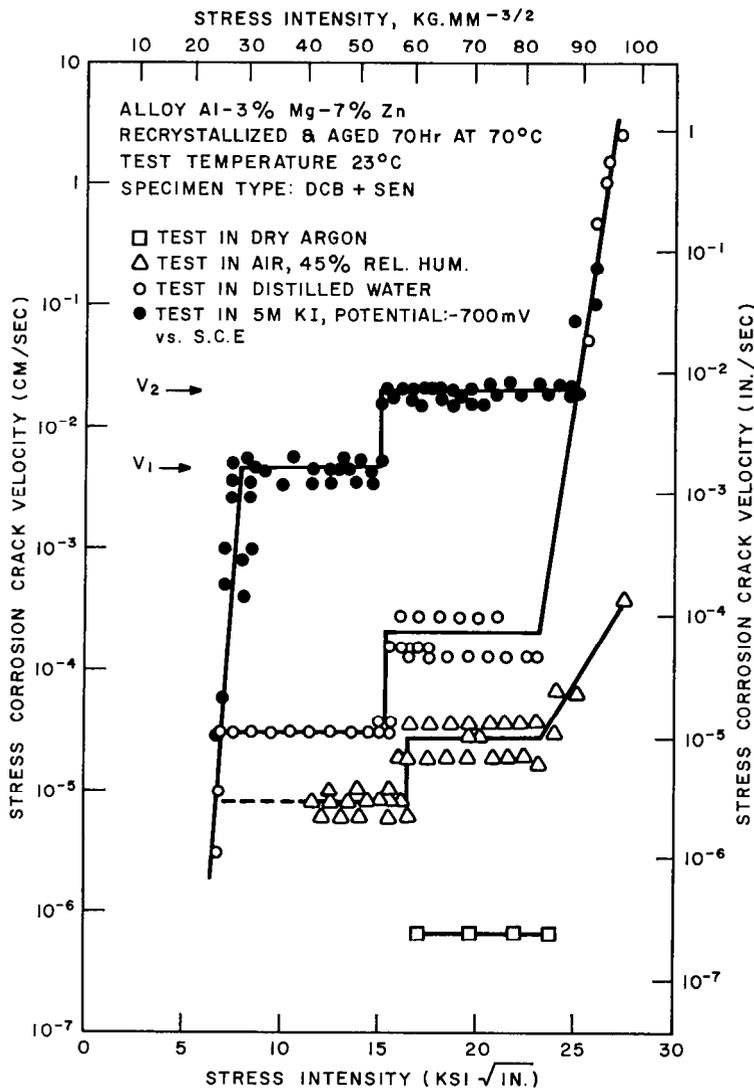


Fig. 1 - The effect of stress intensity on SCC crack velocity

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NRL Report 7329

UNCLASSIFIED

ARPA Coupling Program on Stress-Corrosion Cracking

Final Technical Report: Second Edition

B. F. BROWN

*Physical Metallurgy Branch
Metallurgy Division*

Sponsored by

*Advanced Research Projects Agency
ARPA Order No. 878*

October 27, 1971



NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

The technical background, organization, and *modus operandi* of the ARPA coupling program on stress-corrosion cracking are summarized. The problem of interpreting the data from smooth stress-corrosion cracking specimens is discussed. This is followed by a summary of technical achievement highlights in narrative form treating specimen types, titanium alloys, high-strength steels, aluminum alloys, and surface sciences. An Abstracts of Achievements section (abstracts arranged by organization) is the most important part of this report, for it gives not only indications of technical contributions but also the literature citations where the interested reader can examine the detailed account of a given topical area. The Abstracts of Achievements section includes a subject index.

The program was one of multiple goals, including experimentation involving coupling NRL with academic personnel and amplifying NRL's capabilities by the addition of an industrial contractor. Since the present report is a purely technical one, it does not treat these non-technical goals. The present report represents an updating of NRL Report 7168 to include material published during the phase-out year of the program.

PROBLEM STATUS

This is a final technical report.

AUTHORIZATION

NRL Problem M04-08A
ARPA Order No. 878

Manuscript submitted July 19, 1971.

ARPA COUPLING PROGRAM ON STRESS-CORROSION CRACKING

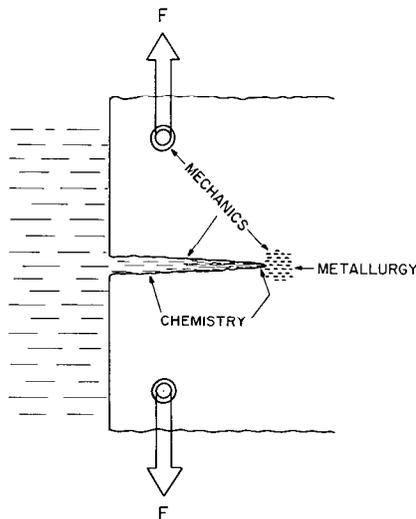
Final Technical Report

INTRODUCTION

History

By 1966 the phenomenon of SCC had affected all the military services (and NASA); had caused serious surprises to the designers of aircraft, submersibles, and rockets; and had involved all three major families of high strength structural alloys—titanium, steels, and aluminum. The Advanced Research Projects Agency (ARPA) of the Department of Defense recognized both the military importance of the problem and its technical complexity, compounding as it does the difficulties of the brittle fracture problem with chemical reactions occurring inside inaccessible cracks (Fig. 1). ARPA also was aware of new developments in surface physics and surface chemistry, some of which might be expected ultimately to afford advances in the science of metallic corrosion. ARPA therefore asked the Naval Research Laboratory to organize an intensive attack on the problem of the SCC of high-strength structural alloys with provision for coupling science to technology and also for coupling academic laboratories with an industrial laboratory and a government laboratory.

Fig. 1 - The three scientific elements of stress-corrosion cracking. Progress requires attention to all three.



Organization

The principal member institutions were NRL, The Boeing Company, Lehigh University, and Carnegie-Mellon University, to which was added Georgia Institute of Technology because of special capabilities in surface physics.

Two other universities had supplementary roles for special purposes: At a time when graduate students specializing in the electrochemistry of corrosion were almost

nil, both in the program and nationally, such students became enrolled at American University under well-qualified thesis supervision; hence, American University became a supplementary member of the program to ensure the involvement of at least a few electrochemistry graduate students, in this case studying the role of anions in corrosion reactions. At the University of Florida, Professor M. Pourbaix became available as a visiting professor and consultant to the program, and for this reason the University became a supplementary member, concentrating on experimental methods to apply Pourbaix' potential-pH method for analyzing the corrosion behavior of complex alloys (commencing with chromium steels).

There were no exclusive charters at any of the institutions, but in general the emphasis at Lehigh was on surface chemistry, that at Carnegie-Mellon was on physical metallurgy, and that at Georgia Tech was on surface physics. NRL contributed to both basic and applied research, and Boeing's role was to amplify the capabilities of NRL. Boeing and NRL filled an additional role by providing opportunities for graduate students to observe and/or participate in applied research in the course of their graduate careers.

SCC, which is caused by the conjoint action of a corrodent and a stress which may be constant, represents one of the limiting cases of corrosion fatigue (as R-1), which differs from SCC in that in corrosion fatigue the stress is necessarily fluctuating. For this reason corrosion fatigue in a limited sense was considered an appropriate subject to be included in the program, and particularly appropriate for a DoD program, since corrosion fatigue is said to be the major cause of failures in vehicles and in moving machinery. Analysis shows that there is no such thing as a simple method of generating the general engineering corrosion-fatigue characteristics of a given alloy, however, and accordingly from midprogram onward the corrosion-fatigue studies were restricted to academic research on mechanisms. Research on corrosion-fatigue mechanisms was also conducted at NRL with Navy funds but associated with the program.

The alloy families of interest were titanium, high-strength steels, and aluminum, and the relative emphasis on the three systems was set at 3:2:1. The reason for this relative emphasis was not alone the relative importance of the problem to DoD, but also the relative amount of accumulated knowledge in the three systems and the activity of producers on the problem in the area of their own products.

Modus Operandi

The program was conducted as a national one in the sense that it was fully integrated into the national technical community. Reports from the program were given unlimited distribution, and attendance at the quarterly meetings (described briefly below) was open to personnel from outside the program, subject only to the limitations of manageability. It was found that keeping the agenda of the quarterly meetings to a single narrow topic (e. g. , titanium alloys) accomplished several ends: It permitted an in-depth review of the subject matter, it eased the problem of limiting outside participants, and it promoted interchange between persons working in different disciplines such as surface physics, electrochemistry, metallurgy, crystallography, and mechanics. The program profited immensely by the regular participation of outsiders.

The program was integrated into the national technological community in another manner, namely, by sharing costs. For example, in studies in which, to have technological significance, portions of large heats (batches) of alloys were required, these alloy heats were sometimes procured by other DoD interests, and the small amounts required for SCC studies were traded to the ARPA project in return for the stress-corrosion information generated. Mixed support of another type was practiced in which students whose stipends were paid from one source had the costs of their laboratory supplies and services paid by the ARPA program. These jointly supported activities

provided not only breadth of contact but also economies which in the case of large alloy heats were of important magnitude.

Also as part of the design of the program to serve the national technological community, personnel in the program were encouraged to present the output of their research at various types of technical meetings. The effectiveness of this policy is evident in the Presentations section of the Abstracts of Achievements.

Documentation

This report is primarily technical, but a brief background account is given here for the interested reader.

As another part of the final reporting sequence, there is in preparation a monograph on the state of the art of stress-corrosion cracking (SCC) of titanium alloys, high-strength steels, and aluminum alloys. That monograph is designed to be not only a summary of what has been contributed to the subject by the ARPA program, but a state-of-the-art summary without restriction as to source of contributions. The monograph will therefore be the most useful technical summary of the program for most purposes, for in it the pertinent output of the program is integrated into the entire literature on the subject.

The present report is limited to contributions from the ARPA program. Such contributions from a program as large and as productive as this one cannot be *detailed* in a manageable fashion in a single document such as the present report, but the key contributions are given herein in a consolidated narrative form. In addition, Abstracts of Achievements, modeled after the Interdisciplinary Laboratory reports, are given, together with references to the literature, so that the reader has a key directly to the technical literature of interest to him. The present report was written at the end of the program, and by the nature of the publication machinery of the technical societies many of the manuscripts generated by the program have not yet been printed. In such cases the journal or society is noted so that the interested reader can monitor the appropriate literature for the appearance of a paper of special interest. Requests for reprints should be directed to the individual authors. Qualified recipients may request from the Defense Documentation Center those reports for which accession numbers are given.

In the present report the author uses the term *stress-corrosion cracking* (SCC) to designate a cracking process caused by the conjoint action of a stress (which need not be fluctuating), and a corrodent. The term *corrosion fatigue* is used to designate a cracking process caused by the conjoint action of a fluctuating stress and a corrodent. The terms are thus based upon macrophenomenology rather than mechanisms, and the introduction of new terms such as *corrosion-assisted crack growth* and *subcritical cracking* becomes unnecessary.

The emphasis on reporting was to get contributions presented expeditiously at standard technical society meetings and published expeditiously in their journals, and the function of the quarterly reports was most importantly to notice the writing and the publication of such manuscripts in the standard literature.

THE PROBLEM OF THE MACROSCOPIC TEST

Regardless of how small the scale of events which may cause SCC, ultimately it is the macroscopic phenomenon which must be controlled. The traditional method for

characterizing SCC was to stress a specimen in a corrosive environment and report time to failure, usually meaning time for complete separation of the specimen. Although this parameter has afforded progress, particularly in the low-strength alloys, it is a defective parameter because it represents the undifferentiated *sum* of the effects of three processes, (a) incubation (usually film breakdown plus corrosion pitting), (b) SCC, and (c) terminal mechanical overload fracturing (Fig. 2). If an alloy is not susceptible to pitting, then a (smooth) specimen may give an indication of an infinite time to failure, i. e., the alloy may appear to be immune to SCC, whereas in fact it may be highly susceptible to stress-corrosion crack *propagation*. (Titanium alloys in water exemplify this behavior.) Alloys with different fracture toughness characteristics require different lengths of stress-corrosion cracks (and hence different exposure times) before the onset of overload fracturing; thus time-to-failure data could lead to grossly erroneous inferences regarding the relative SCC characteristics of these alloys. Some materials are so brittle that if they are stressed and a corrosion pit forms, the pit can initiate "brittle fracture," and an indication of high susceptibility to SCC might be inferred from a test in which in fact no SCC has occurred at all. (The 5% Cr die steel heat treated to maximum strength tends to behave in that fashion.)

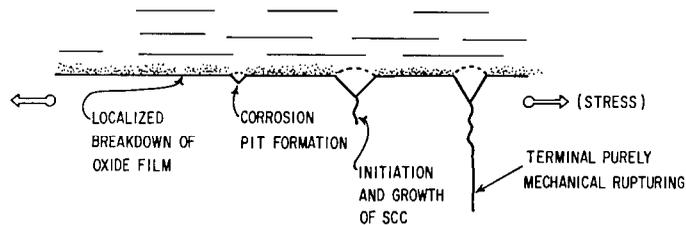


Fig. 2 - Sequence of events (left to right) by which a metal under stress with an originally smooth surface undergoes successively localized film breakdown, corrosion pitting, stress-corrosion cracking, and finally mechanical rupture

The foregoing complications are illustrated in Fig. 3, which is a plot of depth of pitting plus SCC plus mechanical fracturing on the ordinate vs time on the abscissa.

At the beginning of the program, the great bulk of data in the literature and most of that being inserted into the literature were of the undifferentiated time-to-failure type, and as has been shown above, this sort of data can be very misleading about stress-corrosion characteristics. One of the tasks of the program, therefore, was to establish the true SCC characteristics of the structural alloys of most current importance to military designers.

To do this characterization, as well as to conduct other studies both basic and applied, one or more specimen types were used containing pre-existing cracks. This tactic has three advantages: (a) It obviates waiting for a corrosion pit to grow, saving time. (b) It enables one to avoid an erroneous conclusion of immunity to SCC because of a nonpitting combination of alloy and environment. (c) It enables one to get a conservative evaluation by evaluating the material in the presence of the ultimate flaw, namely a sharp crack. There is a fourth advantage, for if the specimen meets certain criteria, the methods of fracture mechanics can be used to predict from the behavior observed in one geometry of specimen and crack what will happen in other geometries.

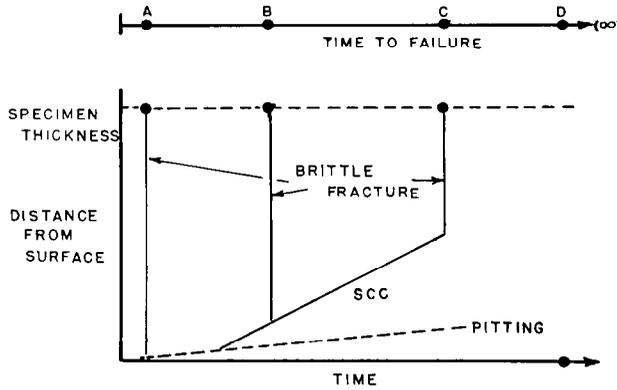


Fig. 3 - The time-to-failure information from stress-corrosion cracking tests of smooth specimens, as plotted in the line at the top, indicates an ascending order of merit with respect to stress-corrosion cracking from A through B and C to D. In point of fact, as shown schematically in the lower portion of the figure, B and C may have the same SCC characteristics but different fracture toughnesses. The SCC characteristics of A and D have not really been measured at all.

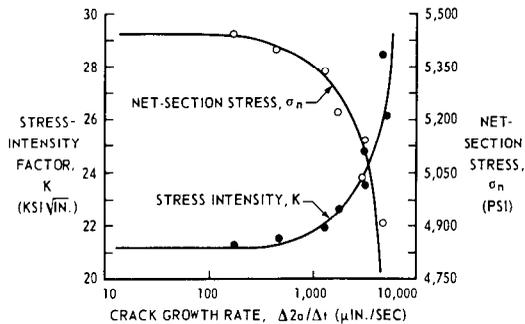
Fortunately for the program, the high level of activity in the fracture mechanics field during the decade preceding the program had produced technological information on various specimen geometries which become useful to the problem of SCC, as will be noted later in this report.

HIGHLIGHTS OF PROGRAM ACHIEVEMENTS

Specimens and Macroscopic Test Methods

During the course of the program the methods of fracture mechanics were demonstrated to afford predictability of stress-corrosion behavior from one geometry of specimen and stress configuration to another, whereas nominal stress was shown to be misleading (Fig. 4). The stress-intensity factor K thus was shown to be the most useful

Fig. 4 - Stress-corrosion cracking data for Ti-8Al-1Mo-1V in salt water. Specimen is stressed at the crack line and the crack growth rate is measured. (Chronologically the experiment proceeds from right to left in this figure.) Experiment shows that as K decreases (because of crack growth), the crack growth rate decreases, but meanwhile the nominal stress (net section stress) increases. This is an illustration of the inability of net section stress to correlate with cracking behavior. Extrapolation of data indicates a K_{ISCC} of about 21 ksi $\sqrt{in.}$.



way to quantify stress in the presence of a stress-corrosion crack. Evidence was found that for titanium alloys there is a threshold value of K below which SCC is not expected (for a given combination of alloy and corrodent), and this threshold was designated $K_{I_{SCC}}$. In the absence of positive knowledge that a true threshold exists, an arbitrarily defined $K_{I_{SCC}}$ (such as "nil crack growth in 1,000 hours") does indeed convey more information than an index of the patience of the experimenter or his skill with instrumentation; for at slightly higher K levels, one can make the positive statement that SCC will occur.

To fully characterize the SCC of a given alloy in a given K corrodent, one would like to have cracking kinetics as a function of K all the way from a threshold ($K_{I_{SCC}}$) if one exists to K_{I_C} , the stress intensity at which brittle fracture occurs. Even if one has only the value $K_{I_{SCC}}$, and even though in a given system this may not be known to be a true threshold but may represent, for example, the minimum K at which SCC is observed in 1,000 hours, the $K_{I_{SCC}}$ numbers can be plotted as a function of yield strength to produce an interesting analysis of the relative merits of various compositions or heat treatments in a given alloy family. In such a plot (Fig. 5), one can simplify the Irwin equation for a surface crack by assuming yield-strength stresses, and assuming that any surface flaw will be long compared with its depth and will lie perpendicular to the stress field, he can then draw a series of straight lines as shown in Fig. 5. Any one of these represents conditions for a given flaw depth, and the line simply means that if one may have a given flaw size as represented by the line, he must have a material with a $K_{I_{SCC}}$ lying above that line to avoid SCC.

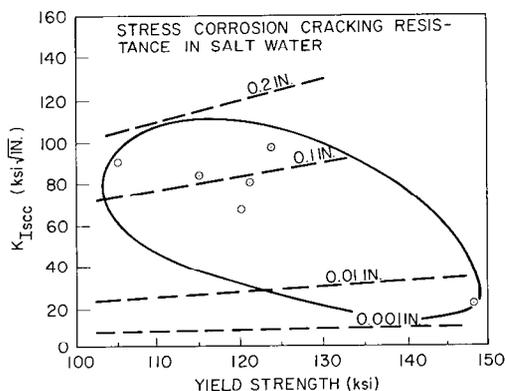


Fig. 5 - $K_{I_{SCC}}$ data in salt water for six commercial heats of Ti-6Al-4V rolled to plates 1-in. thick. All $K_{I_{SCC}}$ data for commercial heats of this alloy have been found to lie within the oval. The broken lines indicate $K_{I_{SCC}}$ values which an alloy must have (or exceed) in order to avoid SCC initiating at a long flaw of the depth shown on the line, assuming yield stresses. (Data show that no commercial alloy can tolerate a flaw as deep as 0.2 in. if the operative stress equals the yield strength.) The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

$K_{I_{SCC}}$ can be determined by a number of specimens, some set at K levels above and others below the $K_{I_{SCC}}$ level. The program showed that there are alternative ways to determine a threshold. For example, one can use the "wedge-loaded" (crack-line-loaded) sheet tensile specimen and await arrest of the stress-corrosion crack, or one can use a load-relaxing system such as an elastic ring to stress a specimen which experiences relaxation as the stress-corrosion crack advances (Fig. 6). It was shown elsewhere during the program that a specimen similar to the one of Fig. 6 can be self-stressed with a bolt and used as a stress-corrosion specimen. During the program the specimen of Fig. 6, self-stressed with a bolt instead of the elastic ring, has been shown to be extremely useful for characterizing the SCC behavior of high-strength aluminum alloys by determining the rate of crack growth as a function of K (Figs. 7, 8). Such a test has been found far more rapid and more discriminating than the traditional methods.

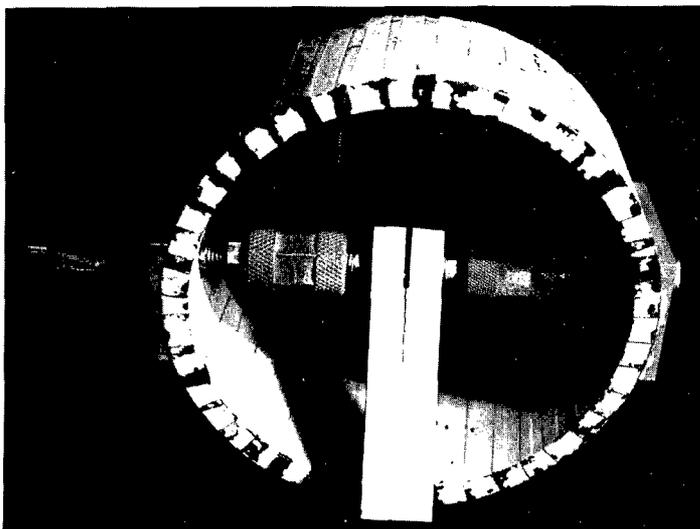


Fig. 6 - DCB aluminum alloy specimen ($1 \times 1 \times 3.5$ in.) stressed by an elastic ring which relaxes as the crack propagates. (Ring is made of high-strength steel wrapped with tape to prevent stress-corrosion cracking.) Load on ring is monitored by strain gage (not shown).

Since K has been shown to be the proper way to quantify stress around a stress-corrosion crack, and since SCC kinetics have been found to be K -dependent, specimens having the property of constant- K conditions regardless of crack length would be of obvious interest. Two such constant- K specimens were studied in the program. One of these, designated the tapered, double-cantilever beam (DCB) specimen, has given experimenters problems with the arms breaking off, and that was found to be true using the specimen for SCC, even though the experimenters were expert with that particular specimen. It was found possible, however, in using this specimen at a number of K levels, to extrapolate the crack rate to zero, which was found to correspond to K_{Isc} for the same steel as determined by a beam specimen. The other constant- K specimen, sometimes designated the double-torsion specimen and sometimes the Outwater specimen (after its inventor), is of additional interest because of its simplicity—it can be satisfactorily prepared from a sheet of metal using a bandsaw. For constant- K conditions the specimen can be satisfactorily stressed by a dead-weight-lever system, and it appears to be well behaved in stress-corrosion tests, at least for high-strength steel.

A small inexpensive self-stressed specimen was developed for possible use as a quality-control specimen for sheet materials.

The newcomer seeing all the various specimens for measuring SCC characteristics might reasonably ask which one he ought to use. It might be helpful to the metallurgist or engineer to regard this selection question somewhat like the question of which *hardness* test one should use. In both cases the answer to the question depends partly on the geometry of the material of interest and partly on the answer one ultimately gets.

Titanium

The resistance to SCC of all the commercial titanium alloys and many developmental and research alloys has been determined using precracked specimens. Electrochemical

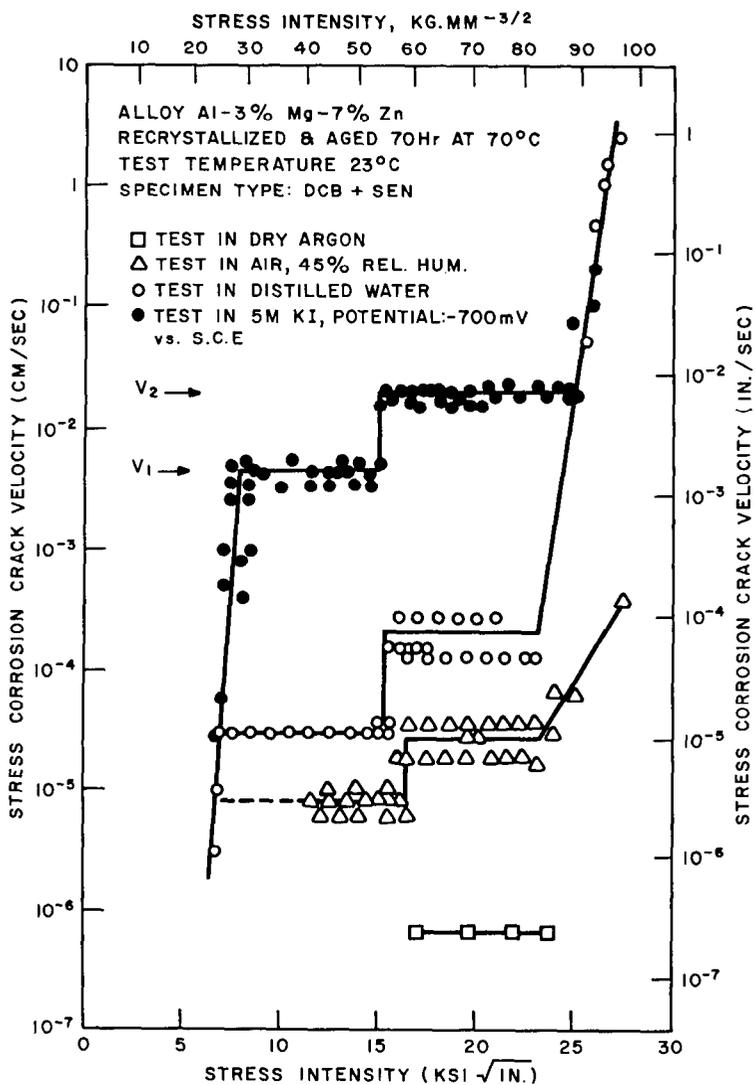


Fig. 7 - Crack-growth rate as a function of K for an aluminum alloy in several environments, illustrating the three stages of the V-K behavior

evidence was interpreted to indicate that for titanium alloys in salt water there is a genuine stress-intensity threshold below which stress-corrosion cracks do not propagate.

The resistance to SCC was found to be strongly dependent upon microstructure and dislocation substructure (Fig. 9). Alpha and alpha-beta alloys that exhibited planar slip in the alpha phase had low resistance to SCC. Beta grains in alpha-beta alloys tended to act as obstructions to the SCC fractures in the alpha phase, but with complications noted below (Fig. 10).

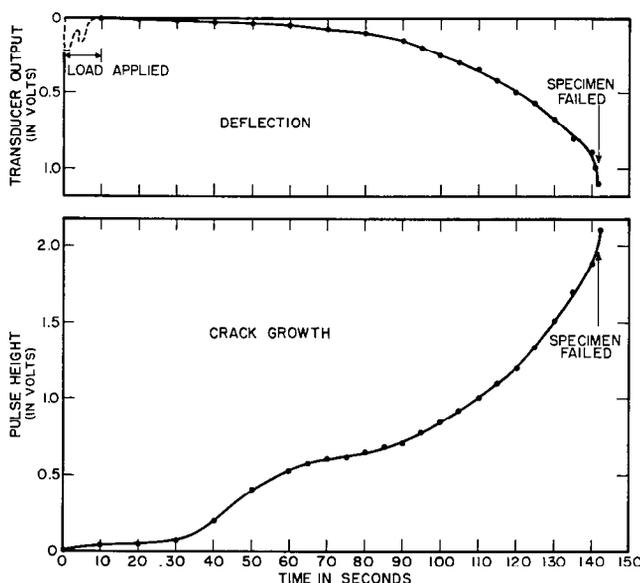


Fig. 8 - Crack-growth rate measurement continues to challenge the experimentalist. An alternative to the clip-gage technique is to monitor the reflection from an ultrasonic pulse (data shown above for a dead-weight-loaded, cantilever-bend specimen of titanium alloy).

Planar slip was found to be characteristic of alloys containing

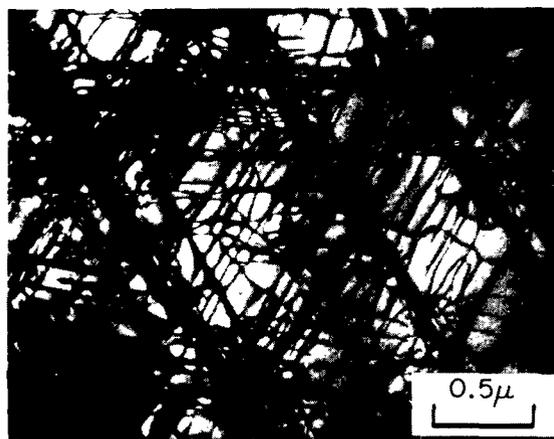
- High oxygen, or
- Aluminum in excess of about 6%, or
- Aluminum in excess of about 5% and tin content of 2.5% or more.

The formation of ordered domains of Ti_3Al or $Ti_3(Al, Sn)$ in the alpha phase further restricted slip and decreased SCC resistance.

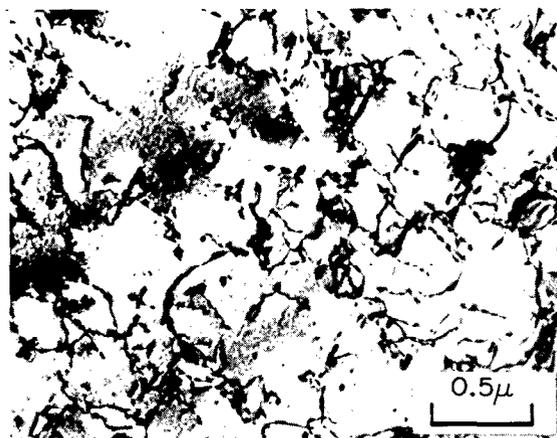
In an alpha-beta alloy, increasing the proportion of beta by increasing the amount of alloying elements such as Mo or V increased SCC resistance, perhaps by the crack-obstructing mechanism mentioned above (Fig. 11). But decomposition of the beta phase (to form omega, Ti_2Cu , or Ti_5Si_3) may embrittle the alloy and markedly lower its SCC resistance.

Of the common commercial alloys, Ti-8Al-1Mo-1V was found to be the least resistant to SCC, Ti-4Al-3Mo-1V was found to be highly resistant, and Ti-6Al-4V was found to have intermediate resistance. These observations were again observed to be correlative to the type of dislocation substructure.

In the all-beta alloy Ti-13V-11Cr-3Al, SCC fractures were observed to occur on or near the (001) plane. The crystallography of twinning of another all-beta alloy (Ti-11.5Mo-6Zr-5Sn) was found to be different from that of most other bcc metals. Mechanical fracture occurs macroscopically parallel to (001), but microscopically the fracture mechanism is not cleavage but microvoid coalescence. Unfortunately, aging this alloy to optimum strength (153 ksi yield) and toughness ($K_{Ic} = 66 \text{ ksi} \sqrt{\text{in.}}$) produced minimum resistance to SCC in halide solutions. The SCC fracture path in this alloy is intercrystalline, in contrast to the transcrystalline fracture path seen in most titanium



(a)



(b)

Fig. 9 - Coplanar dislocation arrays (above, associated with SCC-prone titanium alloys) and tangled dislocations (below, associated with SCC-resistant alloys)

alloys. The formation of omega phase during aging was observed to be an important factor reducing the ductility of the aged alloy; this phase is distributed as small particles (100 to 1,000 Å), but even so may constitute a high volume fraction of the alloy.

The SCC fractures in the alpha phase of alloys lie $15^\circ \pm 2^\circ$ from the basal plane of the hexagonal lattice. This relatively good consistency in crystallographic habit plane has led the resulting flat fracture facets to be termed cleavage (Figs. 12 & 13). The entire SCC fracture surface, however, is not cleavage, but cleavage areas are interspersed with rupture dimples (microvoids) which resemble the dimples of a purely mechanical fracture (Fig. 14). Thus, a stress-corrosion crack appears to be formed by two mechanisms, one (cleavage) involving stress plus an environmental reaction, and the other (dimples) wholly or largely of mechanical origin. The proportion of the dimple areas increases as K increases from $K_{I_{SCC}}$ to K_{I_C} , at which stress intensity the remaining ligament separates entirely by dimple rupture.

Methanol and several other organic fluid environments, including hydrocarbons, were observed to cause the SCC of titanium alloys. Carbon tetrachloride also caused

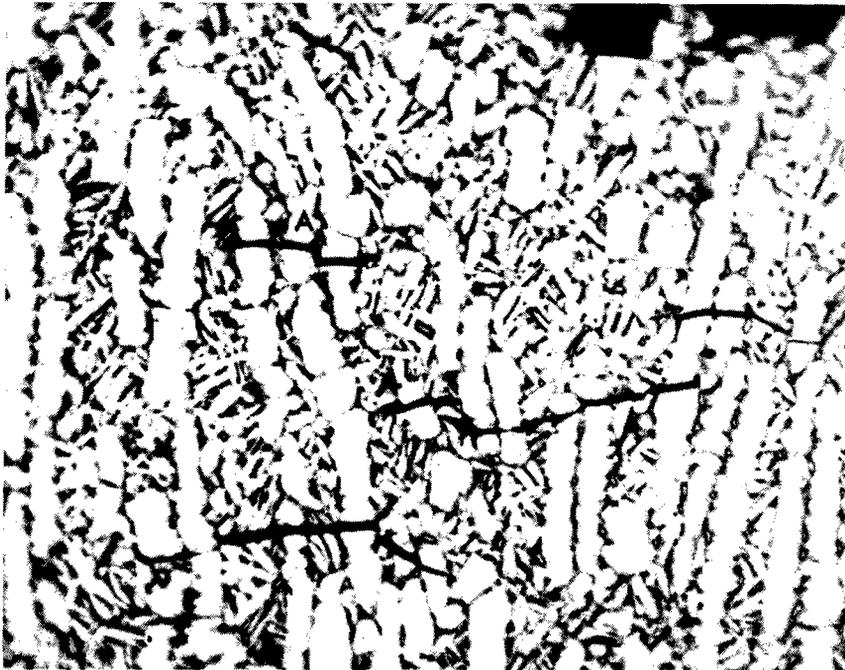
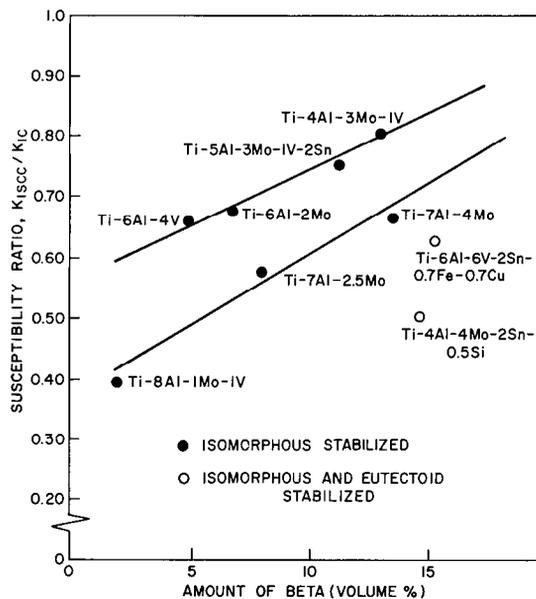


Fig. 10 - Partial stress-corrosion cracks in alpha-beta titanium alloy showing cracks in the alpha phase arrested by the beta phase. 1,000X magnification.

Fig. 11 - Increasing proportion of beta in alpha-beta titanium alloys tends to increase the ratio K_{Isc}/K_{Ic}



severe cracking. These findings have practical implications in the selection of paints and of cleaning and degreasing fluids. Except for liquid metals, carbon tetrachloride is the only environment not containing hydrogen (assuming the CCl_4 was free from HCl), which cracks titanium.



Fig. 12 - Fractograph showing cleavage surface typical of stress-corrosion cracking in titanium alloys in water at a low K level. 6,000X magnification.

Slow crack propagation was observed in titanium alloys in the absence of atmospheric moisture and also in a hard vacuum somewhat better than 10^{-7} torr. In these specimens as in those cracked in organics and in aqueous liquids, the fracture was cleavage interspersed with dimples. Heat treatment which reduced the hydrogen content of the titanium reduced its tendency to slow crack growth in vacuum (Fig. 15).

Methods were developed and applied to elucidate the nature of the corrodent near the advancing crack tip. With neutral salt water as the corrodent, the pH at the advancing crack tip was highly acid (about 1.6). The pH and the potential place the crack tip in a thermodynamic regime in which the hydride may be stable, but not an equilibrium oxide. The addition of FeCl_3 to the salt water increased the SCC resistance of the titanium, perhaps by substituting the reduction of copper for the reduction of hydrogen as the cathodic reaction.

One model which has been proposed for SCC of titanium, in accord with the observations noted above, is the hydrogen model. The reaction of a clean titanium surface with any of the hydrogen-bearing environments studied would release hydrogen which would be expected to react with or dissolve in the titanium. In aqueous salt solutions, the pH at the growing crack tip remains sufficiently acid (because of the occluding action of the SCC path) that repassivation is not possible at the crack tip, which continuously provides clean surfaces for reaction to remove more hydrogen from the corrodent. Thus the function of the precrack in specimens tested in salt water is to provide a little local straining plus the restriction to diffusion which will permit the acidity to remain high locally, whereas smooth specimens tested in salt water would repassivate because of the inability of the geometry to keep the acidity high locally. In methanol, however, the situation is different because the product of the reaction of titanium and methanol is soluble in methanol, i. e., the reaction product does not form a protective film in the

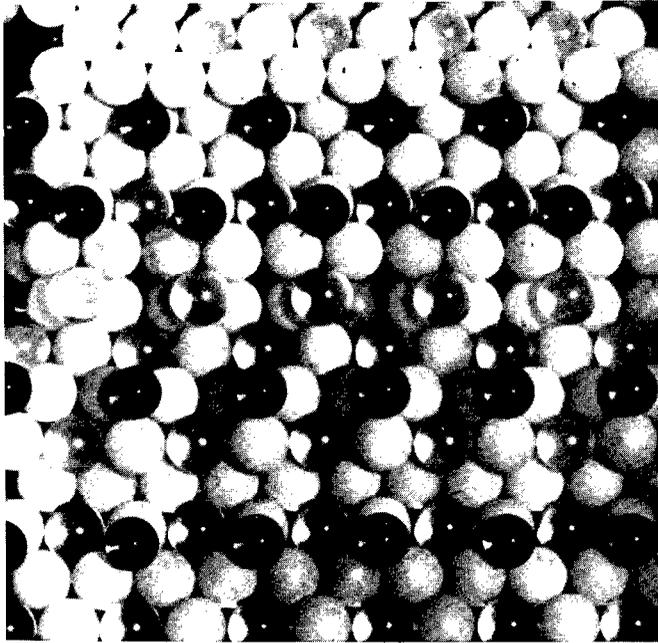


Fig. 13 - Ball model of simulated SCC fracture surface in Ti-Al alloy. Aluminum atoms on base surface are designated by clear balls and on the matching plane by dark balls. The fracture plane occurs where there is the highest concentration of Ti-Al bonds in ordered alpha.

bulk environment. This has been concluded to be the reason *smooth* specimens will initiate SCC in methanol.

Straining Ti-Al alloys in salt water was observed to cause large increases of the active range during anodic polarization, and this too is consistent with the picture of reactions occurring near the crack tip. A computer program has been developed for solving the complex electrochemical transport equations involved in SCC. The aspect ratio was found to dominate all else.

Ti-Al alloys were found to show the same precipitation of hydride at coplanar dislocations in SCC specimens as in slow strain-rate hydrogen-embrittlement specimens, again suggesting the hydrogen model.

Acceptance of the hydrogen model would require a resolution of two apparent anomalies: a) the observation of SCC in reasonably pure CCl_4 (containing traces of water), and b) the observation that increasing $[\text{Cl}^-]$ increases SCC crack-growth rates at a given K level.

Steels

The SCC characteristics of a large number of commercial and near-commercial steels were determined using salt water and natural seawater (Fig. 16). The use of pre-cracked specimens to determine SCC characteristics of alloy steels in seawater can save half a year to a year, which otherwise may be required to generate the pits which in turn initiate SCC. (A precracked specimen may, however, give erroneous data if it is



Fig. 14 - Fractograph showing flat cleavage areas plus dimpled (mechanical rupture) areas typical of SCC in titanium alloys in water at a K level much higher than that of Fig. 12

stressed to a high level before being placed in an SCC test at a lower stress level.) From the data of Fig. 16 it is apparent that the maraging steels and at least some of the precipitation-hardening steels were clearly superior to the conventional martensitic steels at the same strength level.

The following observations were made on low-alloy martensitic steels: Silicon content had no effect on $K_{I_{SCC}}$, but above about 1.5% the increased silicon greatly retarded the cracking kinetics at a given K level. Reducing the grain size also decreased the cracking kinetics, but did not affect $K_{I_{SCC}}$. Increasing the manganese or carbon content caused markedly reduced $K_{I_{SCC}}$ values (Figs. 17, 18). None of the following metallic alloying elements was observed to have a significant effect on $K_{I_{SCC}}$: nickel, cobalt, chromium, and molybdenum.

Fig. 15 - Effect of hydrogen content (varied by vacuum treatment) on fracturing of a commercial titanium alloy in various modes. The line designated K_{IH} represents the stress intensity above which a crack propagates in an inert environment, presumably due to internal hydrogen.

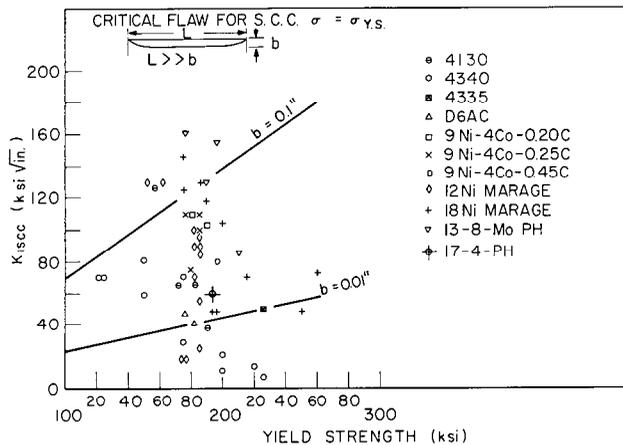
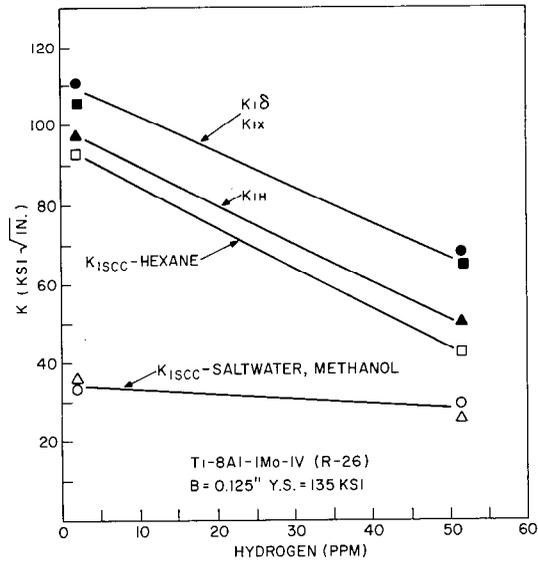


Fig. 16 - K_{ISCC} data in salt water for a number of commercial alloy steels made in production-size heats. The strength range covers strengths of interest to deep-diving submersibles, rockets, and manned aircraft. Flaws of the depth shown in a given steel would propagate stress-corrosion cracks at yield-strength stress unless the K_{ISCC} of that steel lies above the line. The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

The purity of maraging steels with respect to sulfur and phosphorus was not found to have an important effect on SCC characteristics. The same was observed in low-alloy martensitic steels of the 4340 type.

Among the maraging steels, thermal history appears to have an effect above and beyond its effect on strength. Underaging the 350-grade maraging steel was found to be bad for SCC, whereas overaging was helpful. Overaging of 18%-Ni maraging steel

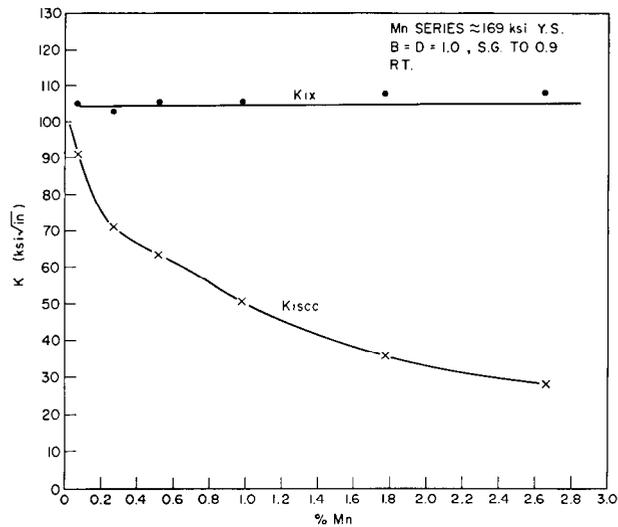


Fig. 17 - Effect of manganese content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

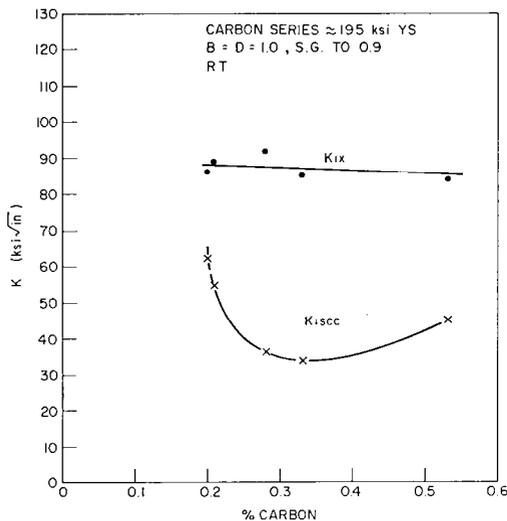


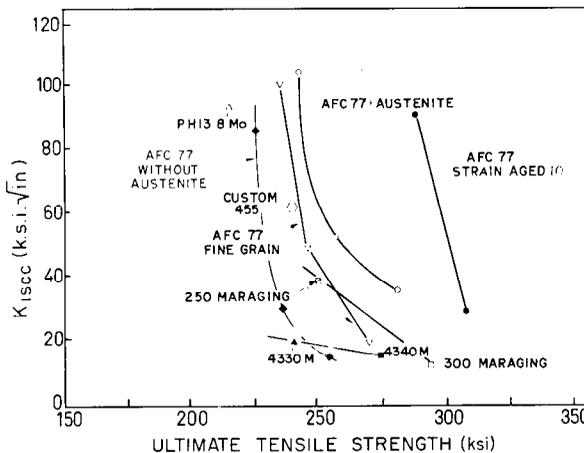
Fig. 18 - Effect of carbon content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

produces reverted austenite, the primary site for which appears to be the compound $Ni_3 Mo$.

$K_{I_{SCC}}$ has a complex curvilinear dependence on strength level, but for a given martensitic steel in the 175- to 185-ksi yield-strength range, a 7% increase in yield strength (by differences in tempering treatment) caused a 20% loss in $K_{I_{SCC}}$, which is linearly proportional to the load-carrying capability of a component containing a standard flaw. The program demonstrated, however, that strengthening by strain aging (in a precipitation-hardening steel) entails a smaller penalty in SCC than the strengthening of martensitic steel by choosing the tempering temperatures, thus providing a possibly useful avenue for further advances for special needs (Fig. 19).

Stress-corrosion cracks are commonly thought to be characteristically multiply branched, because SCC was first observed in cold-worked products, which have complex

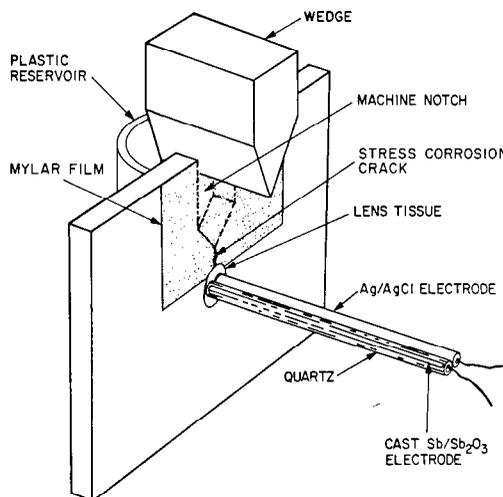
Fig. 19 - K_{Isc} for several commercial steels and one developmental steel (AFC 77) in salt water. Note, for AFC 77 in any given condition, the rapid decrease in K_{Isc} with rising ultimate tensile strength. Note also that by increasing the strength by strain aging, the strength can be increased over that of regular AFC 77 by more than 50 ksi while maintaining the same K_{Isc} .



residual stress patterns that change continuously as the article cracks. In the present program it has been found with many materials that the crack-growth rate rises sharply with increasing K until a point (K_{In}) of apparent process saturation is reached, beyond which the rate is more or less independent of K . If the material is reasonably isotropic, then at a K level of about $2K_{In}$ the crack will tend to divide or branch. This finding is useful in understanding tests in which the crack divides and thereby terminates the utility of the experiment.

During the course of the program, methods were developed which for the first time were successful in measuring the pH near the tips of growing stress-corrosion cracks in steel (Fig. 20). These methods employed successively color-change pH indicators,

Fig. 20 - One method for determining the pH at the tip of a stress-corrosion crack. The potential and pH probes rest against a small paper disk (thin to minimize the solution required to moisten it), and are connected to high-resistance recorders. They do not register a reading until the crack propagates to the disk and moistens it. (The disk does not contain solutes which affect pH.) A glass electrode designed for surface measurements can be used in place of the antimony oxide electrode.



the antimony electrode, and finally the glass electrode, and all three methods gave the same result. This work on crack-tip chemistry gave new insight on SCC (and eventually on most forms of localized corrosion, as will be discussed in a later section). It was found that regardless of the pH of the bulk solution (external to the crack) or the potential impressed upon the steel, the combination of potential and pH at the crack tip are such as to be favorable for the reduction of hydrogen (Fig. 21). This finding makes it unnecessary to postulate any mechanism for SCC in (high-strength) steel other than that commonly termed *hydrogen embrittlement*. The mechanism of hydrogen embrittlement has

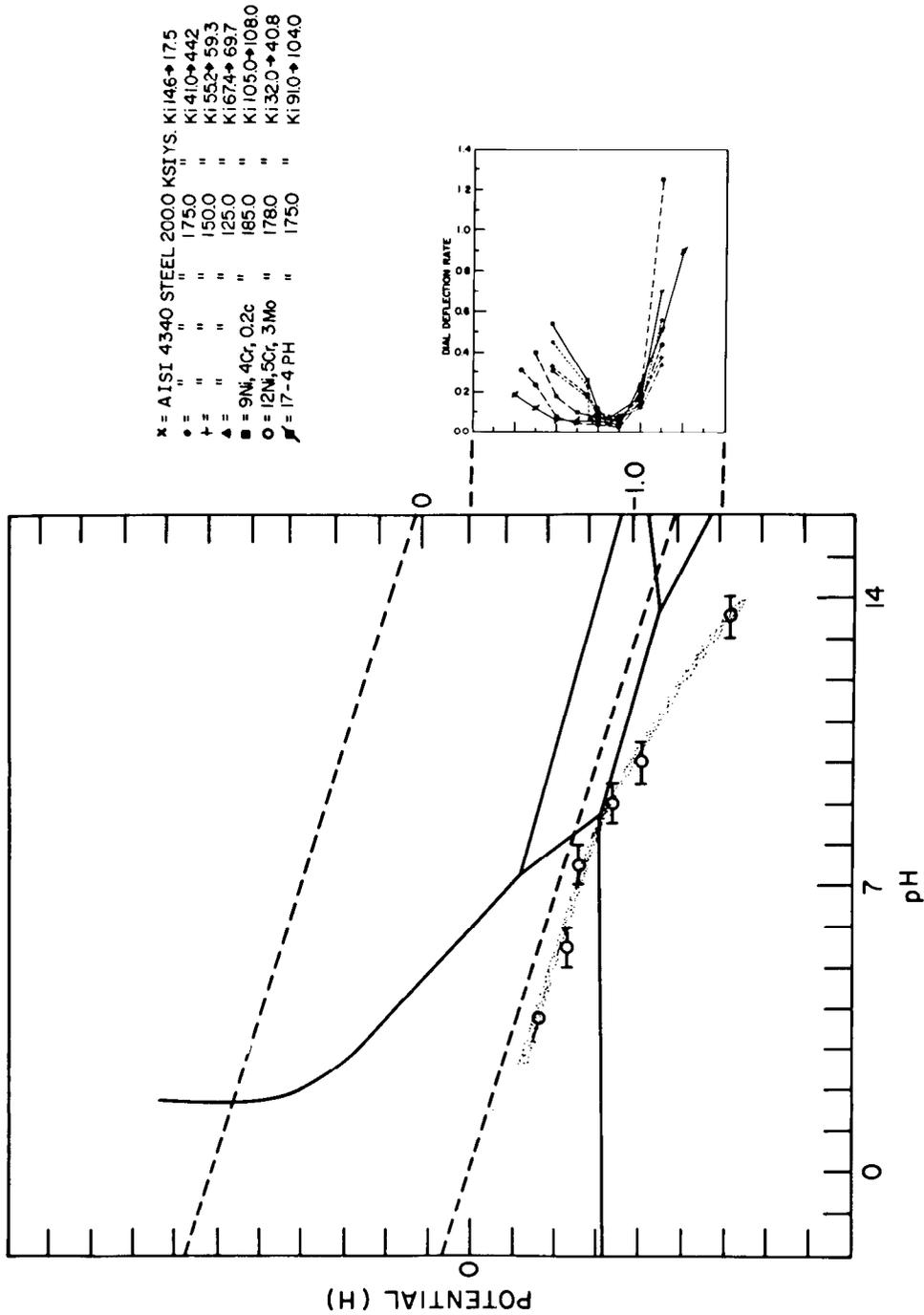


Fig. 21 - pH at the tips of growing cracks in neutral 3.5% NaCl solution, specimens potentiostatted to various levels. Curves at right indicate a function of crack-growth rate (dial deflection rate) at approximately constant K for a given steel (but different K's for different steels). These data were taken by color-change pH indicator technique but have since been confirmed by the glass electrode. Stress-corrosion cracking in steels occurs only under conditions of local pH and potential which place the crack tip under the hydrogen reduction line (lower sloping broken line).

been postulated to involve the formation of an iron hydride, thought to have been prepared and partially characterized, but work during the program has shown that the alleged iron hydride (prepared by a Grignard method) was really an organic compound of iron.

The work on crack-tip chemistry forms the basis for postulating a new role for either a corrosion pit or a pre-existing crack in initiating SCC: Formerly the pit and crack were viewed as stress concentrators, but it is now concluded that their *essential* role is to produce the local acidity which helps establish the conditions for hydrogen reduction. In the corrosion pit the acidity caused by hydrolytic reactions is retained locally by the porous cap of corrosion products, and in the stress-corrosion crack the local acidity is retained because of the long narrow diffusion path between the crack tip and the external corrodent. These observations are consistent with current findings in the program on the nature of pitting of Fe-Cr alloys (Fig. 22).

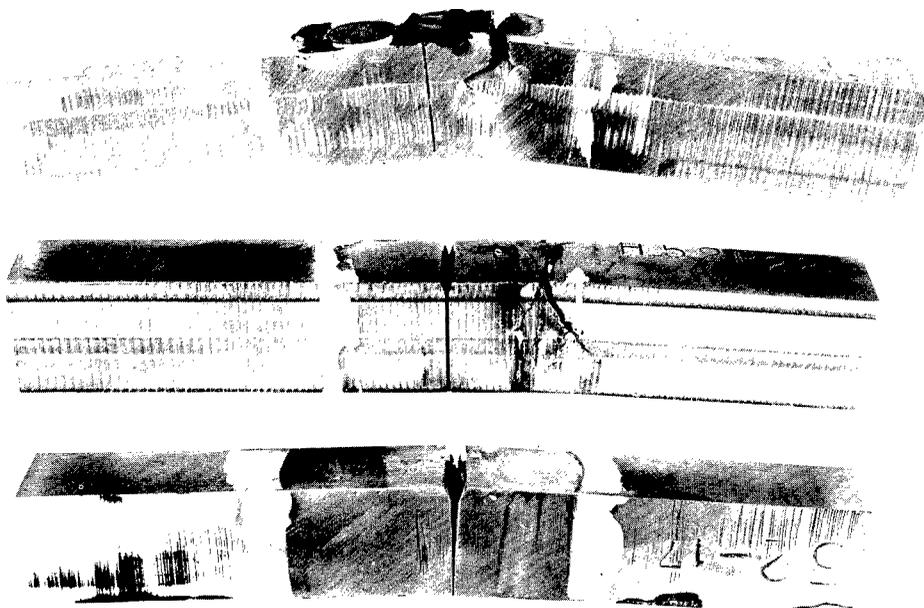


Fig. 22 - Three specimens of a 13-8Mo precipitation-hardening steel whose stress-corrosion cracking characteristics, at first puzzling, become comprehensible in the light of the experiment of Fig. 21. The lower specimen, stressed at a high K , commenced cracking at the notch. At a lower K (center specimen) there was no cracking at the notch but, after a delay of 1300 hours, there was rapid cracking under the wall of the corrodent cell. This was attributed to lowering of pH in the crevice under the wall by crevice corrosion so as to cross the hydrogen reduction curve. The upper specimen also cracked immediately at an unnotched area on which a crystal of ferric chloride had been laid to lower the pH locally.

The acidity role of the corrosion pit suggested that inhibitors and buffers which prevent the formation of the corrosion pit would be effective in preventing SCC of a smooth specimen, and this inference was confirmed experimentally. A specimen containing a precrack, however, responds only to a limited degree to inhibitors and buffers: K_{Isc} cannot be raised to K_{Ic} by such additives, doubtless because not enough of such additives are present inside the crack at the crack tip to fully control the local pH.

Cathodic protection can readily effect changes in pH deep within growing stress-corrosion cracks (contrary to a commonly held rule of cathodic protection technology to the effect that cathodic protection cannot function deeper down a crack than about eight times the crack opening dimension). [Partly because of the foregoing discrepancy, an NRL study in another program showed that the factor of 8 cited above was too pessimistic by at least a factor of 10^3 .] Cathodic protection has not appeared to be a solution to the problem of SCC in high-strength steel because, although the local hydrolytic acidification can be prevented by cathodic polarization, the conditions are still met for hydrogen evolution and cracking does continue to occur. The rate of stress-corrosion crack growth is highly dependent on potential and goes through a minimum at about -0.85 to -0.9 V (SCE) for all alloy steels which have been studied; this minimum in kinetics corresponds approximately to the potential at which iron becomes thermodynamically stable in water, suggesting that the reason for the minimum may be caused by the transfer of the anodic reaction from within the crack (when electropositive to the minimum) to outside the crack (when electronegative to the minimum). As a practical application of this information, one should be able to achieve approximately the minimum in cracking kinetics by plating with cadmium.

If one studies the details on the fracture surfaces using high-resolution replication electron fractography, one finds that regardless of potential, the fracture surface is one of smooth facets (prior austenite grain boundaries) upon which are superimposed plastic tear ridges. The tear ridges increase in number with increasing stress intensity K , until at K_{Ic} the fracture is totally tear ridges surrounding craters (purely mechanical microvoid coalescence, or dimple rupture, fracture). This identical nature of fracture details regardless of which side of the potential minimum one is on is consistent with the conclusion that only one model (hydrogen cracking) is required to account for SCC in high-strength steels.

Consistent with the hydrogen model of SCC in steels, the presence of sulfide in the corrodent (which would tend to promote the entry of hydrogen into the steel) has a strikingly adverse effect on SCC.

One can change the oxide film on the exterior of the specimen from one which is conductive (Fe_3O_4) to one which is poorly conductive ($MnFe_2O_4$), but this change does not appear to have any significant effect on SCC behavior.

The crack tip chemistry studies on *steels* in salt water or in ordinary distilled water showed that the corrodent is concentrated with respect to iron. Thus the newly formed crack surfaces do not behave like pure iron in superpure water, in which environment the iron has been shown to be as inert as platinum.

Large changes in pH locally compared with that of the bulk environment are characteristic of the corrodent in stress-corrosion cracks in all alloy families studied (Fig. 23).

One practical *caveat* appears to be provided by the finding that the behavior of pre-cracked specimens of the stainless steel designated 17-4 PH in (nearly neutral) salt water does not correlate with the poor resistance of this alloy to SCC in service. A possible explanation for this apparent discrepancy is that in service, localized hydrolytic reactions (in crevices, for example) may provide such high local acidity as to create a fundamentally different environment, perhaps also contaminated with sulfur compounds, with a different (and lower) K_{Isc} from that measured in neutral salt water.

Aluminum

The work on aluminum alloys in this program, although by design receiving the least emphasis of the three alloy families, became particularly productive in the more

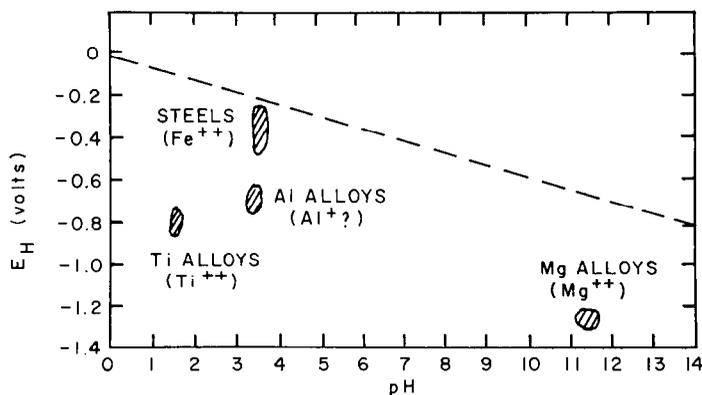


Fig. 23 - Potential and pH data for the tips of growing stress-corrosion cracks in four alloy systems in nearly neutral salt water. Data taken by color-change pH indicator paper technique. Illustrates the large differences between pH of the bulk solution and that at the occluded reaction site. (Hydrogen can be reduced from water below the broken line.)

practical aspects of the problem because of the adoption of the precracked specimen technique (Fig. 24). Wrought products of the Al-Zn-Mg group of alloys which have strengths of special interest to the DoD are highly textured, and SCC is a problem primarily only parallel to this texture. Ordinary bent-beam or tensile specimens cannot be cut in such a fashion as to test this maximum vulnerability direction unless either the plate is very thick or extensions can be welded or otherwise firmly attached to the plate material, which has never been an attractive approach.

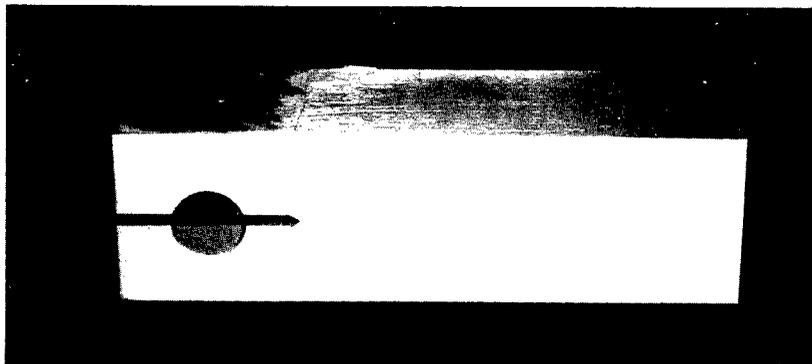


Fig. 24 - Aluminum specimen of Fig. 6 self-stressed (after the method of Novak and Rolfe) by a setscrew. Dark region is paraffin used to insulate the steel setscrew from the crack area. A stress-corrosion crack is seen emanating from the machined notch. This type of specimen was used for most of the characterization data on aluminum alloys in the program.

Early work with the specimen of Fig. 6 suggested that there was a stress intensity below which SCC stopped, but later work has indicated that, although the rate of crack growth diminishes with decreasing K at low levels of K , there does not appear to be any true threshold below which the cracking absolutely stops. Events have shown that the

best way to characterize the SCC behavior of a given alloy is to report the kinetics of crack growth as a function of K, which will be referred to here as V-K characterization.

A contribution from outside the program has been highly beneficial in using the DCB specimen of Fig. 6. This contribution was the demonstration that one could use a bolt to spread apart the two arms of the DCB specimen to stress it without the need for the proving ring, and that stressing in such fashion still permitted quantification of the stress intensity at the root of the crack. This specimen can then be described as a self-stressed DCB specimen, and it has become a most productive research tool, with demonstrated usefulness for sheet material at least as thin as 0.05 in. Among its other advantages, the self-stressed specimen has that of being suitable for wide distribution for readily assessing, say, the effect on SCC of the environment of an airport runway, or of a deep-diving submersible, or of a noxious chemical.

V-K studies have been completed on a large number of commercial and experimental alloys in various tempers (Fig. 25). These studies have shown that at low values of K, log V rises rapidly and linearly with increasing K (Stage I) until a saturation level (Stage II) is reached, after which V is nearly independent of K. In some alloys there is a third stage, near K_{Ic} , in which V is again dependent upon K. Curves of $K \log V$ yield

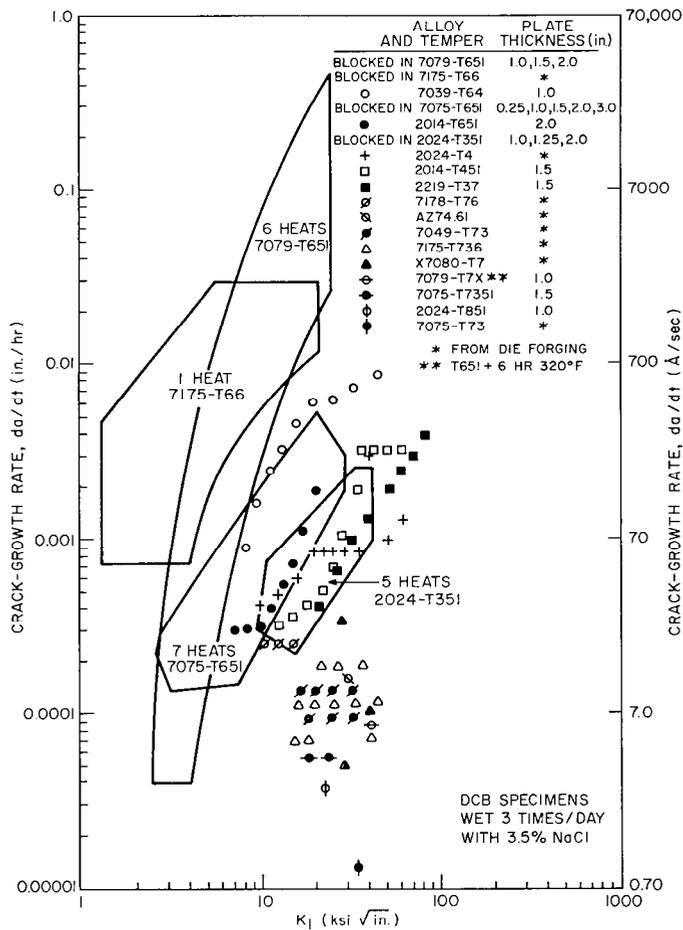


Fig. 25 - Comparison of several commercial and experimental aluminum alloys using the self-stressed DCB specimen and the crack-growth rate method

rangings which agree with established rankings using smooth specimens with two differences: The K-log V rankings are enormously more rapidly obtained, and they are more discriminating than the smooth-specimen rankings when applied to alloys having approximately the same SCC characteristics.

The DCB specimens demonstrated in a very graphic way the magnitude of the effect which quenching stresses can produce in the SCC of aluminum alloys.

The evidence to date is that in Stages I and III the rate of crack growth is little influenced by halide-ion concentration, but the velocity of Stage II apparently can be strongly affected by anion concentration.

Commercial alloys do not experience SCC except when water is present, and only the anions Cl^- , Br^- , and I^- accelerate V (in Stage II) appreciably.

New information was developed on the effects of microstructure on SCC (Fig. 26). It was shown, for example, that the microstructure controlled the cracking process through its effect on the deformation process: Specimens which were strengthened by large Guinier-Preston (G-P) zones exhibited coarse slip characteristics and proved to crack readily, while specimens hardened by small G-P zones exhibited fine slip and cracked slowly. Work on bicrystals revealed that when slip could be transferred across the grain boundary, cracking was slow, but when slip transfer was impeded by the boundary, cracking was rapid.

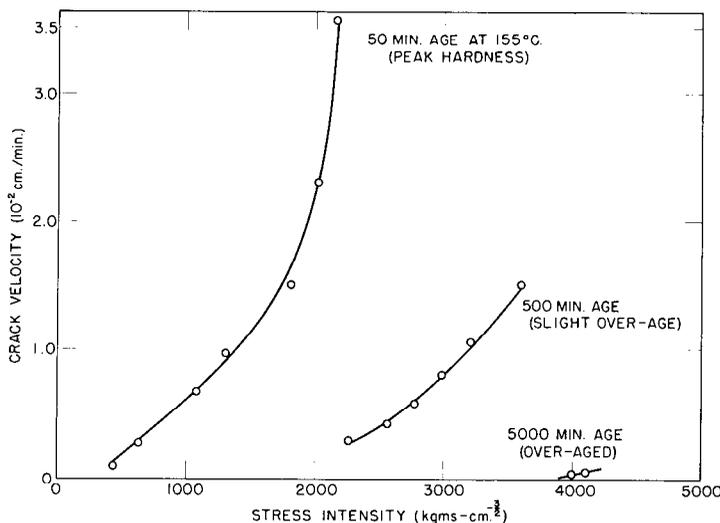


Fig. 26 - Effect of heat treatment on the stress-corrosion cracking kinetics of Al-15%Zn. Transmission electron microscopy shows that the increasing aging time at 155°C causes a progressive decrease in the volume fraction of Guinier-Preston zones.

Neither the presence nor the width of the precipitate-free zone was observed to have any effect on the stress-corrosion susceptibility of a ternary Al-Zn-Mg alloy (Fig. 27). This finding has been explained in terms of slip-band behavior.

Methods have been developed to measure the pH at the tips of growing cracks using both color-change pH indicators and the glass electrode, and in the case of 7000-series

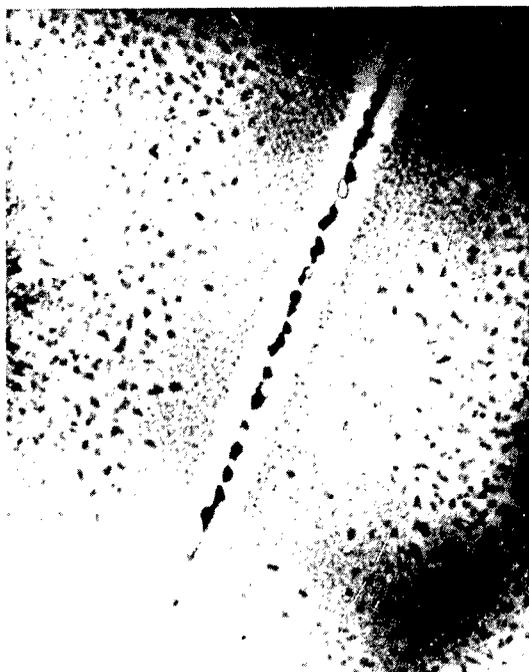


Fig. 27 - The precipitate-free zone adjoining a grain boundary in an Al-6.8% Zn-2.3% Mg alloy. There has been much controversy over the role that this zone plays in stress-corrosion cracking behavior. Studies on high-purity alloys have led to the conclusion that it is primarily the matrix precipitates, and not the grain boundary precipitate, that determine susceptibility to SCC.

aluminum alloys undergoing cracking from nearly neutral salt water, the pH at the crack tip was found to be 3.2 to 3.5. A macroscopic model was also devised to simulate the sides and the base of a stress-corrosion crack, with the simulated base electrically isolated from the simulated walls. This model has given interesting results to date and gives promise of more to come.

In addition to other basic contributions to aluminum corrosion, two reviews were written by program personnel. One of these was concerned with the aluminum-hydrogen system. A second review treated chemical effects in the corrosion of aluminum and aluminum alloys.

An academic study of the corrosion fatigue of an aluminum alloy demonstrated that hydrogen diffusion is not rate controlling (Fig. 28).

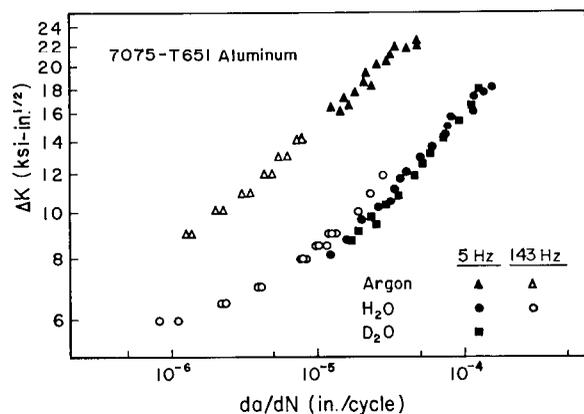


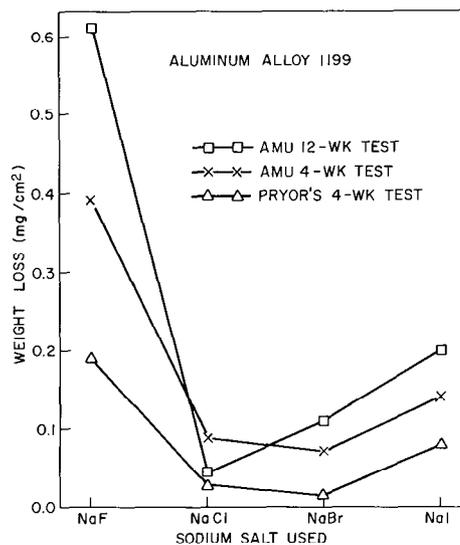
Fig. 28 - Fatigue (in argon) and corrosion fatigue (in water) crack-growth rates in an aluminum alloy. Deuterium studies indicate that hydrogen diffusion is not rate-determining.

Surface Sciences

Various entries in the Abstracts of Achievements identify contributions of some of the subdisciplines which are sometimes called collectively *surface science*. For example, techniques of Low-Energy Electron Diffraction (LEED) have been advanced by the program to enable the experimenter to study the initial reaction of any chosen gas (however corrosive) with a clean metal surface. An international conference was held in which the status of field ion microscopy and field emission microscopy were reviewed by internationally recognized experts, and the proceedings have now been published. Electron spin resonance studies were made on oxide surfaces exposed to various gaseous species.

As indicated by the foregoing, the program was instrumental in drawing to the attention of surface scientists the existence of a challenging technological problem. As a consequence many basic studies were made using various ones of the newer surface science techniques, much new and interesting information was developed, and more techniques were added to those available to the surface scientist (Figs. 29 to 31). The technique of LEED in particular made significant advances because of the program. The experimental and theoretical difficulties of the program area are such, however, that much more work is required before these newer approaches can make their contributions to corrosion technology.

Fig. 29 - Basic study of the role of the chloride ion in the corrosion of aluminum. Kinetic data show that although there are some quantitative differences between the behavior of the various halide ions, there are no qualitative differences, and the role played by chloride is due to its ubiquity rather than any uniqueness.



The electrochemical techniques and concepts, especially those developed and applied by Evans, Hoar, Pourbaix, and their students, have been shown to be of immediate value both in advancing the theory of stress-corrosion cracking and in guiding technological experimentation. Since electrochemistry is generically a surface science, the tenet that surface science would be useful to the stress-corrosion problem at an early date has thus been vindicated. As one example, it has been postulated elsewhere that hydrogen can only be reduced from aqueous solutions at a cathode, that by making a piece of steel an anode one establishes conditions incompatible with hydrogen reduction and that any SCC occurring under such conditions cannot be attributed to hydrogen. A more sophisticated analysis of the situation is as follows: A given site (electrode) can serve as an anode for the dissolution of iron and at the same time function as a cathode for the reduction of hydrogen, if the potential and pH are favorable.



Fig. 30 - Field ion micrograph Ni_4Mo . This is one of several modern techniques in surface physics which are useful to study the ultrafine-scale nature of clean metal surfaces.

The experience of the program, in summary, is that there are numerous new areas of surface science capable of yielding important scientific knowledge about metal surfaces and their reaction with environment. The more mature discipline of electrochemistry has been demonstrated to have immediate utility in the understanding of the processes of aqueous corrosion, including stress-corrosion cracking, and in the guidance of future technological advances.

ABSTRACTS OF ACHIEVEMENTS

Explanatory Notes

These abstracts were prepared by the organization performing the research as a means both of summarizing progress and giving the reader a key to the literature generated by the program. They were modeled after annual reports of Interdisciplinary Laboratories, listing task title, personnel, objective, usually the approach, the achievements, and publications and presentations.

It will be noted that a given task, represented by a single task title, may differ greatly from another in scope, staffing, and productivity. This is due in considerable measure to the broad technical nature of the program and to the fact that each organization grouped its work under a given task title as seemed most effective for conveying the output to the imagined readers.

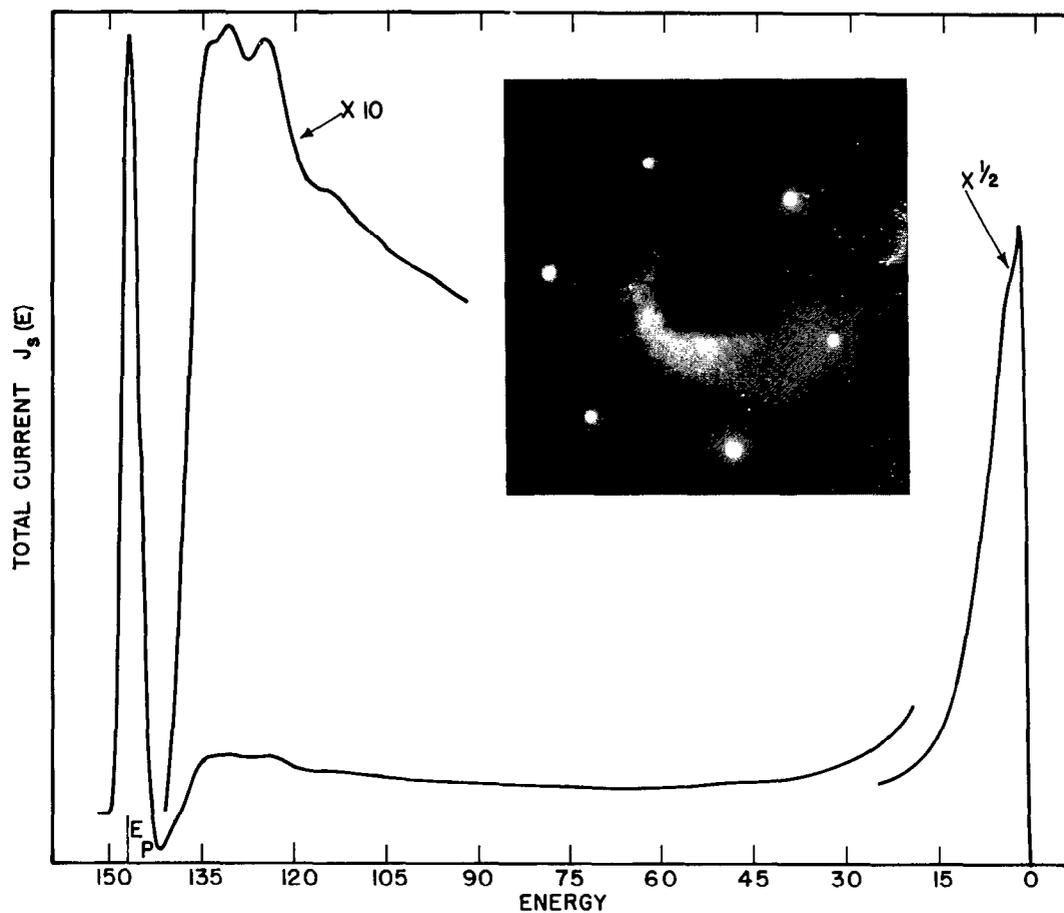


Fig. 31 - Low energy electron diffraction pattern and secondary electron energy distribution curve for an aluminum (111) surface. The curve includes a peak indicating that the elaborate steps used to prepare an entirely clean surface were not quite successful. This observation illustrates one of the many challenges of state-of-the-art surface physics and surface chemistry.

The abstracts are arranged in the following pages by institutions, commencing with The Boeing Company, followed by the universities (alphabetically), and finally the Naval Research Laboratory.

The Boeing Company

USE OF PRECRACKED SPECIMENS IN STRESS-CORROSION TESTING OF HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for several high strength commercial aluminum alloys, and to compare the rating of the alloys based on this data with the ratings established from smooth specimen time to failure data.

Approach

The V-K curves were obtained using bolt-loaded, double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Alloys and tempers tested were 7079-T651, 7079-T651 + 6 hr/325°F, 7075-T651, 7075-T7351, 7175-T66, 7175-T736, 7178-T76, AZ74.61, X7080-T7, 7039-T64, 7049-T7, 2024-T351, 2024-T4, 2024-T851, 2014-T451, 2014-T651, 2219-T37.

Achievements

The V-K curves showed a double slope behavior. At lower crack tip stress intensities the crack velocities were highly dependent on K_I , whereas at the higher K_I levels crack velocities were nearly independent of the applied crack tip stress intensity. Maximum crack velocities ranged from 4×10^{-5} in./hr for the highly susceptible 7079-T651 to 1×10^{-5} in./hr for the highly resistant 7075-T73. Although crack velocities often continued to decrease with decreasing K_I level, true K_{Isc} values (K_I levels below which growth ceases) were not observed for any alloy tested. Rankings of the various alloys based on the V-K curves agreed with established rankings based on smooth specimen time to failure data. In many cases the V-K curves provided more discriminating data than is available from smooth specimen time to failure tests. For example, at the higher K_I levels stress-corrosion crack growth rates in 7079-T651 were one to two orders of magnitude faster than in 7075-T651 even though both alloys show similar behavior in the standard smooth specimen, alternate immersion test.

A relationship between the smooth specimen stress-corrosion threshold stress from time to failure data and the V-K curves is presented.

Publications

"Use of Precracked Specimens in Stress-Corrosion Testing of High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24466, November 1969; submitted to Corrosion

The Boeing Company

USE OF PRECRACKED SPECIMENS IN SELECTING HEAT TREATMENTS FOR STRESS-CORROSION RESISTANCE IN HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for the alloy 7075 after various overaging heat treatments between T6 and T73.

Approach

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Three different techniques were employed. Two techniques used single DCB specimens containing aging gradients along their lengths. The third technique used multiple DCB specimens, each one having a different heat treatment.

Achievements

Results from each technique showed that for the 7075 alloy, overaging to an electrical conductivity of at least 38% IACS is necessary before stress-corrosion crack growth rates approach those of 7075-T73. Stress-corrosion performance was established most rapidly using multiple DCB specimens. After only a few hundred hours the crack growth characteristics were sufficiently established using this technique that the different heat treatments could be rated against the known performance of 7075 in the T6 and T73 tempers.

Publications

"Use of Precracked Specimens in Selecting Heat Treatments for Stress-Corrosion Resistance in High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-2447, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF RESIDUAL STRESSES ON STRESS-CORROSION CRACK GROWTH RATES
IN ALUMINUM ALLOYS

M. V. Hyatt

Objective

To determine the effects of quenched-in residual stresses on the behavior of pre-cracked double cantilever beam (DCB) stress-corrosion specimens of high strength aluminum alloys 7075, 7175, and 7079.

Approach

The V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were obtained using bolt loaded DCB specimens intermittently wetted with an aqueous 3.5% NaCl solution. Tests were conducted on specimens containing quenched-in residual stresses and on specimens which had been stress relieved after quenching by stretching or explosive shocking.

Achievements

Large differences in crack front profiles were observed between specimens with and without residual quenching stresses. Severe crack front bowing occurred in non-stress relieved specimens. In addition the crack opening displacement in the non-stress relieved specimens was effectively increased at the crack tip by the bowing apart of the two DCB specimen arms as the stress-corrosion crack propagated through the material. These effects result primarily from the residual compressive stresses on the surfaces of the non-stress relieved specimens. Both the crack front bowing and the bowing apart of the DCB specimen arms cause errors in the calculated K_I levels. These problems were eliminated by stress relieving DCB specimens after quenching. This work underlines the fact that residual quenching stresses in actual parts susceptible to stress-corrosion cracking not only increase chances of initiating stress-corrosion cracks, but also play an important role in increasing average growth rates. This can result from the increased crack opening displacement (and therefore K_I level) at the crack tip due to deflections caused by the residual stresses.

Publications

"Effect of Residual Stresses on Stress Corrosion Crack Growth Rates in Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24469, November 1969; submitted to Corrosion

The Boeing Company

EFFECTS OF SPECIMEN GEOMETRY AND GRAIN STRUCTURE ON STRESS-CORROSION CRACKING BEHAVIOR OF ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for aluminum alloy double cantilever beam (DCB) specimens with various side grooves, grain structures, and thicknesses.

Approach

DCB specimens with various side grooves, grain structures, and thicknesses were tested in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Branch cracking and arm breakoff may occur during testing of DCB specimens of aluminum alloy materials with equiaxed grain structures. Side grooves on DCB specimens had a negligible effect on crack growth rate data. Double cantilever beam specimens from materials as thin as 0.050 in. can be successfully tested.

Publications

"Effects of Specimen Geometry and Grain Structure on Stress Corrosion Cracking Behavior of Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24470, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF QUENCHING RATE ON STRESS-CORROSION CRACK GROWTH RATES
IN 2024-T4 ALUMINUM

M. V. Hyatt

Objective

To determine the effect of quenching rate on the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for 2024-T4.

Approach

Specimens of 2024 were resolution treated, quenched at two different rates, and naturally aged to the T4 temper.

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution.

Achievements

Actual stress-corrosion crack growth rates were higher in the more slowly quenched 2024-T4 alloy. This behavior agrees with trends observed by others based on percent loss in tensile strengths of pre-exposed specimens which have been quenched at different rates.

Publications

"Effect of Quenching Rate on Stress-Corrosion Crack Growth Rates in 2024-T4 Aluminum," M. V. Hyatt, Boeing Document No. D6-24471, November 1969; submitted to Corrosion

The Boeing Company

DEVELOPMENT OF A HIGH STRENGTH, STRESS-CORROSION RESISTANT ALUMINUM ALLOY FOR USE IN THICK SECTIONS

M. V. Hyatt and H. W. Schimmelbusch

Objective

To develop a new high strength Al-Zn-Mg-Cu alloy with a smooth specimen stress-corrosion threshold stress of 25 ksi, good toughness and fatigue properties, and a quench sensitivity such that the properties can be maintained at a high level in thick plate and forgings.

Approach

To meet the strength goals an alloy with zinc and magnesium contents intermediate between those of 7075 and 7178 was selected. To reduce quench sensitivity the copper content was reduced to about 1.0%, and zirconium and manganese were added in place of chromium which is the normal recrystallization retardant in 7075 and 7178 alloys. The amount of overaging required to meet the stress-corrosion goal was determined using both smooth specimens and precracked double cantilever beam (DCB) specimens. Finally, hand and die forgings, plate, and extrusions of the new alloy were given the selected heat treatment and evaluated to determine mechanical, fracture, fatigue, and stress-corrosion properties.

Achievements

Mechanical, fracture, and stress-corrosion properties for die forgings of the new alloy (alloy 21) and several other forging alloys are compared in the following table.

Alloy	Thickness (in.)	Minimum longitudinal properties		Longitudinal K_{Ic} range (ksi $\sqrt{\text{in.}}$)	Short-transverse stress-corrosion threshold (ksi)	
		F_{tu} (ksi)	0.2% F_{ty} (ksi)		3.5% NaCl alternate immersion	Industrial atmosphere
Alloy 21	6.75	69*	60*	30-38*	> 25*	> 25*
7049-T73	5.0	70	60	30-38*	45	?
X7080-T7	6.0	65	57	27-30	25	15
7075-T73	3.0	66	56	27-38	> 47	> 47
7075-T73	6.0	61	51	27-38	> 47	> 47
7175-T736	3.0 max	76	66	27-38	~ 35	?
7075-T6	3.0 max	75	65	25-32	7	14
7079-T6	6.0	72	62	25-32	7	6

*Estimated values

The mechanical properties of alloy 21 are comparable to those of 7049-T73. The fracture toughness of alloy 21 is as good as or better than that of the other alloys listed. The smooth-specimen short-transverse stress-corrosion threshold appears to be greater than 25 ksi. Test data also indicate that the smooth and notched axial (tension-tension) fatigue properties of alloy 21 are comparable to those of 7075-T6 and 7075-T73.

Publications

"Development of a High-Strength, Stress-Corrosion Resistant Aluminum Alloy for Use in Thick Sections," M. V. Hyatt and H. W. Schimmelbusch, Technical Report AFML-TR-70-109, May 1970, Boeing Document No. D6-60122

The Boeing Company

EFFECT OF EXPOSURE TIME AT 250°F ON STRESS-CORROSION CRACK GROWTH RATES IN 2024-T351 ALUMINUM

M. V. Hyatt and W. E. Quist

Objective

To determine the degree of sensitization to stress-corrosion cracking of 2024-T351 after exposure at 250°F (a temperature commonly used during curing of adhesively bonded assemblies).

Approach

Double cantilever beam (DCB) specimens of 2024-T351 were exposed at 250°F for times up to 300 hours. V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were then obtained in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Stress-corrosion crack velocities were observed to increase in specimens which had been exposed for only 2-5 hours at 250°F. Maximum crack velocity increases of about 60% occurred on specimens which had been exposed from 15 to 100 hours.

The Boeing Company

FUNDAMENTAL ASPECTS OF STRESS-CORROSION CRACKING OF HIGH STRENGTH ALUMINUM ALLOYS

Markus O. Speidel

Objective

At the Boeing Scientific Research Laboratories experimental and theoretical studies of stress-corrosion cracking in high strength aluminum alloys have three aims: (1) to identify the major influential parameters, that is, the conditions under which stress-corrosion cracks can grow; (2) to compare such conditions with those that cause stress-corrosion cracking in other alloy systems, polymers, and glasses, in an attempt to define their limits of applicability; and (3) to increase our understanding of the basic mechanisms of stress-corrosion crack propagation.

Approach

With complementary fractography and metallurgical examination, the main effort was concentrated on the measurement of stress-corrosion crack tip velocity as a function of the following parameters.

1. Mechanical parameters
 - a) applied crack tip stress intensity
 - b) specimen geometry
2. Environmental parameters
 - a) concentration of halide ions
 - b) concentration of other inorganic anions
 - c) concentration of water in the environment
 - d) presence of various gases
 - e) concentration of organic liquids
 - f) concentration of protons
 - g) presence of other cations
 - h) presence of liquid metal in the crack
 - i) temperature
 - j) viscosity of electrolyte
 - k) electrochemical potential
3. Metallurgical parameters
 - a) aging time
 - b) aging temperature
 - c) alloy concentration
 - d) recrystallization

Achievements

Crack propagation was shown to be affected by almost all the parameters listed. The first step in each case was to measure the effect of the variation of just one parameter on the velocity while keeping all the other parameters constant at some "reasonable" value. Our data showed that this can lead to quite different results,

depending on the actual value chosen for those parameters that were kept constant. The interdependence of the effects of various parameters on stress-corrosion crack velocity is illustrated in Figs. 1, 2, and 3.

Effect of Stress on Crack Tip Velocity—Crack tip stress intensity has a decisive effect on stress-corrosion crack velocity. It can cause the velocity to vary from less than 5×10^{-9} cm/sec to more than 2 cm/sec, a range that exceeds by far the lowest and the highest subcritical crack velocity ever before directly observed in aluminum alloys. Although the slowest cracks took a year to become visible, a movie camera had to be used to record the fastest cracks. Generally, there are three regions of the crack velocity versus stress intensity curve: region I at low stress intensities where the crack velocity is strongly stress dependent; region II at intermediate stress intensities where the crack velocity is independent of stress and which subsequently may show one or two plateaus; and region III at stress

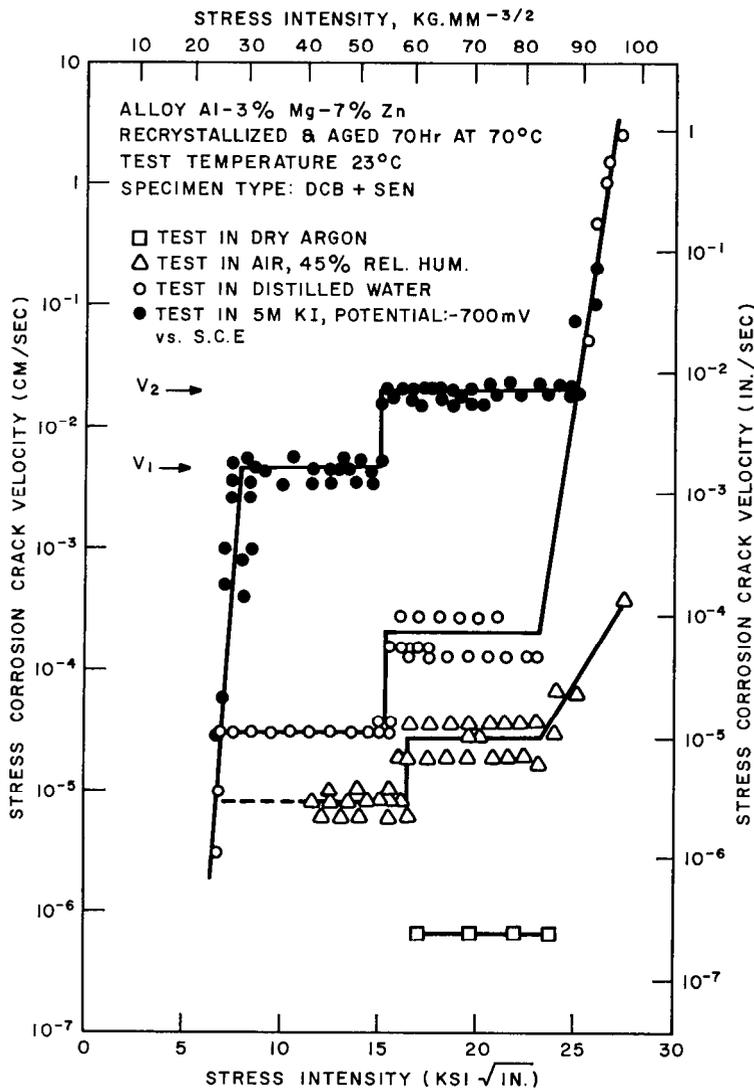


Fig. 1 - The effect of stress intensity on SCC crack velocity

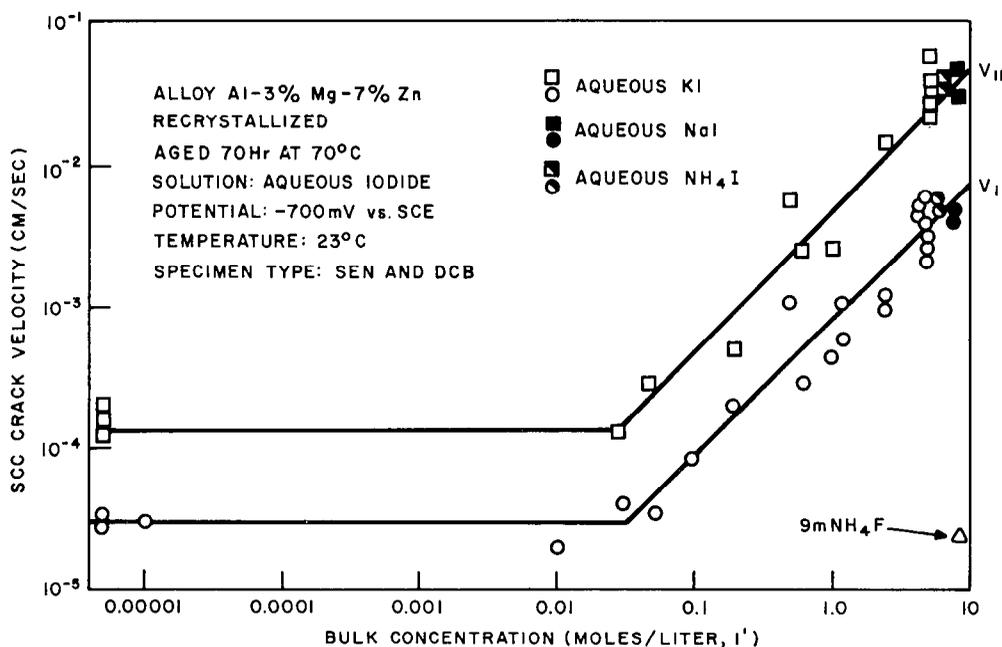


Fig. 2 - The effect of halide ion concentration on SCC crack velocity

intensities close to K_{Ic} where the velocity again is strongly stress dependent. Commercial aluminum alloys show only regions I and II, but a high-purity alloy showed all three regions, as illustrated in Fig. 1. For the experimental conditions listed in Fig. 1, stress-corrosion crack velocity apparently does not depend on halide ion concentration in regions I and III. Region II, however, is strongly affected by halide ion concentration. This is obvious from both Figs. 1 and 2, which are based on hundreds of tests on self-stressed double cantilever beam specimens and single-edge-notched tension specimens. Thus, there is no simple answer to whether halide ion concentration affects stress-corrosion crack velocity. The answer is no for regions I and III, but yes for region II. Velocity in region I is thought to be kinetically limited. Velocity in region II is thought to be limited by mass transport. The existence of region III is thought to be due to additional mechanical components of crack growth.

Effect of Halide Ion Concentration on Stress-Corrosion Crack Velocity—Figure 2 shows the effect of iodide concentration on the two plateau velocities that may be seen in region II in Fig. 1. The linear increase of the plateau velocities at higher iodide concentrations is consistent with the concept of mass transport limited velocity. The constant velocity at low halide ion concentrations can be attributed to water as a stress-corrosion agent. This behavior also occurs in commercial aluminum alloys and is similar for bromide and chloride ions. Fluoride ions, however, do not accelerate stress-corrosion cracking over the rate found in distilled water.

Effect of Electrochemical Potential on Stress-Corrosion Crack Velocity—In Fig. 3 it may be seen that the effect of halide ion concentration on region II velocity applies only at a specific electrochemical potential of the specimen and only at a specific pH value of the bulk electrolyte. For example, at a potential of $E = -1600$ mV, there is no influence whatsoever of iodide concentration on stress-corrosion crack velocity. This is true if the solution is neutral. Under such conditions, the crack propagates even in concentrated solutions with the velocity characteristic of

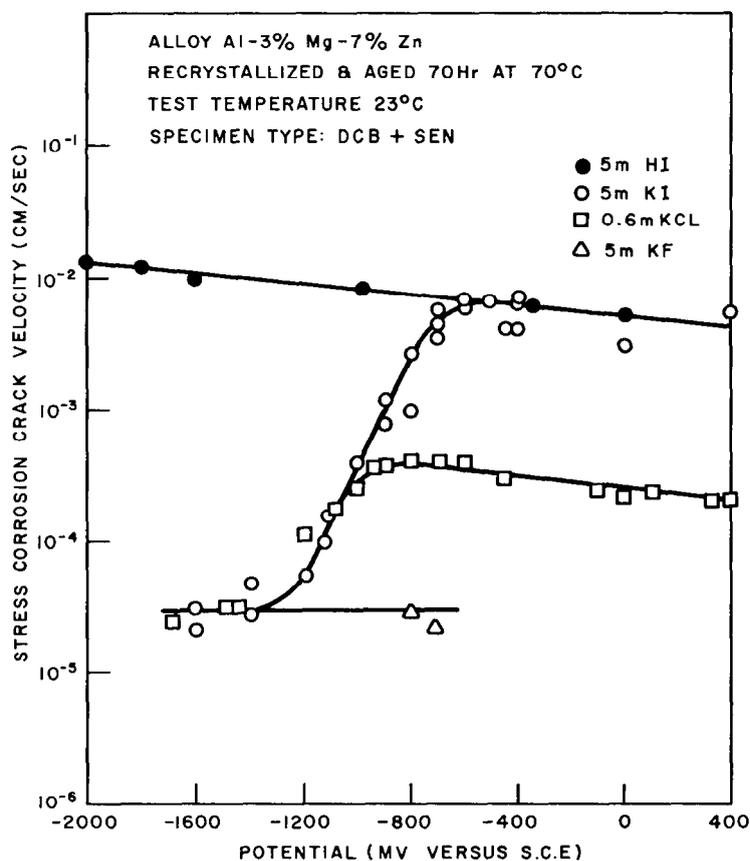


Fig. 3 - The effect of electrochemical potential on SCC crack velocity

propagation in distilled water. (Compare Figs. 1, 2, and 3.) In strongly acidic solutions, however, cathodic protection is impossible, and the crack propagates with the velocity characteristic for propagation in highly concentrated halide solutions. Between the cathodic-protection and the pitting potentials, stress-corrosion crack velocity in neutral Cl^- , Br^- , and I^- solutions increases with potential and finally levels out at rates that are determined by the halide ion concentration. The increase in velocity is attributed to the replacement of OH^- ions by halide ions. The leveling off beyond the pitting potential is attributed to the consumption of halide ions on the crack walls.

Summary of Other Results--

1. Crack-line-loaded and remote-loaded specimens yield comparable crack velocity versus stress intensity curves.
2. Of 20 anions tested, only Cl^- , Br^- , I^- , and, to a much lesser degree, NO_3^- accelerate stress-corrosion crack growth.
3. Ten different cations tested resulted in the same stress-corrosion crack velocity. An exception was H^+ in the cathodic protection range.

4. Liquid metals cause stress-corrosion crack velocities up to 20 cm/sec and K_{Isc} as low as 0.8 ksi $\sqrt{\text{in.}}$.
5. Solution viscosity is inversely proportional to stress-corrosion crack velocity.
6. Overaging causes not only a reduction in velocity, but also an increase in the limiting stress intensity in region I.
7. Alloys recrystallized to large equiaxed grains show stress-corrosion crack velocities 10 to 100 times faster than commercial alloys with the usual flattened grains.
8. There is no true K_{Isc} for aluminum alloys. Cracks just slow down at lower stress intensities, but do not stop.
9. In commercial aluminum alloys, no crack growth occurs in gases and organic liquids unless water is present.

The Boeing Company

ENVIRONMENTAL FATIGUE CRACK PROPAGATION OF ALUMINUM ALLOYS AT LOW STRESS INTENSITY LEVELS

J. A. Feeney, J. C. McMillan, and R. P. Wei

Objective

The objectives of the study were:

- a) To evaluate the performance of commercial aluminum alloys when subjected to cyclic stresses in corrosive and "mild" environments.
- b) To correlate the data within the framework of linear-elastic fracture mechanics using the crack tip stress-intensity factor K to characterize the crack driving force.
- c) To examine fatigue crack growth rates at low values of stress intensity factor where the mechanical aspects of the fatigue process are less dominant.
- d) To correlate the rate of fatigue crack propagation in a particular environment and at a particular K level with the fracture topography.

Approach

Corrosion fatigue experiments were conducted on aluminum alloys 7178-T6, 7075-T6, and 2024-T3. Panels of dimensions $24 \times 9 \times 0.16$ in. were cyclic stressed by wedge force and remote loading techniques. Five different environments were studied: desiccated argon (10 ppm H_2O), dry air ($< 10\%$ relative humidity), wet air ($> 90\%$ relative humidity), distilled water, and 3.5% NaCl solution. Data was plotted as $\log \Delta K$ versus $\log d2a/dN$.

Achievements

Wedge force loading and remote loading techniques were found to be compatible under the test conditions used in this investigation. When the data was plotted as $\log \Delta K$ versus $\log d2a/dN$, two transition regions were exhibited:

- a) The transition at high levels of ΔK was environmentally controlled and reflected a change-over from a plane strain to plane stress mode of propagation.
- b) The transition at low levels of ΔK was not environmentally controlled and reflected some intrinsic property of the material.

The frequency effect was found to be controlled mostly by the environmental influence and was not an intrinsic property of the material. The effects of the environments on the rate of fatigue crack propagation were:

- a) Environmental sensitivity was most pronounced at low levels of cyclic amplitude of stress intensity ΔK .

- b) Alloy 2024-T3 was relatively insensitive to the mild environments when compared to dry air, whereas 7075-T6 and 7178-T6 showed a pronounced acceleration in fatigue crack growth rate when tested in either wet air or distilled water.
- c) All three alloys exhibited a marked susceptibility to environmentally enhanced fatigue crack growth rate in 3.5% NaCl solution. In contrast to 2024-T3 and 7075-T6, however, fatigue crack growth of 7178-T6 was faster in distilled water than in 3.5% NaCl solution.

The most pertinent fractographic observations were:

- a) Ductile striations were not observed at growth rates ($d2a/dN$) less than $250 \text{ \AA}/\text{cycle}$.
- b) Cleavage-like fracture, stepwise growth, and rippled facet fracture were the most pronounced transgranular fracture modes at crack growth rates below $10 \text{ \mu in.}/\text{cycle}$.
- c) Cleavage-like fracture appeared to be environmentally controlled and was more pronounced the less ductile the material.
- d) Intergranular fracture was the most common fracture process in specimens of 2024-T3 and 7178-T6 tested in 3.5% NaCl solution at low ΔK levels. In 7075-T6, however, intergranular fracture did not occur at any ΔK level.
- e) Environmental sensitivity at relatively higher ΔK levels was not always associated with a change in fracture mode from ductile striation formation to brittle striation formation. In 2024-T3, for example, brittle striations did not form in any of the environments used in the investigation.

Publications

"Environmental Fatigue Crack Propagation of Aluminum Alloys at Low Stress Intensity Levels," J. A. Feeney, J. C. McMillan, and R. P. Wei, Boeing Document No. D6-60114, May 1969 (DDC Accession No. AD 692166); published in Metallurgical Transactions 1: 6, June 1970, p. 1741

Presentations

"Environmental Fatigue Crack Propagation of Aluminum Alloys at Low Stress Intensity Levels" by J. A. Feeney, ASM/WESTEC Meeting, Los Angeles, May 1969

The Boeing Company

IMPROVING THE TOUGHNESS AND STRESS-CORROSION RESISTANCE OF AFC 77

D. Webster

Objective

In the past five years the strength of stainless steels has been improved to the point where they are competitive on a strength-to-weight basis with low alloy steels and alloys of titanium and aluminum. The strongest stainless steel available is AFC 77 which contains 0.15C, 14.5Cr, 5.0Mo, 0.5V, and 13.5Co. In spite of its high strength, this alloy has not found widespread use because of its low toughness and stress-corrosion resistance. The objective of this study was to improve the toughness and stress-corrosion resistance of AFC 77.

Approach

New heat treatments and thermomechanical processes were used. The three most promising techniques were as follows:

1. In the first process, heat treatment is controlled to ensure that a small amount of austenite remains after heat treatment. The tough austenite diverts or stops a growing crack so that a large amount of energy is necessary for fracture; in other words, the material has a high fracture toughness. AFC 77 is normally considered to have a fully martensitic structure, but there is an increasing tendency for austenite to be retained as the austenitizing temperature is increased. This happens because the stability of the austenite is related to the alloy content of the matrix, which is greater at high austenitizing temperatures due to increased solution of undissolved carbides and intermetallic compounds. An upper limit on the austenitizing temperature is set by the formation of delta ferrite at about 2100°F. In order to be an efficient crack stopper, it is not only necessary that the second phase be tough, but it must also be well dispersed. The dispersion of austenite is produced automatically during the martensite transformation as new martensite needles repeatedly subdivide the areas of austenite in which they form. A modification of the above technique which allows the retained austenite content to be increased has recently been developed. In this technique higher than normal austenitizing temperatures which are inside the austenite + delta ferrite phase field are used. The delta ferrite is then transformed to austenite at lower temperatures after which the normal heat-treatment practice is followed.
2. A new grain refinement process forms the basis of the second technique. In this process the annealed steel is cold rolled at least 35% in the final stages of manufacture and then re-annealed before delivery to the user. While still in the annealed condition, fabrication of the part is completed and then a normal hardening treatment is given which, because of the prior deformation, will develop a refined grain structure. The explanation for the grain refinement is as follows: The cold rolling ruptures the interface between the hard carbide particles and the matrix and causes voids to form around the particles. These voids, which are stable in the austenite at temperatures up to 1875°F, interact with moving grain boundaries at the austenitizing temperature, resulting in a marked refinement of austenite grain size.

3. The third technique, which involves the strain aging of material containing retained austenite, produces the best combination of strength, toughness, and stress-corrosion resistance. In this process the material is austenitized at a temperature high enough to produce retained austenite, tempered at 500°F, and then strained 10-20% by cold rolling. A second tempering treatment in the range 500°-1000°F is then given to develop tensile strengths from 280,000 psi to 330,000 psi. Because a substantial proportion of the retained austenite remains after strain aging, a high level of fracture toughness is maintained.

Achievements

Using the PH stainless steels as a base, the techniques described above have increased the strength level at which a given toughness (K_{Ic}) can be maintained from the normal 190-230 ksi range to the 310-330 ksi range for strain aged material or the 250-290 ksi range for non-strain aged material. Similar increases in strength level for equivalent stress-corrosion resistance (K_{Isc}) is achieved by these techniques. For example, strain-aged AFC 77 sheet with a yield strength of 277 ksi and an ultimate strength of 288 ksi has a K_{Isc} of 90 ksi $\sqrt{\text{in}}$.

Publications

"The Use of Deformation Voids to Refine the Austenite Grain Size and Improve the Mechanical Properties of AFC 77," D. Webster, Boeing Document No. D6-23870, 1969 (DDC Accession No. AD 687724); also Trans. ASM Quarterly 62, Sept. 1969, p. 759

"The Stress Corrosion Resistance and Fatigue Crack Growth Rate of a High Strength Martensitic Stainless Steel AFC 77," D. Webster, Boeing Document No. D6-23973, 1969 (DDC Accession No. AD 695794)

"Stainless Steels Can Be Strong and Tough," D. Webster, Boeing Document No. D6-24379, 1969 (DDC Accession No. AD 695795); also Space/Aeronautics, Sept. 1969, p. 83

"Effect of Grain Refinement on Mechanical Properties of 4340M Steel," D. Webster, Boeing Document No. D6-25220, Feb. 1970

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NRL Report 7329

UNCLASSIFIED

ARPA Coupling Program on Stress-Corrosion Cracking

Final Technical Report: Second Edition

B. F. BROWN

*Physical Metallurgy Branch
Metallurgy Division*

Sponsored by

*Advanced Research Projects Agency
ARPA Order No. 878*

October 27, 1971



NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

The technical background, organization, and *modus operandi* of the ARPA coupling program on stress-corrosion cracking are summarized. The problem of interpreting the data from smooth stress-corrosion cracking specimens is discussed. This is followed by a summary of technical achievement highlights in narrative form treating specimen types, titanium alloys, high-strength steels, aluminum alloys, and surface sciences. An Abstracts of Achievements section (abstracts arranged by organization) is the most important part of this report, for it gives not only indications of technical contributions but also the literature citations where the interested reader can examine the detailed account of a given topical area. The Abstracts of Achievements section includes a subject index.

The program was one of multiple goals, including experimentation involving coupling NRL with academic personnel and amplifying NRL's capabilities by the addition of an industrial contractor. Since the present report is a purely technical one, it does not treat these non-technical goals. The present report represents an updating of NRL Report 7168 to include material published during the phase-out year of the program.

PROBLEM STATUS

This is a final technical report.

AUTHORIZATION

NRL Problem M04-08A
ARPA Order No. 878

Manuscript submitted July 19, 1971.

ARPA COUPLING PROGRAM ON STRESS-CORROSION CRACKING

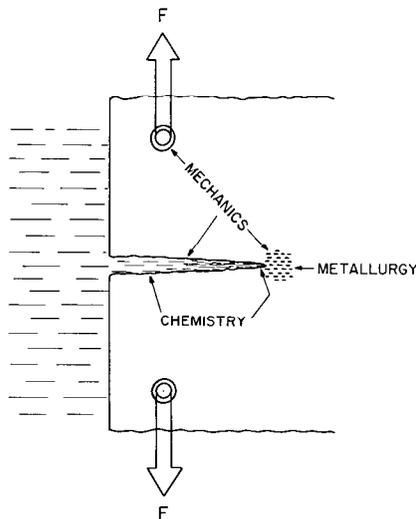
Final Technical Report

INTRODUCTION

History

By 1966 the phenomenon of SCC had affected all the military services (and NASA); had caused serious surprises to the designers of aircraft, submersibles, and rockets; and had involved all three major families of high strength structural alloys—titanium, steels, and aluminum. The Advanced Research Projects Agency (ARPA) of the Department of Defense recognized both the military importance of the problem and its technical complexity, compounding as it does the difficulties of the brittle fracture problem with chemical reactions occurring inside inaccessible cracks (Fig. 1). ARPA also was aware of new developments in surface physics and surface chemistry, some of which might be expected ultimately to afford advances in the science of metallic corrosion. ARPA therefore asked the Naval Research Laboratory to organize an intensive attack on the problem of the SCC of high-strength structural alloys with provision for coupling science to technology and also for coupling academic laboratories with an industrial laboratory and a government laboratory.

Fig. 1 - The three scientific elements of stress-corrosion cracking. Progress requires attention to all three.



Organization

The principal member institutions were NRL, The Boeing Company, Lehigh University, and Carnegie-Mellon University, to which was added Georgia Institute of Technology because of special capabilities in surface physics.

Two other universities had supplementary roles for special purposes: At a time when graduate students specializing in the electrochemistry of corrosion were almost

nil, both in the program and nationally, such students became enrolled at American University under well-qualified thesis supervision; hence, American University became a supplementary member of the program to ensure the involvement of at least a few electrochemistry graduate students, in this case studying the role of anions in corrosion reactions. At the University of Florida, Professor M. Pourbaix became available as a visiting professor and consultant to the program, and for this reason the University became a supplementary member, concentrating on experimental methods to apply Pourbaix' potential-pH method for analyzing the corrosion behavior of complex alloys (commencing with chromium steels).

There were no exclusive charters at any of the institutions, but in general the emphasis at Lehigh was on surface chemistry, that at Carnegie-Mellon was on physical metallurgy, and that at Georgia Tech was on surface physics. NRL contributed to both basic and applied research, and Boeing's role was to amplify the capabilities of NRL. Boeing and NRL filled an additional role by providing opportunities for graduate students to observe and/or participate in applied research in the course of their graduate careers.

SCC, which is caused by the conjoint action of a corrodent and a stress which may be constant, represents one of the limiting cases of corrosion fatigue (as R-1), which differs from SCC in that in corrosion fatigue the stress is necessarily fluctuating. For this reason corrosion fatigue in a limited sense was considered an appropriate subject to be included in the program, and particularly appropriate for a DoD program, since corrosion fatigue is said to be the major cause of failures in vehicles and in moving machinery. Analysis shows that there is no such thing as a simple method of generating the general engineering corrosion-fatigue characteristics of a given alloy, however, and accordingly from midprogram onward the corrosion-fatigue studies were restricted to academic research on mechanisms. Research on corrosion-fatigue mechanisms was also conducted at NRL with Navy funds but associated with the program.

The alloy families of interest were titanium, high-strength steels, and aluminum, and the relative emphasis on the three systems was set at 3:2:1. The reason for this relative emphasis was not alone the relative importance of the problem to DoD, but also the relative amount of accumulated knowledge in the three systems and the activity of producers on the problem in the area of their own products.

Modus Operandi

The program was conducted as a national one in the sense that it was fully integrated into the national technical community. Reports from the program were given unlimited distribution, and attendance at the quarterly meetings (described briefly below) was open to personnel from outside the program, subject only to the limitations of manageability. It was found that keeping the agenda of the quarterly meetings to a single narrow topic (e. g., titanium alloys) accomplished several ends: It permitted an in-depth review of the subject matter, it eased the problem of limiting outside participants, and it promoted interchange between persons working in different disciplines such as surface physics, electrochemistry, metallurgy, crystallography, and mechanics. The program profited immensely by the regular participation of outsiders.

The program was integrated into the national technological community in another manner, namely, by sharing costs. For example, in studies in which, to have technological significance, portions of large heats (batches) of alloys were required, these alloy heats were sometimes procured by other DoD interests, and the small amounts required for SCC studies were traded to the ARPA project in return for the stress-corrosion information generated. Mixed support of another type was practiced in which students whose stipends were paid from one source had the costs of their laboratory supplies and services paid by the ARPA program. These jointly supported activities

provided not only breadth of contact but also economies which in the case of large alloy heats were of important magnitude.

Also as part of the design of the program to serve the national technological community, personnel in the program were encouraged to present the output of their research at various types of technical meetings. The effectiveness of this policy is evident in the Presentations section of the Abstracts of Achievements.

Documentation

This report is primarily technical, but a brief background account is given here for the interested reader.

As another part of the final reporting sequence, there is in preparation a monograph on the state of the art of stress-corrosion cracking (SCC) of titanium alloys, high-strength steels, and aluminum alloys. That monograph is designed to be not only a summary of what has been contributed to the subject by the ARPA program, but a state-of-the-art summary without restriction as to source of contributions. The monograph will therefore be the most useful technical summary of the program for most purposes, for in it the pertinent output of the program is integrated into the entire literature on the subject.

The present report is limited to contributions from the ARPA program. Such contributions from a program as large and as productive as this one cannot be *detailed* in a manageable fashion in a single document such as the present report, but the key contributions are given herein in a consolidated narrative form. In addition, Abstracts of Achievements, modeled after the Interdisciplinary Laboratory reports, are given, together with references to the literature, so that the reader has a key directly to the technical literature of interest to him. The present report was written at the end of the program, and by the nature of the publication machinery of the technical societies many of the manuscripts generated by the program have not yet been printed. In such cases the journal or society is noted so that the interested reader can monitor the appropriate literature for the appearance of a paper of special interest. Requests for reprints should be directed to the individual authors. Qualified recipients may request from the Defense Documentation Center those reports for which accession numbers are given.

In the present report the author uses the term *stress-corrosion cracking* (SCC) to designate a cracking process caused by the conjoint action of a stress (which need not be fluctuating), and a corrodent. The term *corrosion fatigue* is used to designate a cracking process caused by the conjoint action of a fluctuating stress and a corrodent. The terms are thus based upon macrophenomenology rather than mechanisms, and the introduction of new terms such as *corrosion-assisted crack growth* and *subcritical cracking* becomes unnecessary.

The emphasis on reporting was to get contributions presented expeditiously at standard technical society meetings and published expeditiously in their journals, and the function of the quarterly reports was most importantly to notice the writing and the publication of such manuscripts in the standard literature.

THE PROBLEM OF THE MACROSCOPIC TEST

Regardless of how small the scale of events which may cause SCC, ultimately it is the macroscopic phenomenon which must be controlled. The traditional method for

characterizing SCC was to stress a specimen in a corrosive environment and report time to failure, usually meaning time for complete separation of the specimen. Although this parameter has afforded progress, particularly in the low-strength alloys, it is a defective parameter because it represents the undifferentiated *sum* of the effects of three processes, (a) incubation (usually film breakdown plus corrosion pitting), (b) SCC, and (c) terminal mechanical overload fracturing (Fig. 2). If an alloy is not susceptible to pitting, then a (smooth) specimen may give an indication of an infinite time to failure, i. e., the alloy may appear to be immune to SCC, whereas in fact it may be highly susceptible to stress-corrosion crack *propagation*. (Titanium alloys in water exemplify this behavior.) Alloys with different fracture toughness characteristics require different lengths of stress-corrosion cracks (and hence different exposure times) before the onset of overload fracturing; thus time-to-failure data could lead to grossly erroneous inferences regarding the relative SCC characteristics of these alloys. Some materials are so brittle that if they are stressed and a corrosion pit forms, the pit can initiate "brittle fracture," and an indication of high susceptibility to SCC might be inferred from a test in which in fact no SCC has occurred at all. (The 5% Cr die steel heat treated to maximum strength tends to behave in that fashion.)

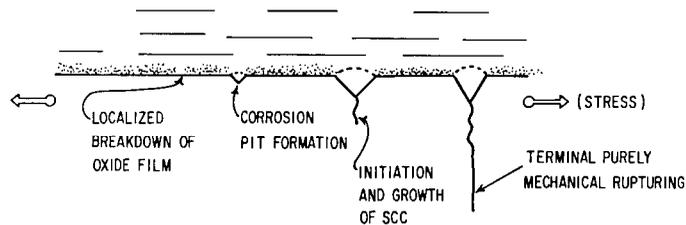


Fig. 2 - Sequence of events (left to right) by which a metal under stress with an originally smooth surface undergoes successively localized film breakdown, corrosion pitting, stress-corrosion cracking, and finally mechanical rupture

The foregoing complications are illustrated in Fig. 3, which is a plot of depth of pitting plus SCC plus mechanical fracturing on the ordinate vs time on the abscissa.

At the beginning of the program, the great bulk of data in the literature and most of that being inserted into the literature were of the undifferentiated time-to-failure type, and as has been shown above, this sort of data can be very misleading about stress-corrosion characteristics. One of the tasks of the program, therefore, was to establish the true SCC characteristics of the structural alloys of most current importance to military designers.

To do this characterization, as well as to conduct other studies both basic and applied, one or more specimen types were used containing pre-existing cracks. This tactic has three advantages: (a) It obviates waiting for a corrosion pit to grow, saving time. (b) It enables one to avoid an erroneous conclusion of immunity to SCC because of a nonpitting combination of alloy and environment. (c) It enables one to get a conservative evaluation by evaluating the material in the presence of the ultimate flaw, namely a sharp crack. There is a fourth advantage, for if the specimen meets certain criteria, the methods of fracture mechanics can be used to predict from the behavior observed in one geometry of specimen and crack what will happen in other geometries.

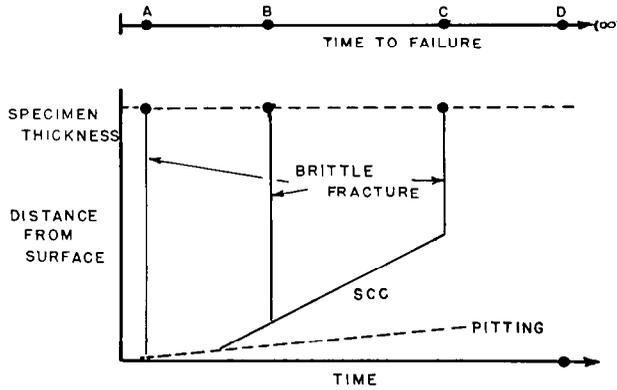


Fig. 3 - The time-to-failure information from stress-corrosion cracking tests of smooth specimens, as plotted in the line at the top, indicates an ascending order of merit with respect to stress-corrosion cracking from A through B and C to D. In point of fact, as shown schematically in the lower portion of the figure, B and C may have the same SCC characteristics but different fracture toughnesses. The SCC characteristics of A and D have not really been measured at all.

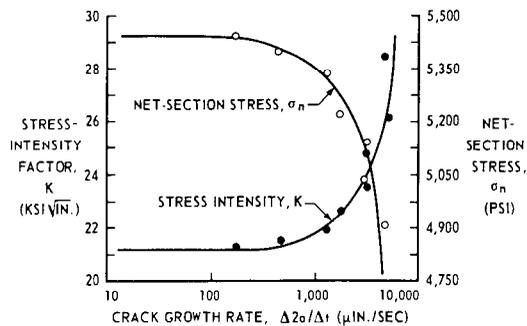
Fortunately for the program, the high level of activity in the fracture mechanics field during the decade preceding the program had produced technological information on various specimen geometries which become useful to the problem of SCC, as will be noted later in this report.

HIGHLIGHTS OF PROGRAM ACHIEVEMENTS

Specimens and Macroscopic Test Methods

During the course of the program the methods of fracture mechanics were demonstrated to afford predictability of stress-corrosion behavior from one geometry of specimen and stress configuration to another, whereas nominal stress was shown to be misleading (Fig. 4). The stress-intensity factor K thus was shown to be the most useful

Fig. 4 - Stress-corrosion cracking data for Ti-8Al-1Mo-1V in salt water. Specimen is stressed at the crack line and the crack growth rate is measured. (Chronologically the experiment proceeds from right to left in this figure.) Experiment shows that as K decreases (because of crack growth), the crack growth rate decreases, but meanwhile the nominal stress (net section stress) increases. This is an illustration of the inability of net section stress to correlate with cracking behavior. Extrapolation of data indicates a K_{ISCC} of about 21 $\text{ksi}\sqrt{\text{in.}}$.



way to quantify stress in the presence of a stress-corrosion crack. Evidence was found that for titanium alloys there is a threshold value of K below which SCC is not expected (for a given combination of alloy and corrodent), and this threshold was designated $K_{I_{SCC}}$. In the absence of positive knowledge that a true threshold exists, an arbitrarily defined $K_{I_{SCC}}$ (such as "nil crack growth in 1,000 hours") does indeed convey more information than an index of the patience of the experimenter or his skill with instrumentation; for at slightly higher K levels, one can make the positive statement that SCC will occur.

To fully characterize the SCC of a given alloy in a given K corrodent, one would like to have cracking kinetics as a function of K all the way from a threshold ($K_{I_{SCC}}$) if one exists to K_{I_C} , the stress intensity at which brittle fracture occurs. Even if one has only the value $K_{I_{SCC}}$, and even though in a given system this may not be known to be a true threshold but may represent, for example, the minimum K at which SCC is observed in 1,000 hours, the $K_{I_{SCC}}$ numbers can be plotted as a function of yield strength to produce an interesting analysis of the relative merits of various compositions or heat treatments in a given alloy family. In such a plot (Fig. 5), one can simplify the Irwin equation for a surface crack by assuming yield-strength stresses, and assuming that any surface flaw will be long compared with its depth and will lie perpendicular to the stress field, he can then draw a series of straight lines as shown in Fig. 5. Any one of these represents conditions for a given flaw depth, and the line simply means that if one may have a given flaw size as represented by the line, he must have a material with a $K_{I_{SCC}}$ lying above that line to avoid SCC.

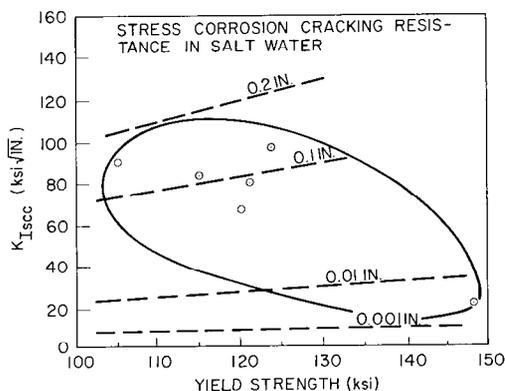


Fig. 5 - $K_{I_{SCC}}$ data in salt water for six commercial heats of Ti-6Al-4V rolled to plates 1-in. thick. All $K_{I_{SCC}}$ data for commercial heats of this alloy have been found to lie within the oval. The broken lines indicate $K_{I_{SCC}}$ values which an alloy must have (or exceed) in order to avoid SCC initiating at a long flaw of the depth shown on the line, assuming yield stresses. (Data show that no commercial alloy can tolerate a flaw as deep as 0.2 in. if the operative stress equals the yield strength.) The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

$K_{I_{SCC}}$ can be determined by a number of specimens, some set at K levels above and others below the $K_{I_{SCC}}$ level. The program showed that there are alternative ways to determine a threshold. For example, one can use the "wedge-loaded" (crack-line-loaded) sheet tensile specimen and await arrest of the stress-corrosion crack, or one can use a load-relaxing system such as an elastic ring to stress a specimen which experiences relaxation as the stress-corrosion crack advances (Fig. 6). It was shown elsewhere during the program that a specimen similar to the one of Fig. 6 can be self-stressed with a bolt and used as a stress-corrosion specimen. During the program the specimen of Fig. 6, self-stressed with a bolt instead of the elastic ring, has been shown to be extremely useful for characterizing the SCC behavior of high-strength aluminum alloys by determining the rate of crack growth as a function of K (Figs. 7, 8). Such a test has been found far more rapid and more discriminating than the traditional methods.

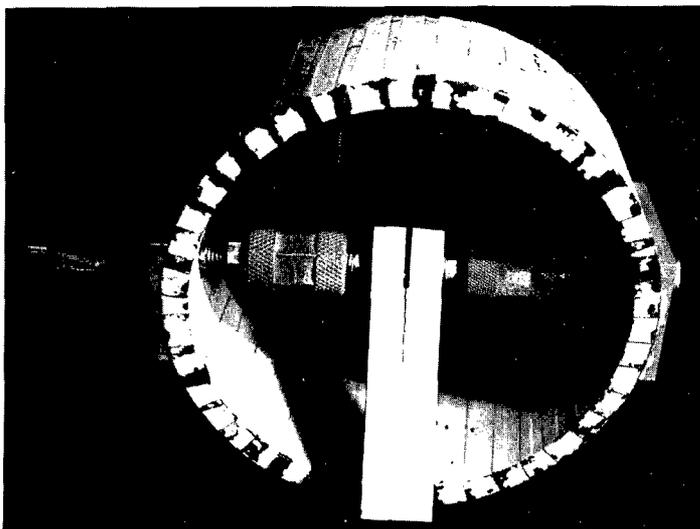


Fig. 6 - DCB aluminum alloy specimen ($1 \times 1 \times 3.5$ in.) stressed by an elastic ring which relaxes as the crack propagates. (Ring is made of high-strength steel wrapped with tape to prevent stress-corrosion cracking.) Load on ring is monitored by strain gage (not shown).

Since K has been shown to be the proper way to quantify stress around a stress-corrosion crack, and since SCC kinetics have been found to be K -dependent, specimens having the property of constant- K conditions regardless of crack length would be of obvious interest. Two such constant- K specimens were studied in the program. One of these, designated the tapered, double-cantilever beam (DCB) specimen, has given experimenters problems with the arms breaking off, and that was found to be true using the specimen for SCC, even though the experimenters were expert with that particular specimen. It was found possible, however, in using this specimen at a number of K levels, to extrapolate the crack rate to zero, which was found to correspond to K_{Isc} for the same steel as determined by a beam specimen. The other constant- K specimen, sometimes designated the double-torsion specimen and sometimes the Outwater specimen (after its inventor), is of additional interest because of its simplicity—it can be satisfactorily prepared from a sheet of metal using a bandsaw. For constant- K conditions the specimen can be satisfactorily stressed by a dead-weight-lever system, and it appears to be well behaved in stress-corrosion tests, at least for high-strength steel.

A small inexpensive self-stressed specimen was developed for possible use as a quality-control specimen for sheet materials.

The newcomer seeing all the various specimens for measuring SCC characteristics might reasonably ask which one he ought to use. It might be helpful to the metallurgist or engineer to regard this selection question somewhat like the question of which *hardness* test one should use. In both cases the answer to the question depends partly on the geometry of the material of interest and partly on the answer one ultimately gets.

Titanium

The resistance to SCC of all the commercial titanium alloys and many developmental and research alloys has been determined using precracked specimens. Electrochemical

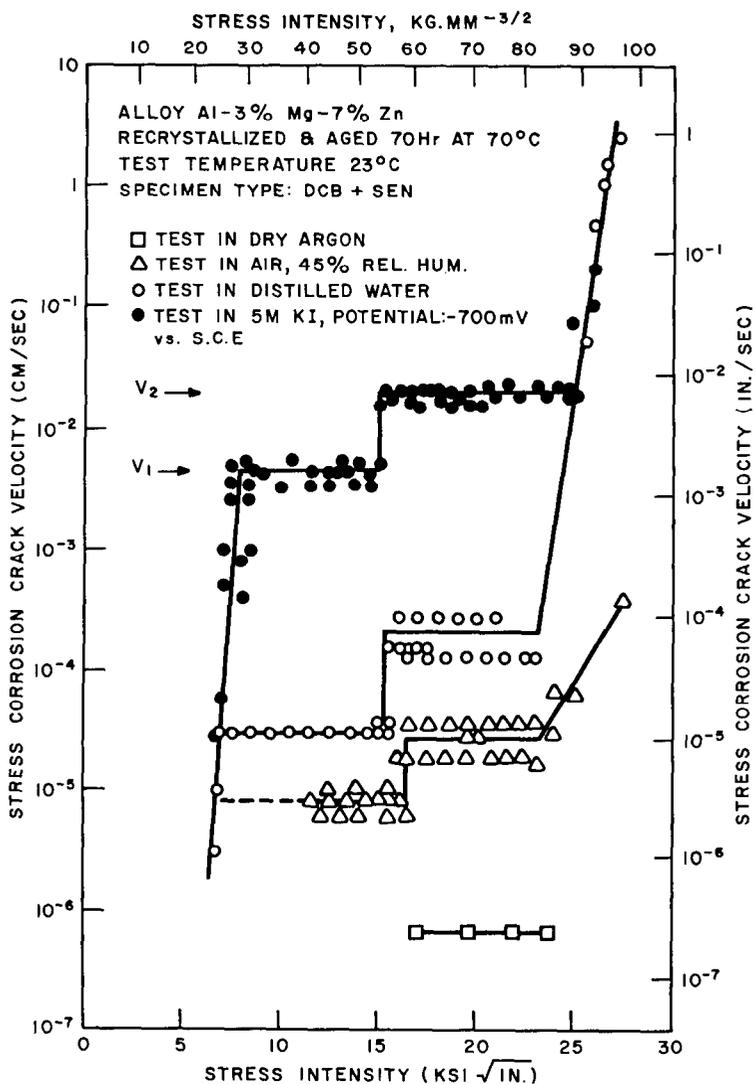


Fig. 7 - Crack-growth rate as a function of K for an aluminum alloy in several environments, illustrating the three stages of the V-K behavior

evidence was interpreted to indicate that for titanium alloys in salt water there is a genuine stress-intensity threshold below which stress-corrosion cracks do not propagate.

The resistance to SCC was found to be strongly dependent upon microstructure and dislocation substructure (Fig. 9). Alpha and alpha-beta alloys that exhibited planar slip in the alpha phase had low resistance to SCC. Beta grains in alpha-beta alloys tended to act as obstructions to the SCC fractures in the alpha phase, but with complications noted below (Fig. 10).

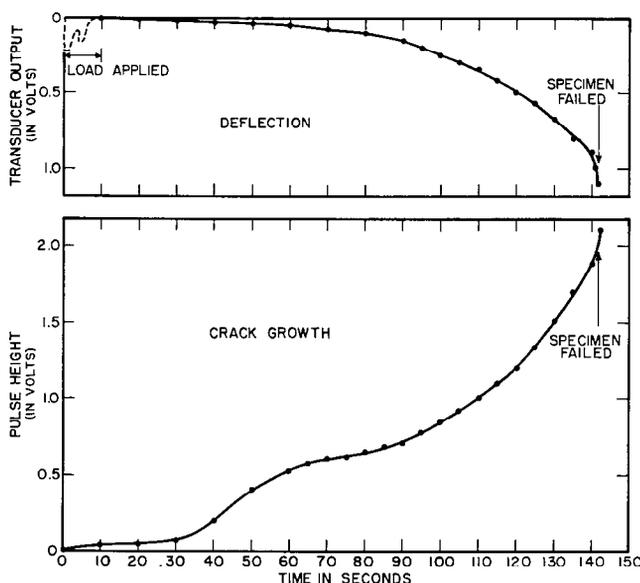


Fig. 8 - Crack-growth rate measurement continues to challenge the experimentalist. An alternative to the clip-gage technique is to monitor the reflection from an ultrasonic pulse (data shown above for a dead-weight-loaded, cantilever-bend specimen of titanium alloy).

Planar slip was found to be characteristic of alloys containing

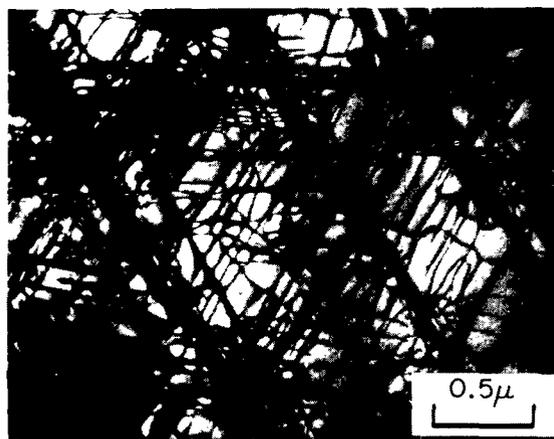
- High oxygen, or
- Aluminum in excess of about 6%, or
- Aluminum in excess of about 5% and tin content of 2.5% or more.

The formation of ordered domains of Ti_3Al or $Ti_3(Al, Sn)$ in the alpha phase further restricted slip and decreased SCC resistance.

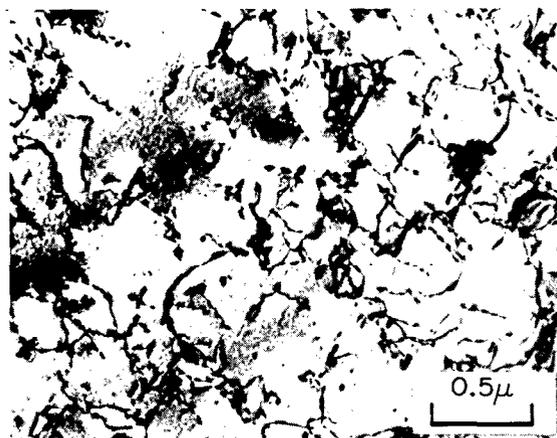
In an alpha-beta alloy, increasing the proportion of beta by increasing the amount of alloying elements such as Mo or V increased SCC resistance, perhaps by the crack-obstructing mechanism mentioned above (Fig. 11). But decomposition of the beta phase (to form omega, Ti_2Cu , or Ti_5Si_3) may embrittle the alloy and markedly lower its SCC resistance.

Of the common commercial alloys, Ti-8Al-1Mo-1V was found to be the least resistant to SCC, Ti-4Al-3Mo-1V was found to be highly resistant, and Ti-6Al-4V was found to have intermediate resistance. These observations were again observed to be correlative to the type of dislocation substructure.

In the all-beta alloy Ti-13V-11Cr-3Al, SCC fractures were observed to occur on or near the (001) plane. The crystallography of twinning of another all-beta alloy (Ti-11.5Mo-6Zr-5Sn) was found to be different from that of most other bcc metals. Mechanical fracture occurs macroscopically parallel to (001), but microscopically the fracture mechanism is not cleavage but microvoid coalescence. Unfortunately, aging this alloy to optimum strength (153 ksi yield) and toughness ($K_{Ic} = 66 \text{ ksi} \sqrt{\text{in.}}$) produced minimum resistance to SCC in halide solutions. The SCC fracture path in this alloy is intercrystalline, in contrast to the transcrystalline fracture path seen in most titanium



(a)



(b)

Fig. 9 - Coplanar dislocation arrays (above, associated with SCC-prone titanium alloys) and tangled dislocations (below, associated with SCC-resistant alloys)

alloys. The formation of omega phase during aging was observed to be an important factor reducing the ductility of the aged alloy; this phase is distributed as small particles (100 to 1,000 Å), but even so may constitute a high volume fraction of the alloy.

The SCC fractures in the alpha phase of alloys lie $15^\circ \pm 2^\circ$ from the basal plane of the hexagonal lattice. This relatively good consistency in crystallographic habit plane has led the resulting flat fracture facets to be termed cleavage (Figs. 12 & 13). The entire SCC fracture surface, however, is not cleavage, but cleavage areas are interspersed with rupture dimples (microvoids) which resemble the dimples of a purely mechanical fracture (Fig. 14). Thus, a stress-corrosion crack appears to be formed by two mechanisms, one (cleavage) involving stress plus an environmental reaction, and the other (dimples) wholly or largely of mechanical origin. The proportion of the dimple areas increases as K increases from $K_{I_{SCC}}$ to K_{I_C} , at which stress intensity the remaining ligament separates entirely by dimple rupture.

Methanol and several other organic fluid environments, including hydrocarbons, were observed to cause the SCC of titanium alloys. Carbon tetrachloride also caused

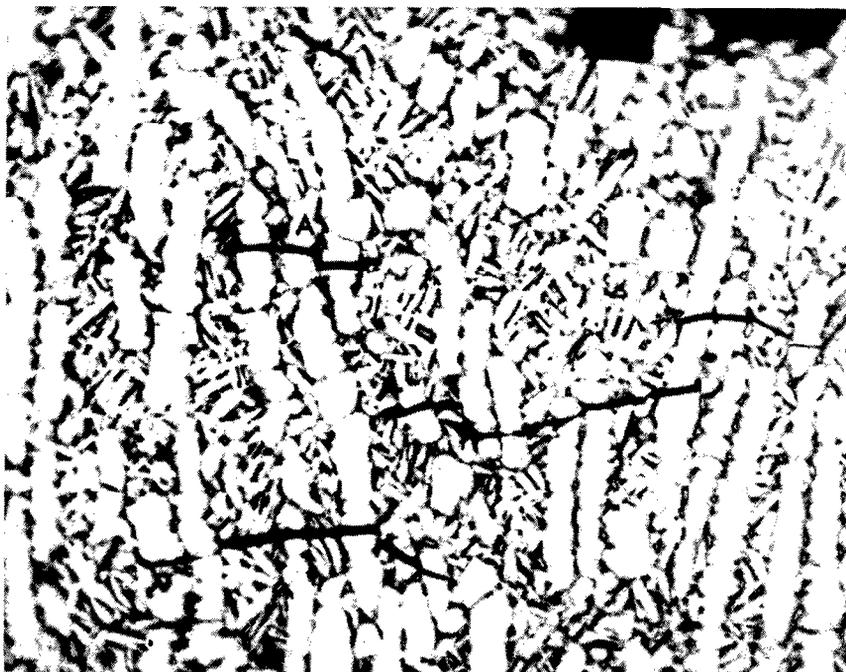
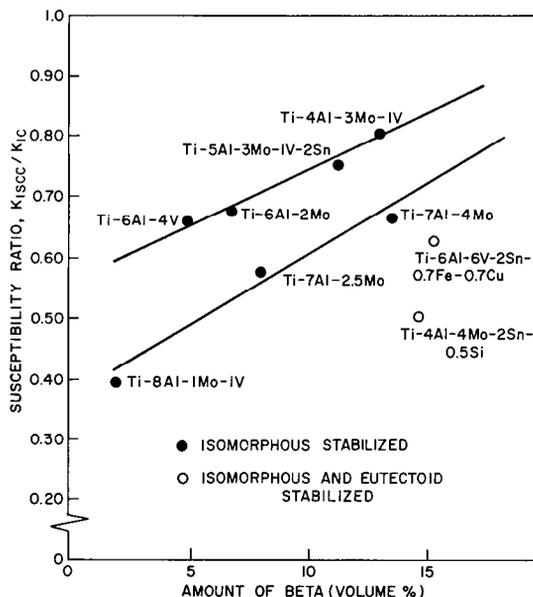


Fig. 10 - Partial stress-corrosion cracks in alpha-beta titanium alloy showing cracks in the alpha phase arrested by the beta phase. 1,000X magnification.

Fig. 11 - Increasing proportion of beta in alpha-beta titanium alloys tends to increase the ratio K_{Isc}/K_{Ic}



severe cracking. These findings have practical implications in the selection of paints and of cleaning and degreasing fluids. Except for liquid metals, carbon tetrachloride is the only environment not containing hydrogen (assuming the CCl_4 was free from HCl), which cracks titanium.



Fig. 12 - Fractograph showing cleavage surface typical of stress-corrosion cracking in titanium alloys in water at a low K level. 6,000X magnification.

Slow crack propagation was observed in titanium alloys in the absence of atmospheric moisture and also in a hard vacuum somewhat better than 10^{-7} torr. In these specimens as in those cracked in organics and in aqueous liquids, the fracture was cleavage interspersed with dimples. Heat treatment which reduced the hydrogen content of the titanium reduced its tendency to slow crack growth in vacuum (Fig. 15).

Methods were developed and applied to elucidate the nature of the corrodent near the advancing crack tip. With neutral salt water as the corrodent, the pH at the advancing crack tip was highly acid (about 1.6). The pH and the potential place the crack tip in a thermodynamic regime in which the hydride may be stable, but not an equilibrium oxide. The addition of FeCl_3 to the salt water increased the SCC resistance of the titanium, perhaps by substituting the reduction of copper for the reduction of hydrogen as the cathodic reaction.

One model which has been proposed for SCC of titanium, in accord with the observations noted above, is the hydrogen model. The reaction of a clean titanium surface with any of the hydrogen-bearing environments studied would release hydrogen which would be expected to react with or dissolve in the titanium. In aqueous salt solutions, the pH at the growing crack tip remains sufficiently acid (because of the occluding action of the SCC path) that repassivation is not possible at the crack tip, which continuously provides clean surfaces for reaction to remove more hydrogen from the corrodent. Thus the function of the precrack in specimens tested in salt water is to provide a little local straining plus the restriction to diffusion which will permit the acidity to remain high locally, whereas smooth specimens tested in salt water would repassivate because of the inability of the geometry to keep the acidity high locally. In methanol, however, the situation is different because the product of the reaction of titanium and methanol is soluble in methanol, i. e., the reaction product does not form a protective film in the

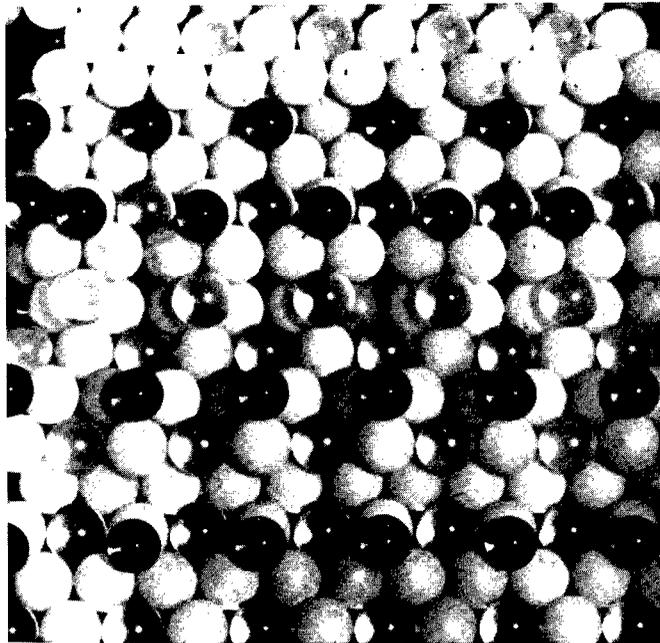


Fig. 13 - Ball model of simulated SCC fracture surface in Ti-Al alloy. Aluminum atoms on base surface are designated by clear balls and on the matching plane by dark balls. The fracture plane occurs where there is the highest concentration of Ti-Al bonds in ordered alpha.

bulk environment. This has been concluded to be the reason *smooth* specimens will initiate SCC in methanol.

Straining Ti-Al alloys in salt water was observed to cause large increases of the active range during anodic polarization, and this too is consistent with the picture of reactions occurring near the crack tip. A computer program has been developed for solving the complex electrochemical transport equations involved in SCC. The aspect ratio was found to dominate all else.

Ti-Al alloys were found to show the same precipitation of hydride at coplanar dislocations in SCC specimens as in slow strain-rate hydrogen-embrittlement specimens, again suggesting the hydrogen model.

Acceptance of the hydrogen model would require a resolution of two apparent anomalies: a) the observation of SCC in reasonably pure CCl_4 (containing traces of water), and b) the observation that increasing $[\text{Cl}^-]$ increases SCC crack-growth rates at a given K level.

Steels

The SCC characteristics of a large number of commercial and near-commercial steels were determined using salt water and natural seawater (Fig. 16). The use of pre-cracked specimens to determine SCC characteristics of alloy steels in seawater can save half a year to a year, which otherwise may be required to generate the pits which in turn initiate SCC. (A precracked specimen may, however, give erroneous data if it is



Fig. 14 - Fractograph showing flat cleavage areas plus dimpled (mechanical rupture) areas typical of SCC in titanium alloys in water at a K level much higher than that of Fig. 12

stressed to a high level before being placed in an SCC test at a lower stress level.) From the data of Fig. 16 it is apparent that the maraging steels and at least some of the precipitation-hardening steels were clearly superior to the conventional martensitic steels at the same strength level.

The following observations were made on low-alloy martensitic steels: Silicon content had no effect on $K_{I_{SCC}}$, but above about 1.5% the increased silicon greatly retarded the cracking kinetics at a given K level. Reducing the grain size also decreased the cracking kinetics, but did not affect $K_{I_{SCC}}$. Increasing the manganese or carbon content caused markedly reduced $K_{I_{SCC}}$ values (Figs. 17, 18). None of the following metallic alloying elements was observed to have a significant effect on $K_{I_{SCC}}$: nickel, cobalt, chromium, and molybdenum.

Fig. 15 - Effect of hydrogen content (varied by vacuum treatment) on fracturing of a commercial titanium alloy in various modes. The line designated K_{IH} represents the stress intensity above which a crack propagates in an inert environment, presumably due to internal hydrogen.

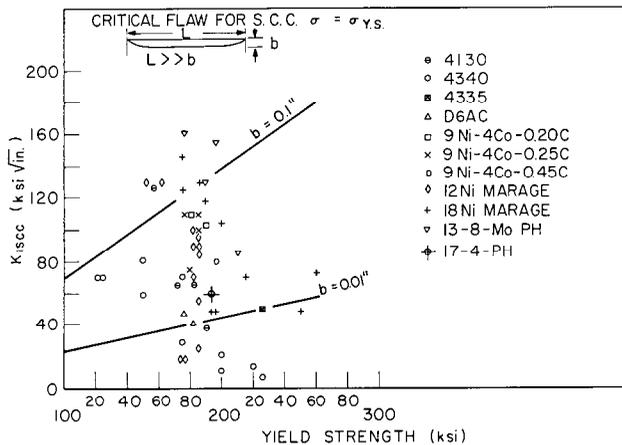
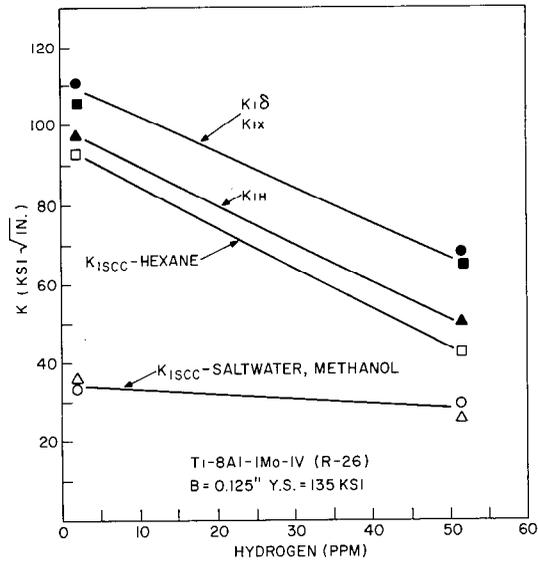


Fig. 16 - $K_{I SCC}$ data in salt water for a number of commercial alloy steels made in production-size heats. The strength range covers strengths of interest to deep-diving submersibles, rockets, and manned aircraft. Flaws of the depth shown in a given steel would propagate stress-corrosion cracks at yield-strength stress unless the $K_{I SCC}$ of that steel lies above the line. The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

The purity of maraging steels with respect to sulfur and phosphorus was not found to have an important effect on SCC characteristics. The same was observed in low-alloy martensitic steels of the 4340 type.

Among the maraging steels, thermal history appears to have an effect above and beyond its effect on strength. Underaging the 350-grade maraging steel was found to be bad for SCC, whereas overaging was helpful. Overaging of 18%-Ni maraging steel

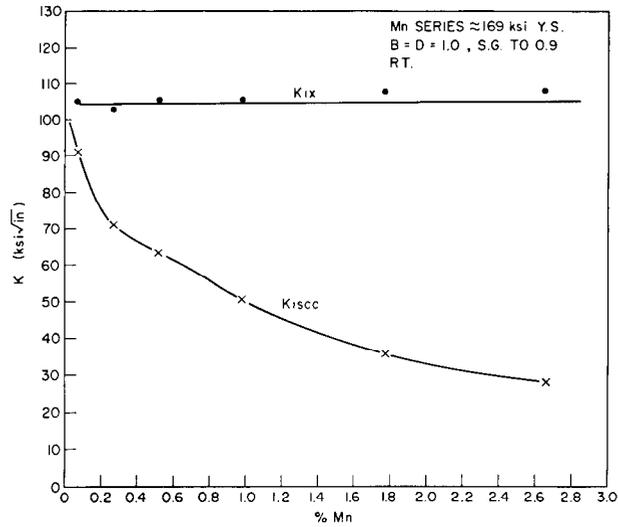


Fig. 17 - Effect of manganese content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

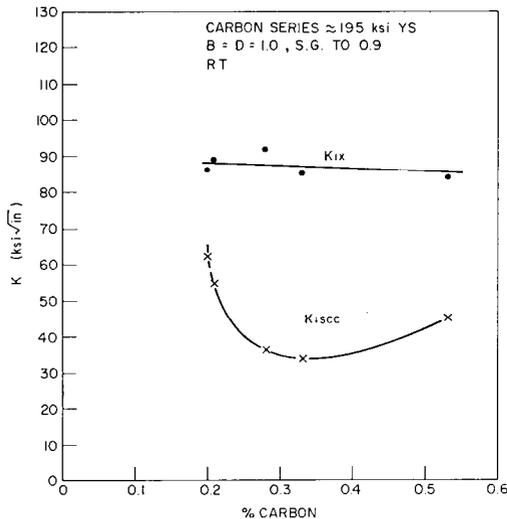


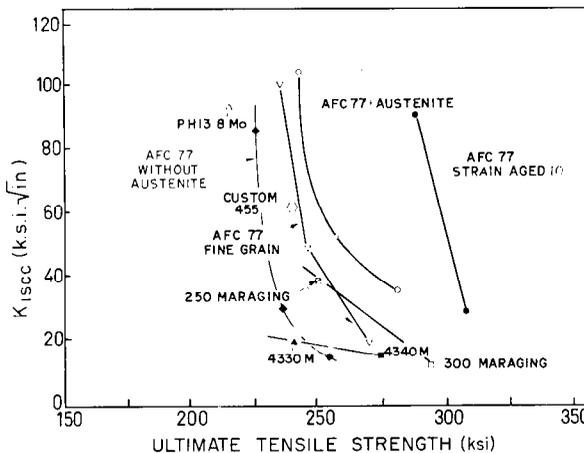
Fig. 18 - Effect of carbon content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

produces reverted austenite, the primary site for which appears to be the compound $Ni_3 Mo$.

$K_{I_{SCC}}$ has a complex curvilinear dependence on strength level, but for a given martensitic steel in the 175- to 185-ksi yield-strength range, a 7% increase in yield strength (by differences in tempering treatment) caused a 20% loss in $K_{I_{SCC}}$, which is linearly proportional to the load-carrying capability of a component containing a standard flaw. The program demonstrated, however, that strengthening by strain aging (in a precipitation-hardening steel) entails a smaller penalty in SCC than the strengthening of martensitic steel by choosing the tempering temperatures, thus providing a possibly useful avenue for further advances for special needs (Fig. 19).

Stress-corrosion cracks are commonly thought to be characteristically multiply branched, because SCC was first observed in cold-worked products, which have complex

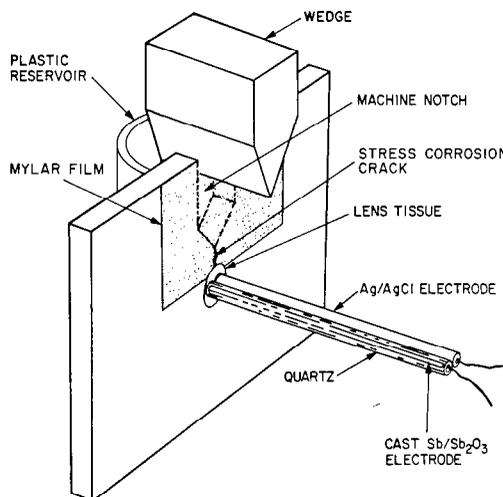
Fig. 19 - K_{Isc} for several commercial steels and one developmental steel (AFC 77) in salt water. Note, for AFC 77 in any given condition, the rapid decrease in K_{Isc} with rising ultimate tensile strength. Note also that by increasing the strength by strain aging, the strength can be increased over that of regular AFC 77 by more than 50 ksi while maintaining the same K_{Isc} .



residual stress patterns that change continuously as the article cracks. In the present program it has been found with many materials that the crack-growth rate rises sharply with increasing K until a point (K_{In}) of apparent process saturation is reached, beyond which the rate is more or less independent of K . If the material is reasonably isotropic, then at a K level of about $2K_{In}$ the crack will tend to divide or branch. This finding is useful in understanding tests in which the crack divides and thereby terminates the utility of the experiment.

During the course of the program, methods were developed which for the first time were successful in measuring the pH near the tips of growing stress-corrosion cracks in steel (Fig. 20). These methods employed successively color-change pH indicators,

Fig. 20 - One method for determining the pH at the tip of a stress-corrosion crack. The potential and pH probes rest against a small paper disk (thin to minimize the solution required to moisten it), and are connected to high-resistance recorders. They do not register a reading until the crack propagates to the disk and moistens it. (The disk does not contain solutes which affect pH.) A glass electrode designed for surface measurements can be used in place of the antimony oxide electrode.



the antimony electrode, and finally the glass electrode, and all three methods gave the same result. This work on crack-tip chemistry gave new insight on SCC (and eventually on most forms of localized corrosion, as will be discussed in a later section). It was found that regardless of the pH of the bulk solution (external to the crack) or the potential impressed upon the steel, the combination of potential and pH at the crack tip are such as to be favorable for the reduction of hydrogen (Fig. 21). This finding makes it unnecessary to postulate any mechanism for SCC in (high-strength) steel other than that commonly termed *hydrogen embrittlement*. The mechanism of hydrogen embrittlement has

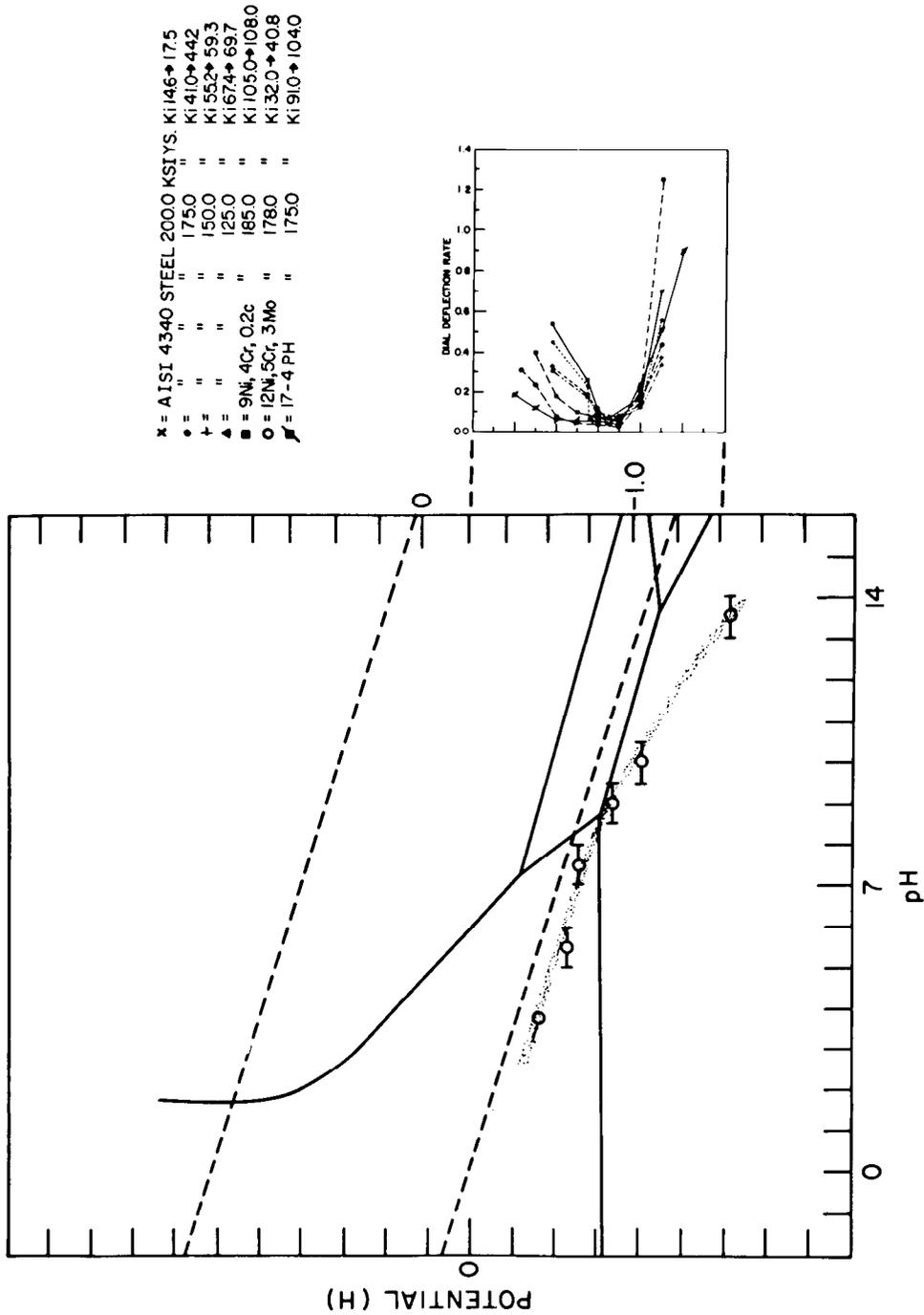


Fig. 21 - pH at the tips of growing cracks in neutral 3.5% NaCl solution, specimens potentiostatted to various levels. Curves at right indicate a function of crack-growth rate (dial deflection rate) at approximately constant K for a given steel (but different K's for different steels). These data were taken by color-change pH indicator technique but have since been confirmed by the glass electrode. Stress-corrosion cracking in steels occurs only under conditions of local pH and potential which place the crack tip under the hydrogen reduction line (lower sloping broken line).

been postulated to involve the formation of an iron hydride, thought to have been prepared and partially characterized, but work during the program has shown that the alleged iron hydride (prepared by a Grignard method) was really an organic compound of iron.

The work on crack-tip chemistry forms the basis for postulating a new role for either a corrosion pit or a pre-existing crack in initiating SCC: Formerly the pit and crack were viewed as stress concentrators, but it is now concluded that their *essential* role is to produce the local acidity which helps establish the conditions for hydrogen reduction. In the corrosion pit the acidity caused by hydrolytic reactions is retained locally by the porous cap of corrosion products, and in the stress-corrosion crack the local acidity is retained because of the long narrow diffusion path between the crack tip and the external corrodent. These observations are consistent with current findings in the program on the nature of pitting of Fe-Cr alloys (Fig. 22).

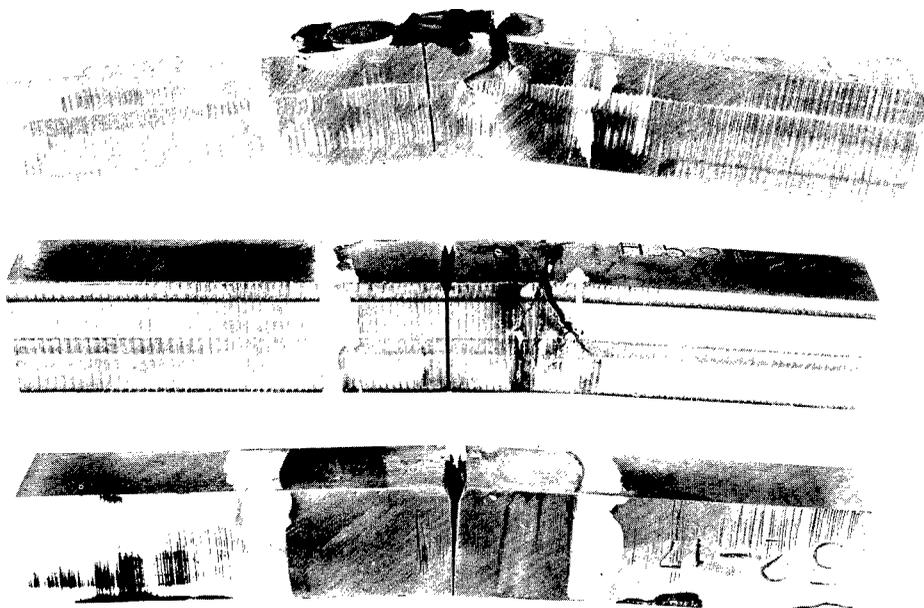


Fig. 22 - Three specimens of a 13-8Mo precipitation-hardening steel whose stress-corrosion cracking characteristics, at first puzzling, become comprehensible in the light of the experiment of Fig. 21. The lower specimen, stressed at a high K , commenced cracking at the notch. At a lower K (center specimen) there was no cracking at the notch but, after a delay of 1300 hours, there was rapid cracking under the wall of the corrodent cell. This was attributed to lowering of pH in the crevice under the wall by crevice corrosion so as to cross the hydrogen reduction curve. The upper specimen also cracked immediately at an unnotched area on which a crystal of ferric chloride had been laid to lower the pH locally.

The acidity role of the corrosion pit suggested that inhibitors and buffers which prevent the formation of the corrosion pit would be effective in preventing SCC of a smooth specimen, and this inference was confirmed experimentally. A specimen containing a precrack, however, responds only to a limited degree to inhibitors and buffers: K_{Isc} cannot be raised to K_{Ic} by such additives, doubtless because not enough of such additives are present inside the crack at the crack tip to fully control the local pH.

Cathodic protection can readily effect changes in pH deep within growing stress-corrosion cracks (contrary to a commonly held rule of cathodic protection technology to the effect that cathodic protection cannot function deeper down a crack than about eight times the crack opening dimension). [Partly because of the foregoing discrepancy, an NRL study in another program showed that the factor of 8 cited above was too pessimistic by at least a factor of 10^3 .] Cathodic protection has not appeared to be a solution to the problem of SCC in high-strength steel because, although the local hydrolytic acidification can be prevented by cathodic polarization, the conditions are still met for hydrogen evolution and cracking does continue to occur. The rate of stress-corrosion crack growth is highly dependent on potential and goes through a minimum at about -0.85 to -0.9 V (SCE) for all alloy steels which have been studied; this minimum in kinetics corresponds approximately to the potential at which iron becomes thermodynamically stable in water, suggesting that the reason for the minimum may be caused by the transfer of the anodic reaction from within the crack (when electropositive to the minimum) to outside the crack (when electronegative to the minimum). As a practical application of this information, one should be able to achieve approximately the minimum in cracking kinetics by plating with cadmium.

If one studies the details on the fracture surfaces using high-resolution replication electron fractography, one finds that regardless of potential, the fracture surface is one of smooth facets (prior austenite grain boundaries) upon which are superimposed plastic tear ridges. The tear ridges increase in number with increasing stress intensity K , until at K_{Ic} the fracture is totally tear ridges surrounding craters (purely mechanical microvoid coalescence, or dimple rupture, fracture). This identical nature of fracture details regardless of which side of the potential minimum one is on is consistent with the conclusion that only one model (hydrogen cracking) is required to account for SCC in high-strength steels.

Consistent with the hydrogen model of SCC in steels, the presence of sulfide in the corrodent (which would tend to promote the entry of hydrogen into the steel) has a strikingly adverse effect on SCC.

One can change the oxide film on the exterior of the specimen from one which is conductive (Fe_3O_4) to one which is poorly conductive ($MnFe_2O_4$), but this change does not appear to have any significant effect on SCC behavior.

The crack tip chemistry studies on *steels* in salt water or in ordinary distilled water showed that the corrodent is concentrated with respect to iron. Thus the newly formed crack surfaces do not behave like pure iron in superpure water, in which environment the iron has been shown to be as inert as platinum.

Large changes in pH locally compared with that of the bulk environment are characteristic of the corrodent in stress-corrosion cracks in all alloy families studied (Fig. 23).

One practical *caveat* appears to be provided by the finding that the behavior of pre-cracked specimens of the stainless steel designated 17-4 PH in (nearly neutral) salt water does not correlate with the poor resistance of this alloy to SCC in service. A possible explanation for this apparent discrepancy is that in service, localized hydrolytic reactions (in crevices, for example) may provide such high local acidity as to create a fundamentally different environment, perhaps also contaminated with sulfur compounds, with a different (and lower) K_{Isc} from that measured in neutral salt water.

Aluminum

The work on aluminum alloys in this program, although by design receiving the least emphasis of the three alloy families, became particularly productive in the more

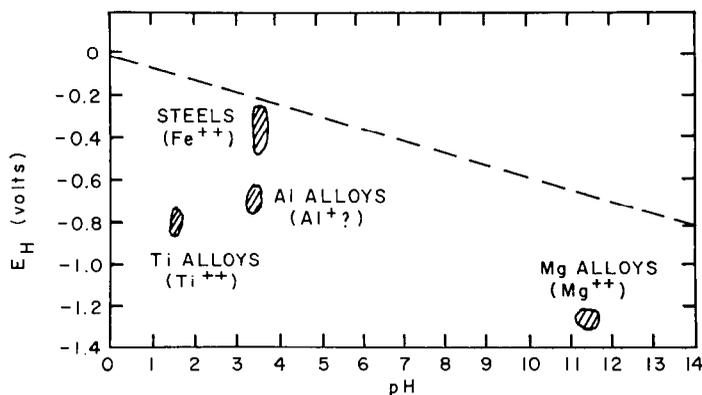


Fig. 23 - Potential and pH data for the tips of growing stress-corrosion cracks in four alloy systems in nearly neutral salt water. Data taken by color-change pH indicator paper technique. Illustrates the large differences between pH of the bulk solution and that at the occluded reaction site. (Hydrogen can be reduced from water below the broken line.)

practical aspects of the problem because of the adoption of the precracked specimen technique (Fig. 24). Wrought products of the Al-Zn-Mg group of alloys which have strengths of special interest to the DoD are highly textured, and SCC is a problem primarily only parallel to this texture. Ordinary bent-beam or tensile specimens cannot be cut in such a fashion as to test this maximum vulnerability direction unless either the plate is very thick or extensions can be welded or otherwise firmly attached to the plate material, which has never been an attractive approach.

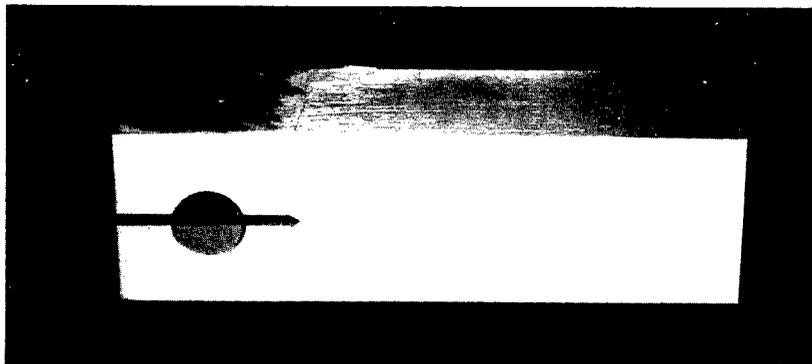


Fig. 24 - Aluminum specimen of Fig. 6 self-stressed (after the method of Novak and Rolfe) by a setscrew. Dark region is paraffin used to insulate the steel setscrew from the crack area. A stress-corrosion crack is seen emanating from the machined notch. This type of specimen was used for most of the characterization data on aluminum alloys in the program.

Early work with the specimen of Fig. 6 suggested that there was a stress intensity below which SCC stopped, but later work has indicated that, although the rate of crack growth diminishes with decreasing K at low levels of K , there does not appear to be any true threshold below which the cracking absolutely stops. Events have shown that the

best way to characterize the SCC behavior of a given alloy is to report the kinetics of crack growth as a function of K, which will be referred to here as V-K characterization.

A contribution from outside the program has been highly beneficial in using the DCB specimen of Fig. 6. This contribution was the demonstration that one could use a bolt to spread apart the two arms of the DCB specimen to stress it without the need for the proving ring, and that stressing in such fashion still permitted quantification of the stress intensity at the root of the crack. This specimen can then be described as a self-stressed DCB specimen, and it has become a most productive research tool, with demonstrated usefulness for sheet material at least as thin as 0.05 in. Among its other advantages, the self-stressed specimen has that of being suitable for wide distribution for readily assessing, say, the effect on SCC of the environment of an airport runway, or of a deep-diving submersible, or of a noxious chemical.

V-K studies have been completed on a large number of commercial and experimental alloys in various tempers (Fig. 25). These studies have shown that at low values of K, log V rises rapidly and linearly with increasing K (Stage I) until a saturation level (Stage II) is reached, after which V is nearly independent of K. In some alloys there is a third stage, near K_{Ic} , in which V is again dependent upon K. Curves of $K \log V$ yield

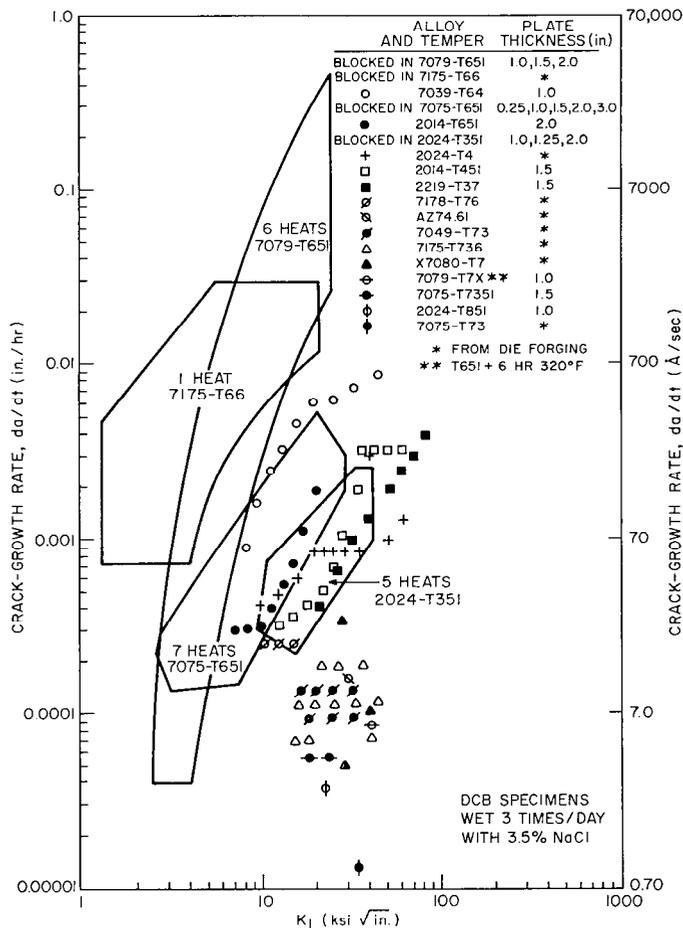


Fig. 25 - Comparison of several commercial and experimental aluminum alloys using the self-stressed DCB specimen and the crack-growth rate method

rangings which agree with established rankings using smooth specimens with two differences: The K-log V rankings are enormously more rapidly obtained, and they are more discriminating than the smooth-specimen rankings when applied to alloys having approximately the same SCC characteristics.

The DCB specimens demonstrated in a very graphic way the magnitude of the effect which quenching stresses can produce in the SCC of aluminum alloys.

The evidence to date is that in Stages I and III the rate of crack growth is little influenced by halide-ion concentration, but the velocity of Stage II apparently can be strongly affected by anion concentration.

Commercial alloys do not experience SCC except when water is present, and only the anions Cl^- , Br^- , and I^- accelerate V (in Stage II) appreciably.

New information was developed on the effects of microstructure on SCC (Fig. 26). It was shown, for example, that the microstructure controlled the cracking process through its effect on the deformation process: Specimens which were strengthened by large Guinier-Preston (G-P) zones exhibited coarse slip characteristics and proved to crack readily, while specimens hardened by small G-P zones exhibited fine slip and cracked slowly. Work on bicrystals revealed that when slip could be transferred across the grain boundary, cracking was slow, but when slip transfer was impeded by the boundary, cracking was rapid.

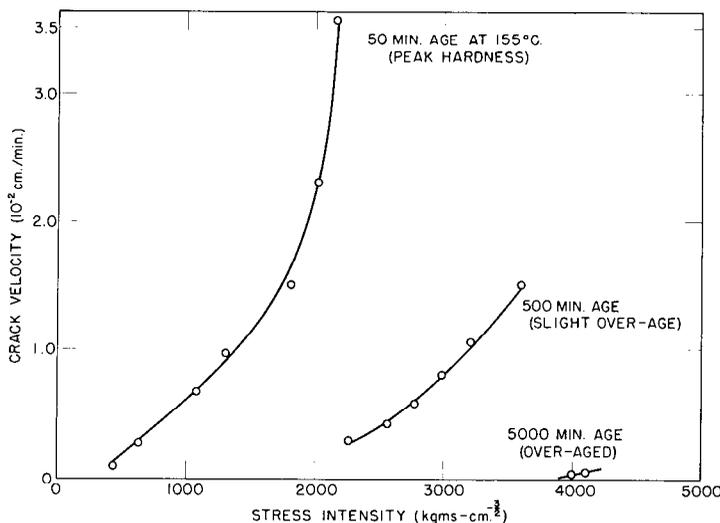


Fig. 26 - Effect of heat treatment on the stress-corrosion cracking kinetics of Al-15%Zn. Transmission electron microscopy shows that the increasing aging time at 155°C causes a progressive decrease in the volume fraction of Guinier-Preston zones.

Neither the presence nor the width of the precipitate-free zone was observed to have any effect on the stress-corrosion susceptibility of a ternary Al-Zn-Mg alloy (Fig. 27). This finding has been explained in terms of slip-band behavior.

Methods have been developed to measure the pH at the tips of growing cracks using both color-change pH indicators and the glass electrode, and in the case of 7000-series

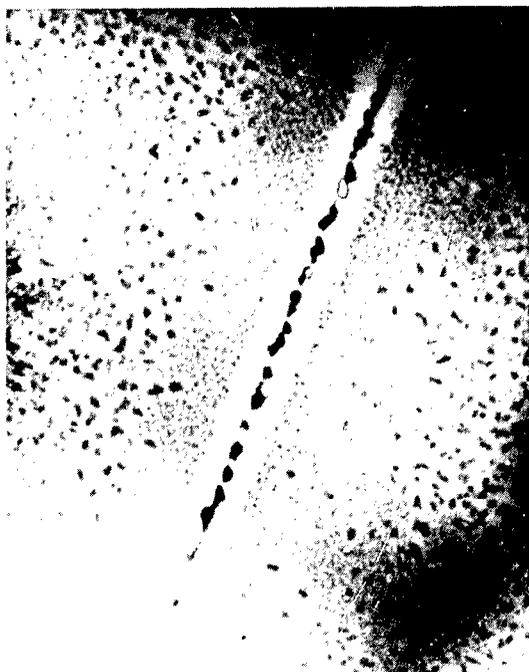


Fig. 27 - The precipitate-free zone adjoining a grain boundary in an Al-6.8% Zn-2.3% Mg alloy. There has been much controversy over the role that this zone plays in stress-corrosion cracking behavior. Studies on high-purity alloys have led to the conclusion that it is primarily the matrix precipitates, and not the grain boundary precipitate, that determine susceptibility to SCC.

aluminum alloys undergoing cracking from nearly neutral salt water, the pH at the crack tip was found to be 3.2 to 3.5. A macroscopic model was also devised to simulate the sides and the base of a stress-corrosion crack, with the simulated base electrically isolated from the simulated walls. This model has given interesting results to date and gives promise of more to come.

In addition to other basic contributions to aluminum corrosion, two reviews were written by program personnel. One of these was concerned with the aluminum-hydrogen system. A second review treated chemical effects in the corrosion of aluminum and aluminum alloys.

An academic study of the corrosion fatigue of an aluminum alloy demonstrated that hydrogen diffusion is not rate controlling (Fig. 28).

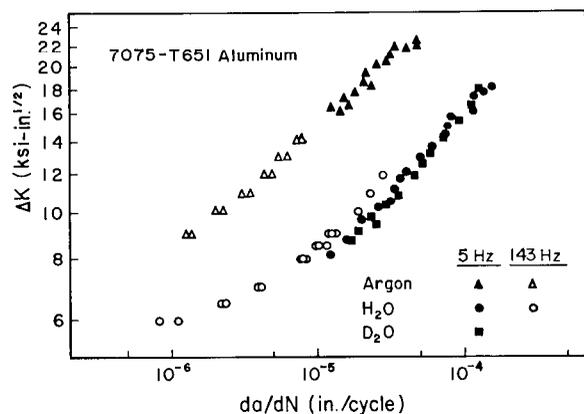


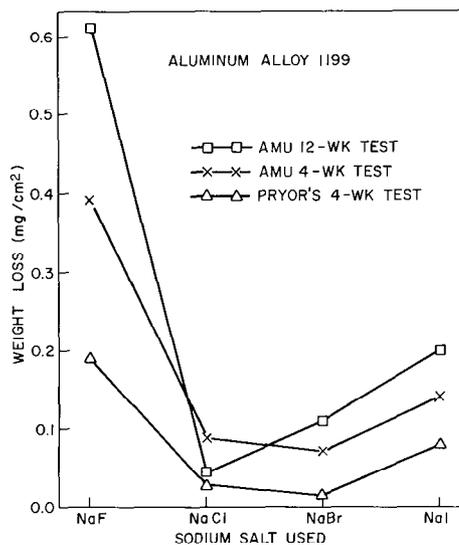
Fig. 28 - Fatigue (in argon) and corrosion fatigue (in water) crack-growth rates in an aluminum alloy. Deuterium studies indicate that hydrogen diffusion is not rate-determining.

Surface Sciences

Various entries in the Abstracts of Achievements identify contributions of some of the subdisciplines which are sometimes called collectively *surface science*. For example, techniques of Low-Energy Electron Diffraction (LEED) have been advanced by the program to enable the experimenter to study the initial reaction of any chosen gas (however corrosive) with a clean metal surface. An international conference was held in which the status of field ion microscopy and field emission microscopy were reviewed by internationally recognized experts, and the proceedings have now been published. Electron spin resonance studies were made on oxide surfaces exposed to various gaseous species.

As indicated by the foregoing, the program was instrumental in drawing to the attention of surface scientists the existence of a challenging technological problem. As a consequence many basic studies were made using various ones of the newer surface science techniques, much new and interesting information was developed, and more techniques were added to those available to the surface scientist (Figs. 29 to 31). The technique of LEED in particular made significant advances because of the program. The experimental and theoretical difficulties of the program area are such, however, that much more work is required before these newer approaches can make their contributions to corrosion technology.

Fig. 29 - Basic study of the role of the chloride ion in the corrosion of aluminum. Kinetic data show that although there are some quantitative differences between the behavior of the various halide ions, there are no qualitative differences, and the role played by chloride is due to its ubiquity rather than any uniqueness.



The electrochemical techniques and concepts, especially those developed and applied by Evans, Hoar, Pourbaix, and their students, have been shown to be of immediate value both in advancing the theory of stress-corrosion cracking and in guiding technological experimentation. Since electrochemistry is generically a surface science, the tenet that surface science would be useful to the stress-corrosion problem at an early date has thus been vindicated. As one example, it has been postulated elsewhere that hydrogen can only be reduced from aqueous solutions at a cathode, that by making a piece of steel an anode one establishes conditions incompatible with hydrogen reduction and that any SCC occurring under such conditions cannot be attributed to hydrogen. A more sophisticated analysis of the situation is as follows: A given site (electrode) can serve as an anode for the dissolution of iron and at the same time function as a cathode for the reduction of hydrogen, if the potential and pH are favorable.



Fig. 30 - Field ion micrograph Ni₄Mo. This is one of several modern techniques in surface physics which are useful to study the ultrafine-scale nature of clean metal surfaces.

The experience of the program, in summary, is that there are numerous new areas of surface science capable of yielding important scientific knowledge about metal surfaces and their reaction with environment. The more mature discipline of electrochemistry has been demonstrated to have immediate utility in the understanding of the processes of aqueous corrosion, including stress-corrosion cracking, and in the guidance of future technological advances.

ABSTRACTS OF ACHIEVEMENTS

Explanatory Notes

These abstracts were prepared by the organization performing the research as a means both of summarizing progress and giving the reader a key to the literature generated by the program. They were modeled after annual reports of Interdisciplinary Laboratories, listing task title, personnel, objective, usually the approach, the achievements, and publications and presentations.

It will be noted that a given task, represented by a single task title, may differ greatly from another in scope, staffing, and productivity. This is due in considerable measure to the broad technical nature of the program and to the fact that each organization grouped its work under a given task title as seemed most effective for conveying the output to the imagined readers.

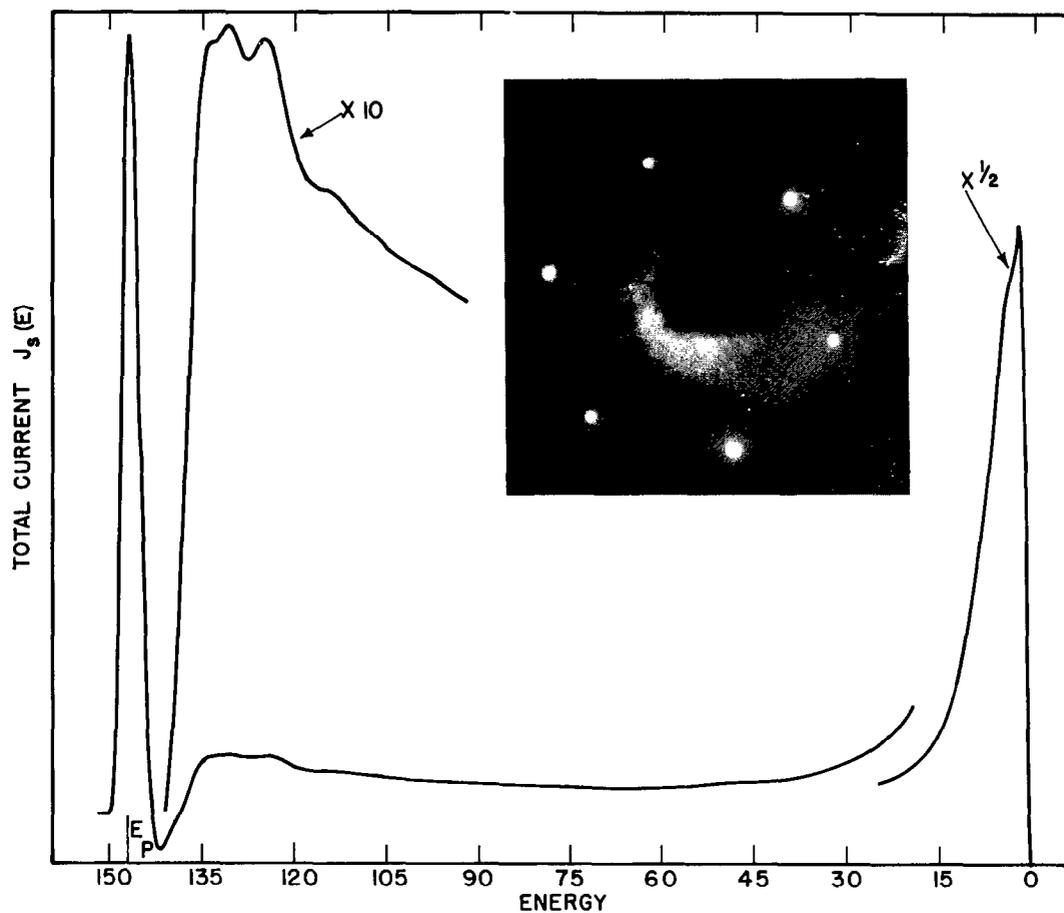


Fig. 31 - Low energy electron diffraction pattern and secondary electron energy distribution curve for an aluminum (111) surface. The curve includes a peak indicating that the elaborate steps used to prepare an entirely clean surface were not quite successful. This observation illustrates one of the many challenges of state-of-the-art surface physics and surface chemistry.

The abstracts are arranged in the following pages by institutions, commencing with The Boeing Company, followed by the universities (alphabetically), and finally the Naval Research Laboratory.

The Boeing Company

USE OF PRECRACKED SPECIMENS IN STRESS-CORROSION TESTING OF HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for several high strength commercial aluminum alloys, and to compare the rating of the alloys based on this data with the ratings established from smooth specimen time to failure data.

Approach

The V-K curves were obtained using bolt-loaded, double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Alloys and tempers tested were 7079-T651, 7079-T651 + 6 hr/325°F, 7075-T651, 7075-T7351, 7175-T66, 7175-T736, 7178-T76, AZ74.61, X7080-T7, 7039-T64, 7049-T7, 2024-T351, 2024-T4, 2024-T851, 2014-T451, 2014-T651, 2219-T37.

Achievements

The V-K curves showed a double slope behavior. At lower crack tip stress intensities the crack velocities were highly dependent on K_I , whereas at the higher K_I levels crack velocities were nearly independent of the applied crack tip stress intensity. Maximum crack velocities ranged from 4×10^{-5} in./hr for the highly susceptible 7079-T651 to 1×10^{-5} in./hr for the highly resistant 7075-T73. Although crack velocities often continued to decrease with decreasing K_I level, true K_{Isc} values (K_I levels below which growth ceases) were not observed for any alloy tested. Rankings of the various alloys based on the V-K curves agreed with established rankings based on smooth specimen time to failure data. In many cases the V-K curves provided more discriminating data than is available from smooth specimen time to failure tests. For example, at the higher K_I levels stress-corrosion crack growth rates in 7079-T651 were one to two orders of magnitude faster than in 7075-T651 even though both alloys show similar behavior in the standard smooth specimen, alternate immersion test.

A relationship between the smooth specimen stress-corrosion threshold stress from time to failure data and the V-K curves is presented.

Publications

"Use of Precracked Specimens in Stress-Corrosion Testing of High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24466, November 1969; submitted to Corrosion

The Boeing Company

USE OF PRECRACKED SPECIMENS IN SELECTING HEAT TREATMENTS FOR STRESS-CORROSION RESISTANCE IN HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for the alloy 7075 after various overaging heat treatments between T6 and T73.

Approach

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Three different techniques were employed. Two techniques used single DCB specimens containing aging gradients along their lengths. The third technique used multiple DCB specimens, each one having a different heat treatment.

Achievements

Results from each technique showed that for the 7075 alloy, overaging to an electrical conductivity of at least 38% IACS is necessary before stress-corrosion crack growth rates approach those of 7075-T73. Stress-corrosion performance was established most rapidly using multiple DCB specimens. After only a few hundred hours the crack growth characteristics were sufficiently established using this technique that the different heat treatments could be rated against the known performance of 7075 in the T6 and T73 tempers.

Publications

"Use of Precracked Specimens in Selecting Heat Treatments for Stress-Corrosion Resistance in High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-2447, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF RESIDUAL STRESSES ON STRESS-CORROSION CRACK GROWTH RATES
IN ALUMINUM ALLOYS

M. V. Hyatt

Objective

To determine the effects of quenched-in residual stresses on the behavior of pre-cracked double cantilever beam (DCB) stress-corrosion specimens of high strength aluminum alloys 7075, 7175, and 7079.

Approach

The V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were obtained using bolt loaded DCB specimens intermittently wetted with an aqueous 3.5% NaCl solution. Tests were conducted on specimens containing quenched-in residual stresses and on specimens which had been stress relieved after quenching by stretching or explosive shocking.

Achievements

Large differences in crack front profiles were observed between specimens with and without residual quenching stresses. Severe crack front bowing occurred in non-stress relieved specimens. In addition the crack opening displacement in the non-stress relieved specimens was effectively increased at the crack tip by the bowing apart of the two DCB specimen arms as the stress-corrosion crack propagated through the material. These effects result primarily from the residual compressive stresses on the surfaces of the non-stress relieved specimens. Both the crack front bowing and the bowing apart of the DCB specimen arms cause errors in the calculated K_I levels. These problems were eliminated by stress relieving DCB specimens after quenching. This work underlines the fact that residual quenching stresses in actual parts susceptible to stress-corrosion cracking not only increase chances of initiating stress-corrosion cracks, but also play an important role in increasing average growth rates. This can result from the increased crack opening displacement (and therefore K_I level) at the crack tip due to deflections caused by the residual stresses.

Publications

"Effect of Residual Stresses on Stress Corrosion Crack Growth Rates in Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24469, November 1969; submitted to Corrosion

The Boeing Company

EFFECTS OF SPECIMEN GEOMETRY AND GRAIN STRUCTURE ON STRESS-CORROSION CRACKING BEHAVIOR OF ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for aluminum alloy double cantilever beam (DCB) specimens with various side grooves, grain structures, and thicknesses.

Approach

DCB specimens with various side grooves, grain structures, and thicknesses were tested in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Branch cracking and arm breakoff may occur during testing of DCB specimens of aluminum alloy materials with equiaxed grain structures. Side grooves on DCB specimens had a negligible effect on crack growth rate data. Double cantilever beam specimens from materials as thin as 0.050 in. can be successfully tested.

Publications

"Effects of Specimen Geometry and Grain Structure on Stress Corrosion Cracking Behavior of Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24470, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF QUENCHING RATE ON STRESS-CORROSION CRACK GROWTH RATES
IN 2024-T4 ALUMINUM

M. V. Hyatt

Objective

To determine the effect of quenching rate on the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for 2024-T4.

Approach

Specimens of 2024 were resolution treated, quenched at two different rates, and naturally aged to the T4 temper.

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution.

Achievements

Actual stress-corrosion crack growth rates were higher in the more slowly quenched 2024-T4 alloy. This behavior agrees with trends observed by others based on percent loss in tensile strengths of pre-exposed specimens which have been quenched at different rates.

Publications

"Effect of Quenching Rate on Stress-Corrosion Crack Growth Rates in 2024-T4 Aluminum," M. V. Hyatt, Boeing Document No. D6-24471, November 1969; submitted to Corrosion

The Boeing Company

DEVELOPMENT OF A HIGH STRENGTH, STRESS-CORROSION RESISTANT ALUMINUM ALLOY FOR USE IN THICK SECTIONS

M. V. Hyatt and H. W. Schimmelbusch

Objective

To develop a new high strength Al-Zn-Mg-Cu alloy with a smooth specimen stress-corrosion threshold stress of 25 ksi, good toughness and fatigue properties, and a quench sensitivity such that the properties can be maintained at a high level in thick plate and forgings.

Approach

To meet the strength goals an alloy with zinc and magnesium contents intermediate between those of 7075 and 7178 was selected. To reduce quench sensitivity the copper content was reduced to about 1.0%, and zirconium and manganese were added in place of chromium which is the normal recrystallization retardant in 7075 and 7178 alloys. The amount of overaging required to meet the stress-corrosion goal was determined using both smooth specimens and precracked double cantilever beam (DCB) specimens. Finally, hand and die forgings, plate, and extrusions of the new alloy were given the selected heat treatment and evaluated to determine mechanical, fracture, fatigue, and stress-corrosion properties.

Achievements

Mechanical, fracture, and stress-corrosion properties for die forgings of the new alloy (alloy 21) and several other forging alloys are compared in the following table.

Alloy	Thickness (in.)	Minimum longitudinal properties		Longitudinal K_{Ic} range (ksi $\sqrt{\text{in.}}$)	Short-transverse stress-corrosion threshold (ksi)	
		F_{tu} (ksi)	0.2% F_{ty} (ksi)		3.5% NaCl alternate immersion	Industrial atmosphere
Alloy 21	6.75	69*	60*	30-38*	> 25*	> 25*
7049-T73	5.0	70	60	30-38*	45	?
X7080-T7	6.0	65	57	27-30	25	15
7075-T73	3.0	66	56	27-38	> 47	> 47
7075-T73	6.0	61	51	27-38	> 47	> 47
7175-T736	3.0 max	76	66	27-38	~ 35	?
7075-T6	3.0 max	75	65	25-32	7	14
7079-T6	6.0	72	62	25-32	7	6

*Estimated values

The mechanical properties of alloy 21 are comparable to those of 7049-T73. The fracture toughness of alloy 21 is as good as or better than that of the other alloys listed. The smooth-specimen short-transverse stress-corrosion threshold appears to be greater than 25 ksi. Test data also indicate that the smooth and notched axial (tension-tension) fatigue properties of alloy 21 are comparable to those of 7075-T6 and 7075-T73.

Publications

"Development of a High-Strength, Stress-Corrosion Resistant Aluminum Alloy for Use in Thick Sections," M. V. Hyatt and H. W. Schimmelbusch, Technical Report AFML-TR-70-109, May 1970, Boeing Document No. D6-60122

The Boeing Company

EFFECT OF EXPOSURE TIME AT 250°F ON STRESS-CORROSION CRACK GROWTH RATES IN 2024-T351 ALUMINUM

M. V. Hyatt and W. E. Quist

Objective

To determine the degree of sensitization to stress-corrosion cracking of 2024-T351 after exposure at 250°F (a temperature commonly used during curing of adhesively bonded assemblies).

Approach

Double cantilever beam (DCB) specimens of 2024-T351 were exposed at 250°F for times up to 300 hours. V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were then obtained in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Stress-corrosion crack velocities were observed to increase in specimens which had been exposed for only 2-5 hours at 250°F. Maximum crack velocity increases of about 60% occurred on specimens which had been exposed from 15 to 100 hours.

The Boeing Company

FUNDAMENTAL ASPECTS OF STRESS-CORROSION CRACKING OF HIGH STRENGTH ALUMINUM ALLOYS

Markus O. Speidel

Objective

At the Boeing Scientific Research Laboratories experimental and theoretical studies of stress-corrosion cracking in high strength aluminum alloys have three aims: (1) to identify the major influential parameters, that is, the conditions under which stress-corrosion cracks can grow; (2) to compare such conditions with those that cause stress-corrosion cracking in other alloy systems, polymers, and glasses, in an attempt to define their limits of applicability; and (3) to increase our understanding of the basic mechanisms of stress-corrosion crack propagation.

Approach

With complementary fractography and metallurgical examination, the main effort was concentrated on the measurement of stress-corrosion crack tip velocity as a function of the following parameters.

1. Mechanical parameters
 - a) applied crack tip stress intensity
 - b) specimen geometry
2. Environmental parameters
 - a) concentration of halide ions
 - b) concentration of other inorganic anions
 - c) concentration of water in the environment
 - d) presence of various gases
 - e) concentration of organic liquids
 - f) concentration of protons
 - g) presence of other cations
 - h) presence of liquid metal in the crack
 - i) temperature
 - j) viscosity of electrolyte
 - k) electrochemical potential
3. Metallurgical parameters
 - a) aging time
 - b) aging temperature
 - c) alloy concentration
 - d) recrystallization

Achievements

Crack propagation was shown to be affected by almost all the parameters listed. The first step in each case was to measure the effect of the variation of just one parameter on the velocity while keeping all the other parameters constant at some "reasonable" value. Our data showed that this can lead to quite different results,

depending on the actual value chosen for those parameters that were kept constant. The interdependence of the effects of various parameters on stress-corrosion crack velocity is illustrated in Figs. 1, 2, and 3.

Effect of Stress on Crack Tip Velocity—Crack tip stress intensity has a decisive effect on stress-corrosion crack velocity. It can cause the velocity to vary from less than 5×10^{-9} cm/sec to more than 2 cm/sec, a range that exceeds by far the lowest and the highest subcritical crack velocity ever before directly observed in aluminum alloys. Although the slowest cracks took a year to become visible, a movie camera had to be used to record the fastest cracks. Generally, there are three regions of the crack velocity versus stress intensity curve: region I at low stress intensities where the crack velocity is strongly stress dependent; region II at intermediate stress intensities where the crack velocity is independent of stress and which subsequently may show one or two plateaus; and region III at stress

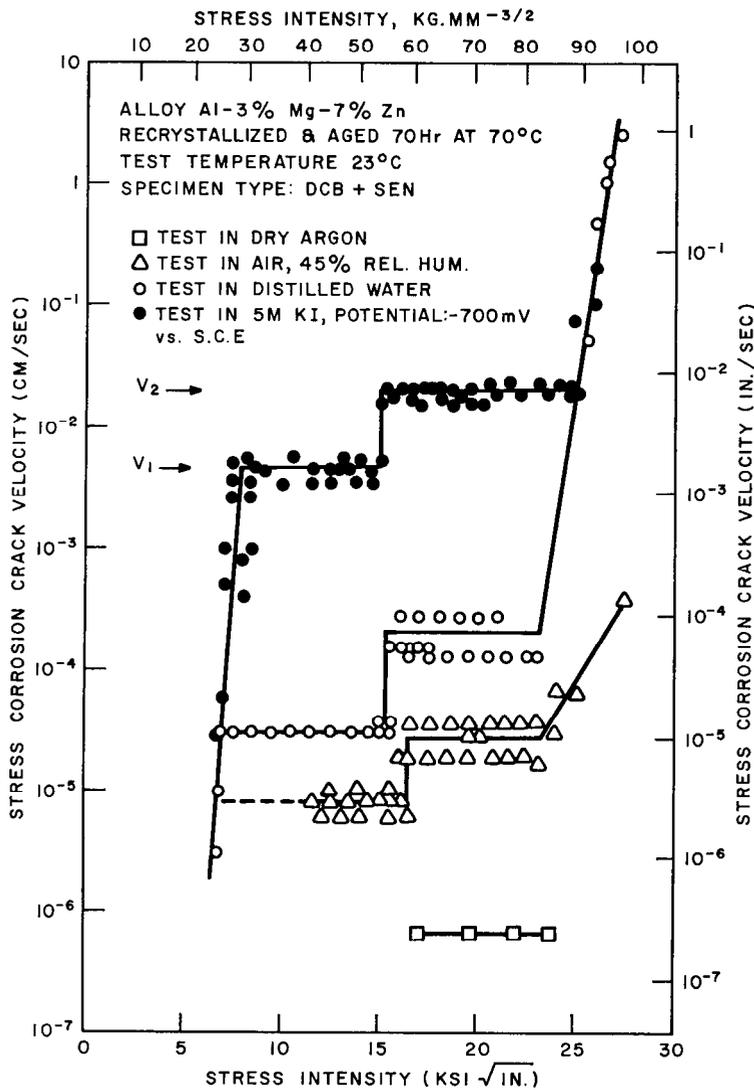


Fig. 1 - The effect of stress intensity on SCC crack velocity

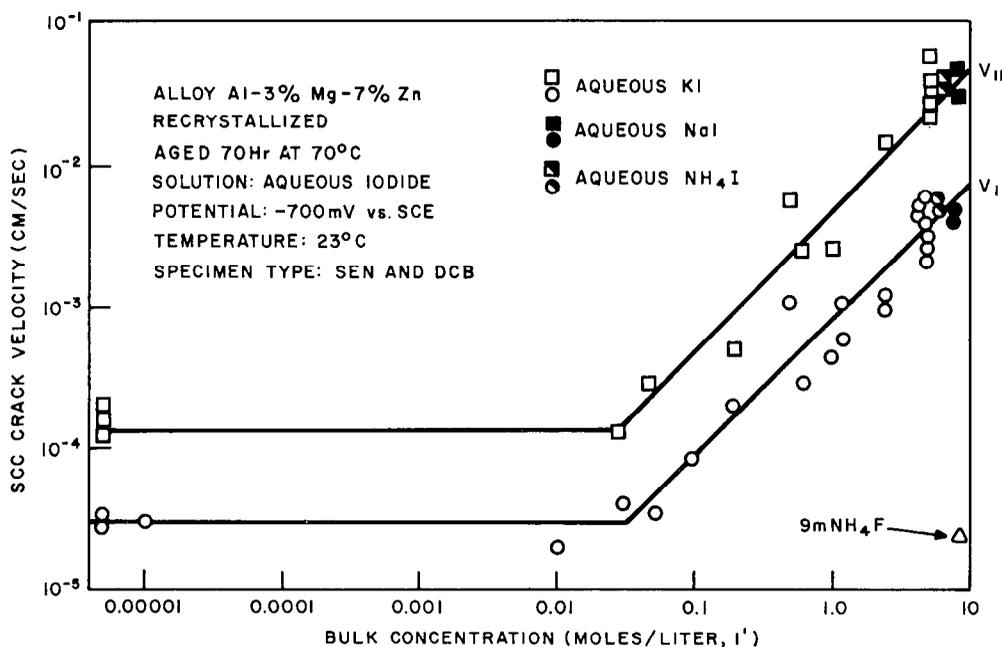


Fig. 2 - The effect of halide ion concentration on SCC crack velocity

intensities close to K_{Ic} where the velocity again is strongly stress dependent. Commercial aluminum alloys show only regions I and II, but a high-purity alloy showed all three regions, as illustrated in Fig. 1. For the experimental conditions listed in Fig. 1, stress-corrosion crack velocity apparently does not depend on halide ion concentration in regions I and III. Region II, however, is strongly affected by halide ion concentration. This is obvious from both Figs. 1 and 2, which are based on hundreds of tests on self-stressed double cantilever beam specimens and single-edge-notched tension specimens. Thus, there is no simple answer to whether halide ion concentration affects stress-corrosion crack velocity. The answer is no for regions I and III, but yes for region II. Velocity in region I is thought to be kinetically limited. Velocity in region II is thought to be limited by mass transport. The existence of region III is thought to be due to additional mechanical components of crack growth.

Effect of Halide Ion Concentration on Stress-Corrosion Crack Velocity—Figure 2 shows the effect of iodide concentration on the two plateau velocities that may be seen in region II in Fig. 1. The linear increase of the plateau velocities at higher iodide concentrations is consistent with the concept of mass transport limited velocity. The constant velocity at low halide ion concentrations can be attributed to water as a stress-corrosion agent. This behavior also occurs in commercial aluminum alloys and is similar for bromide and chloride ions. Fluoride ions, however, do not accelerate stress-corrosion cracking over the rate found in distilled water.

Effect of Electrochemical Potential on Stress-Corrosion Crack Velocity—In Fig. 3 it may be seen that the effect of halide ion concentration on region II velocity applies only at a specific electrochemical potential of the specimen and only at a specific pH value of the bulk electrolyte. For example, at a potential of $E = -1600$ mV, there is no influence whatsoever of iodide concentration on stress-corrosion crack velocity. This is true if the solution is neutral. Under such conditions, the crack propagates even in concentrated solutions with the velocity characteristic of

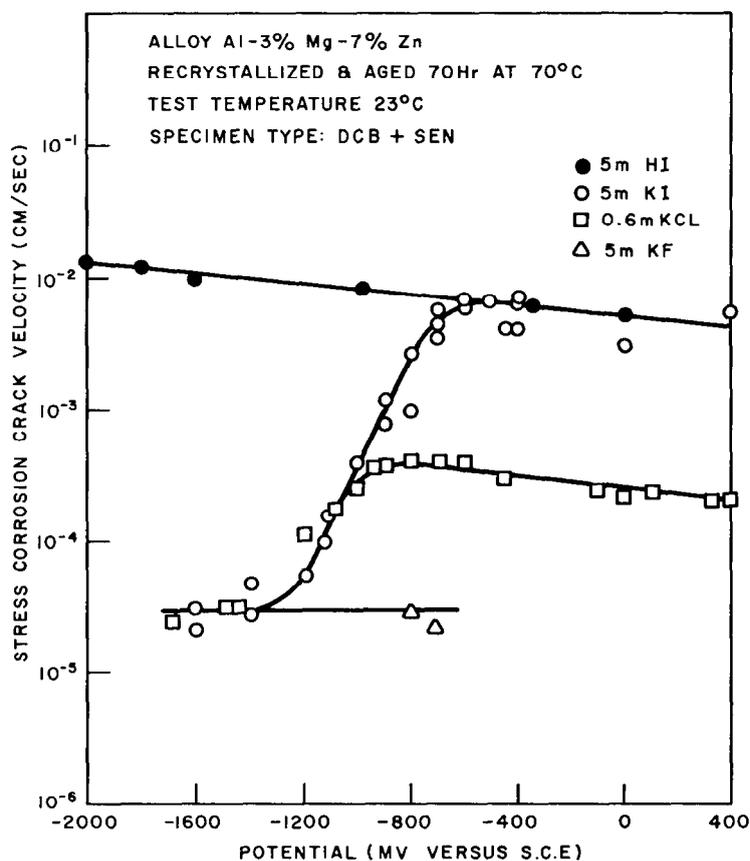


Fig. 3 - The effect of electrochemical potential on SCC crack velocity

propagation in distilled water. (Compare Figs. 1, 2, and 3.) In strongly acidic solutions, however, cathodic protection is impossible, and the crack propagates with the velocity characteristic for propagation in highly concentrated halide solutions. Between the cathodic-protection and the pitting potentials, stress-corrosion crack velocity in neutral Cl^- , Br^- , and I^- solutions increases with potential and finally levels out at rates that are determined by the halide ion concentration. The increase in velocity is attributed to the replacement of OH^- ions by halide ions. The leveling off beyond the pitting potential is attributed to the consumption of halide ions on the crack walls.

Summary of Other Results--

1. Crack-line-loaded and remote-loaded specimens yield comparable crack velocity versus stress intensity curves.
2. Of 20 anions tested, only Cl^- , Br^- , I^- , and, to a much lesser degree, NO_3^- accelerate stress-corrosion crack growth.
3. Ten different cations tested resulted in the same stress-corrosion crack velocity. An exception was H^+ in the cathodic protection range.

4. Liquid metals cause stress-corrosion crack velocities up to 20 cm/sec and K_{Isc} as low as 0.8 ksi $\sqrt{\text{in.}}$.
5. Solution viscosity is inversely proportional to stress-corrosion crack velocity.
6. Overaging causes not only a reduction in velocity, but also an increase in the limiting stress intensity in region I.
7. Alloys recrystallized to large equiaxed grains show stress-corrosion crack velocities 10 to 100 times faster than commercial alloys with the usual flattened grains.
8. There is no true K_{Isc} for aluminum alloys. Cracks just slow down at lower stress intensities, but do not stop.
9. In commercial aluminum alloys, no crack growth occurs in gases and organic liquids unless water is present.

The Boeing Company

ENVIRONMENTAL FATIGUE CRACK PROPAGATION OF ALUMINUM ALLOYS AT LOW STRESS INTENSITY LEVELS

J. A. Feeney, J. C. McMillan, and R. P. Wei

Objective

The objectives of the study were:

- a) To evaluate the performance of commercial aluminum alloys when subjected to cyclic stresses in corrosive and "mild" environments.
- b) To correlate the data within the framework of linear-elastic fracture mechanics using the crack tip stress-intensity factor K to characterize the crack driving force.
- c) To examine fatigue crack growth rates at low values of stress intensity factor where the mechanical aspects of the fatigue process are less dominant.
- d) To correlate the rate of fatigue crack propagation in a particular environment and at a particular K level with the fracture topography.

Approach

Corrosion fatigue experiments were conducted on aluminum alloys 7178-T6, 7075-T6, and 2024-T3. Panels of dimensions $24 \times 9 \times 0.16$ in. were cyclic stressed by wedge force and remote loading techniques. Five different environments were studied: desiccated argon (10 ppm H_2O), dry air ($< 10\%$ relative humidity), wet air ($> 90\%$ relative humidity), distilled water, and 3.5% NaCl solution. Data was plotted as $\log \Delta K$ versus $\log d2a/dN$.

Achievements

Wedge force loading and remote loading techniques were found to be compatible under the test conditions used in this investigation. When the data was plotted as $\log \Delta K$ versus $\log d2a/dN$, two transition regions were exhibited:

- a) The transition at high levels of ΔK was environmentally controlled and reflected a change-over from a plane strain to plane stress mode of propagation.
- b) The transition at low levels of ΔK was not environmentally controlled and reflected some intrinsic property of the material.

The frequency effect was found to be controlled mostly by the environmental influence and was not an intrinsic property of the material. The effects of the environments on the rate of fatigue crack propagation were:

- a) Environmental sensitivity was most pronounced at low levels of cyclic amplitude of stress intensity ΔK .

- b) Alloy 2024-T3 was relatively insensitive to the mild environments when compared to dry air, whereas 7075-T6 and 7178-T6 showed a pronounced acceleration in fatigue crack growth rate when tested in either wet air or distilled water.
- c) All three alloys exhibited a marked susceptibility to environmentally enhanced fatigue crack growth rate in 3.5% NaCl solution. In contrast to 2024-T3 and 7075-T6, however, fatigue crack growth of 7178-T6 was faster in distilled water than in 3.5% NaCl solution.

The most pertinent fractographic observations were:

- a) Ductile striations were not observed at growth rates ($d2a/dN$) less than $250 \text{ \AA}/\text{cycle}$.
- b) Cleavage-like fracture, stepwise growth, and rippled facet fracture were the most pronounced transgranular fracture modes at crack growth rates below $10 \text{ \mu in.}/\text{cycle}$.
- c) Cleavage-like fracture appeared to be environmentally controlled and was more pronounced the less ductile the material.
- d) Intergranular fracture was the most common fracture process in specimens of 2024-T3 and 7178-T6 tested in 3.5% NaCl solution at low ΔK levels. In 7075-T6, however, intergranular fracture did not occur at any ΔK level.
- e) Environmental sensitivity at relatively higher ΔK levels was not always associated with a change in fracture mode from ductile striation formation to brittle striation formation. In 2024-T3, for example, brittle striations did not form in any of the environments used in the investigation.

Publications

"Environmental Fatigue Crack Propagation of Aluminum Alloys at Low Stress Intensity Levels," J. A. Feeney, J. C. McMillan, and R. P. Wei, Boeing Document No. D6-60114, May 1969 (DDC Accession No. AD 692166); published in Metallurgical Transactions 1: 6, June 1970, p. 1741

Presentations

"Environmental Fatigue Crack Propagation of Aluminum Alloys at Low Stress Intensity Levels" by J. A. Feeney, ASM/WESTEC Meeting, Los Angeles, May 1969

The Boeing Company

IMPROVING THE TOUGHNESS AND STRESS-CORROSION RESISTANCE OF AFC 77

D. Webster

Objective

In the past five years the strength of stainless steels has been improved to the point where they are competitive on a strength-to-weight basis with low alloy steels and alloys of titanium and aluminum. The strongest stainless steel available is AFC 77 which contains 0.15C, 14.5Cr, 5.0Mo, 0.5V, and 13.5Co. In spite of its high strength, this alloy has not found widespread use because of its low toughness and stress-corrosion resistance. The objective of this study was to improve the toughness and stress-corrosion resistance of AFC 77.

Approach

New heat treatments and thermomechanical processes were used. The three most promising techniques were as follows:

1. In the first process, heat treatment is controlled to ensure that a small amount of austenite remains after heat treatment. The tough austenite diverts or stops a growing crack so that a large amount of energy is necessary for fracture; in other words, the material has a high fracture toughness. AFC 77 is normally considered to have a fully martensitic structure, but there is an increasing tendency for austenite to be retained as the austenitizing temperature is increased. This happens because the stability of the austenite is related to the alloy content of the matrix, which is greater at high austenitizing temperatures due to increased solution of undissolved carbides and intermetallic compounds. An upper limit on the austenitizing temperature is set by the formation of delta ferrite at about 2100°F. In order to be an efficient crack stopper, it is not only necessary that the second phase be tough, but it must also be well dispersed. The dispersion of austenite is produced automatically during the martensite transformation as new martensite needles repeatedly subdivide the areas of austenite in which they form. A modification of the above technique which allows the retained austenite content to be increased has recently been developed. In this technique higher than normal austenitizing temperatures which are inside the austenite + delta ferrite phase field are used. The delta ferrite is then transformed to austenite at lower temperatures after which the normal heat-treatment practice is followed.
2. A new grain refinement process forms the basis of the second technique. In this process the annealed steel is cold rolled at least 35% in the final stages of manufacture and then re-annealed before delivery to the user. While still in the annealed condition, fabrication of the part is completed and then a normal hardening treatment is given which, because of the prior deformation, will develop a refined grain structure. The explanation for the grain refinement is as follows: The cold rolling ruptures the interface between the hard carbide particles and the matrix and causes voids to form around the particles. These voids, which are stable in the austenite at temperatures up to 1875°F, interact with moving grain boundaries at the austenitizing temperature, resulting in a marked refinement of austenite grain size.

3. The third technique, which involves the strain aging of material containing retained austenite, produces the best combination of strength, toughness, and stress-corrosion resistance. In this process the material is austenitized at a temperature high enough to produce retained austenite, tempered at 500°F, and then strained 10-20% by cold rolling. A second tempering treatment in the range 500°-1000°F is then given to develop tensile strengths from 280,000 psi to 330,000 psi. Because a substantial proportion of the retained austenite remains after strain aging, a high level of fracture toughness is maintained.

Achievements

Using the PH stainless steels as a base, the techniques described above have increased the strength level at which a given toughness (K_{Ic}) can be maintained from the normal 190-230 ksi range to the 310-330 ksi range for strain aged material or the 250-290 ksi range for non-strain aged material. Similar increases in strength level for equivalent stress-corrosion resistance (K_{Isc}) is achieved by these techniques. For example, strain-aged AFC 77 sheet with a yield strength of 277 ksi and an ultimate strength of 288 ksi has a K_{Isc} of 90 ksi $\sqrt{\text{in}}$.

Publications

"The Use of Deformation Voids to Refine the Austenite Grain Size and Improve the Mechanical Properties of AFC 77," D. Webster, Boeing Document No. D6-23870, 1969 (DDC Accession No. AD 687724); also Trans. ASM Quarterly 62, Sept. 1969, p. 759

"The Stress Corrosion Resistance and Fatigue Crack Growth Rate of a High Strength Martensitic Stainless Steel AFC 77," D. Webster, Boeing Document No. D6-23973, 1969 (DDC Accession No. AD 695794)

"Stainless Steels Can Be Strong and Tough," D. Webster, Boeing Document No. D6-24379, 1969 (DDC Accession No. AD 695795); also Space/Aeronautics, Sept. 1969, p. 83

"Effect of Grain Refinement on Mechanical Properties of 4340M Steel," D. Webster, Boeing Document No. D6-25220, Feb. 1970

The Boeing Company

THE EFFECT OF SILICON ON THE STRESS-CORROSION RESISTANCE OF LOW ALLOY HIGH STRENGTH STEELS

C. S. Carter

Objective

Silicon modified 4340 steel has exhibited superior service performance to 4340 at the 260-280 ksi ultimate strength range. The purpose of this investigation was to determine if this could be attributed to a beneficial effect of silicon on the stress-corrosion resistance of low alloy type steels.

Approach

Five 100 lb. heats of 4340 containing 0.09, 0.54, 1.08, 1.58, and 2.15 percent silicon were prepared by vacuum melting. The fracture toughness K_{Ic} , stress-corrosion threshold K_{Isc} , and stress-corrosion crack velocity characteristics were determined for each heat for two ultimate tensile strength ranges: 220-240 ksi and 280-300 ksi. Commercial heats of 4340 and 4340 modified were also evaluated. Stress-corrosion tests were conducted in 3.5% NaCl solution.

Achievements

Silicon did not improve the threshold stress intensity K_{Isc} . However, in the 280-300 ksi strength range the stress-corrosion crack velocity was significantly decreased when the silicon content exceeded 1.5%. In the lower strength range the stress corrosion was reduced by increasing the silicon content. Strength level had a significant effect on the kinetics of stress-corrosion crack growth. In the highest strength range the velocity was proportional to the crack tip stress intensity. On the other hand, the velocity was constant over a wide range of stress intensity when the steels were tempered to 220-240 ksi.

Publications

"The Effect of Silicon on the Stress-Corrosion Resistance of Low Alloy High Strength Steels," C. S. Carter, Boeing Document No. D6-23872, March 1969; (DDC Accession No. AD 687726); published in *Corrosion* 25, 1969, p. 423

Presentations

"The Effect of Silicon on the Stress-Corrosion Resistance of Low Alloy High Strength Steels" presented by C. S. Carter at ASM/WESTEC Meeting, Los Angeles, March 1969

The Boeing Company

STRESS-CORROSION CRACK BRANCHING IN HIGH STRENGTH STEELS

C. S. Carter

Objective

To establish the cause of stress-corrosion crack bifurcation in high strength steels.

Approach

Stress-corrosion crack morphology was determined in several high strength steels loaded in 3.5% aqueous sodium chloride and related to the applied stress intensity and velocity characteristics of the materials.

Achievements

It has been established that the criteria for crack branching are an essentially constant crack velocity (i. e., independent of stress intensity) and the attainment of a critical stress intensity level, K_{IB} . These criteria must be achieved simultaneously for bifurcation. The stress intensity of branching has been empirically expressed as $K_{IB} \sim (2-4) K_{I_{sc}}$ and is in good agreement with a branching criteria proposed by Anthony and Congleton. However, a more applicable relationship appears to be $K_{IB} = 2 K_{I_m}$ where K_{I_m} is the minimum stress intensity for constant crack velocity.

This study has also shown that the stress-corrosion curve of K_{I_i} versus time to failure quantitatively reflects the crack velocity characteristics. For constant crack velocity the time to failure shows only a slight dependence on K_{I_i} , provided that the ratio of initial crack length to specimen width is similar for the specimens used to construct the stress-corrosion curve. Similarly, when the velocity is dependent upon stress intensity the time to failure shows a marked dependence on K_{I_i} . A simple technique, using pairs of dissimilar size specimens, has been devised to quantitatively determine the constant crack velocity and eliminate the incubation time variable.

There is no correlation between $K_{I_{sc}}$ and the crack velocity in the region of stress intensity independence.

Publications

"Stress Corrosion Crack Branching in High Strength Steels," C. S. Carter, Boeing Document No. D6-23871, March 1969 (DDC Accession No. 687725); to be published in Journal of Engineering Fracture Mechanics

"Crack Extension in Several High Strength Steels Loaded in 3.5% Sodium Chloride Solution," C. S. Carter, Boeing Document No. D6-19770, 1967 (DDC Accession No. AD 685377)

Presentations

"Stress Corrosion Crack Branching in High Strength Steels," presented by C.S. Carter at National Symposium on Fracture Mechanics, Lehigh University, August 1969

The Boeing Company

THE EFFECT OF HEAT TREATMENT ON THE FRACTURE TOUGHNESS AND SUB-CRITICAL CRACK GROWTH CHARACTERISTICS OF A 350 GRADE MARAGING STEEL

C. S. Carter

Objective

To determine the effect of heat-treatment variables on a recently introduced 350 grade steel and establish its potential for structural application.

Approach

The 350 grade steel (nominal composition 18.5Ni, 12Co, 4.6Mo, 1.4Ti) was obtained in billet and bar form. The optimum solution treatment was initially established and the effect of aging on stress-corrosion resistance in 3.5% NaCl solution and on fracture toughness was determined.

Achievements

A double solution anneal at 1700°F/1500°F gave the best combination of properties. When aged at temperatures below 900°F the subcritical crack growth resistance was so low that growth occurred in unnotched tension specimens loaded at slow strain rates in laboratory air. Reduced crack growth resistance at low aging temperatures appears to be a characteristic of the 18% Ni maraging system and is possibly related to the precipitate distribution. Aging at, and above, 900°F increased $K_{I_{SCC}}$ and reduced the subcritical crack growth rate. Austenite reversion occurred at aging temperatures exceeding 1000°F (aging time 3 hours) and significantly reduced strength. However, the fracture toughness only slightly improved.

Aging to peak strength gave ultimate tensile strength values within the range 335-347 ksi. The fracture toughness K_{I_C} and stress-corrosion threshold $K_{I_{SCC}}$ at this strength level were 35 and 10 ksi $\sqrt{\text{in}}$. respectively. Because of this low fracture toughness the risk of brittle fracture in service will be greater than with currently used ultrahigh strength steels.

Publications

"The Effect of Heat Treatment on the Fracture Toughness and Sub-Critical Crack Growth Characteristics of a 350 Grade Maraging Steel," C. S. Carter, Boeing Document No. D6-22978, June 1969 (DDC Accession No. AD 692165); published in Metallurgical Transactions 1, 1970, p. 1551

The Boeing Company

THE INFLUENCE OF PRE-STRESSING ON THE STRESS-CORROSION RESISTANCE OF DEFECT-CONTAINING HIGH STRENGTH STEELS

C. S. Carter

Objective

To determine the effect of pre-stressing on the stress-corrosion resistance of high strength steels containing cracks.

Approach

Fatigue precracked single-edge notch specimens of 4340 (project alloy heat treated to 194 ksi yield strength) and 300 grade maraging steel were pre-loaded in air to selected stress intensity levels within the range 0-90% K_{Ic} (72 ksi $\sqrt{\text{in.}}$). After unloading, a stress-corrosion curve of K_{Ii} versus time to failure and the threshold stress intensity level K_{Isc} were determined for each pre-load condition in 3.5% aqueous sodium chloride solution.

Achievements

Without pre-load, the K_{Isc} for the 4340 steel was 8 ksi $\sqrt{\text{in.}}$. The threshold increased in proportion to the pre-load stress intensity level such that K_{Isc} exceeded 25 ksi $\sqrt{\text{in.}}$ with a pre-load of 90% K_{Ic} . The time to failure for applied stress intensities (K_{Ii}) above the threshold(s) was independent of the pre-load. Tests on maraging steel suggest pre-loading has little effect on K_{Isc} in this steel. The observations are attributed to compressive stresses at the crack tip which result from the pre-loading.

The Boeing Company

THE STRESS-CORROSION RESISTANCE OF PRECIPITATION HARDENING STAINLESS STEEL IN 3.5% SODIUM CHLORIDE SOLUTION

C. S. Carter, D. A. Farwick, A. M. Ross, and J. M. Uchida

Objective

To determine the stress-corrosion resistance of commercially available high strength precipitation hardening stainless steels in 3.5% aqueous sodium chloride solution using precracked specimens. There were three goals: (1) to provide design oriented information, (2) to determine the influence of microstructure and alloy content, and (3) to compare the precracked specimen results with reported smooth specimen data and known service performance.

Approach

The following stainless steels, mostly in bar form, were evaluated: 17-7PH, PH15-7Mo, 17-4PH, PH13-8Mo, AM355, AM362, AM364, and Custom 455. Most of the steels were evaluated in two heat-treatment conditions (maximum strength and overaged). Stress-corrosion curves and threshold K_{Isc} values were determined. Fractographic and microstructural studies were conducted for alloy/heat-treatment condition.

Achievements

The semi-austenitic steels 17-7PH and PH15-7Mo were particularly sensitive to stress-corrosion cracking. Most of the martensitic steels were very resistant, with K_{Isc}/K_{Ic} values close to unity. An exception to this was AM362 which was very susceptible. The steels with low K_{Isc} values had low fracture toughness, and all stress-corrosion cracks propagated in an intergranular manner. The effect of alloy content could not be clearly defined. However, it did appear that a high Cr/Ni ratio and titanium had an adverse effect on fracture toughness. Overaging significantly increased fracture toughness and stress-corrosion resistance. Correlation with service performance was good except in one case; the alloy 17-4PH showed no stress-corrosion susceptibility whereas service failures have been experienced. Comparison of precracked specimen and smooth specimen data for certain materials revealed discrepancies. These are explained in terms of the necessity for pit development in the smooth specimens.

Publications

"Stress Corrosion Properties of High-Strength Precipitation Hardening Stainless Steels in 3.5% Aqueous Sodium Chloride Solution," C. S. Carter, D. G. Farwick, A. M. Ross, and J. M. Uchida, Boeing Document D6-25219, February 1970

The Boeing Company

DEVELOPMENT OF TEST SPECIMENS AND TEST PROCEDURES FOR
COMMERCIAL STEELS

H. R. Smith

Objective

Stress-corrosion testing techniques have not been standardized to the extent that data are reproducible from facility to facility. It is also difficult for a specification to gain acceptance if it contains procedures which are time-consuming and costly. Therefore it is desirable to find new specimens which will yield results rapidly. The objectives of the programs described in this section were to determine the variables that influence the level of K_{Isc} in steel alloys and to study the feasibility of using a more effective system to assess susceptibility to stress-corrosion cracking.

Approach

An important consideration affecting the determination of K_{Isc} appears to be the state of stress at the crack tip as it is affected by the thickness of the specimen. Specimens varying in thickness from 0.005 in. to 1.0 in. were prepared and tested in sodium chloride solution to find K_{Isc} . The tapered double cantilever beam configuration was investigated as a means of obtaining crack growth rates in salt solution at constant K_I levels. The reason for performing this test was to obtain rates in short periods of time and to obtain K_{Isc} by extrapolating the curve of K_I as a function of crack growth rate to zero rate. A characteristic of this specimen is that the K_I level does not change as the crack extends, and the crack growth rate can be established over a measured amount of extension. Other systems require that the rate be determined by finding the slope at any point on the curve of crack length as a function of time, a process which may introduce errors.

Achievements

It was found that K_{Isc} of 4340 steel alloy heat treated to a tensile strength of 205 ksi increases with decreasing thicknesses. The minimum value of K_{Isc} occurred when the thickness was equal to or greater than $2.5 (K_{Isc}/F_{tys})^2$.

Curves of crack growth rate as a function of K_I were obtained for 4340M, Maraging 250, and 9Ni-4Co-0.45C (bainitic) steels using the tapered double cantilever beam specimen. When these curves were extrapolated to zero growth rate, the equivalent K_I values agreed with K_{Isc} values reported for these materials. The maximum time required for a complete determination was two weeks.

Publications

"A Note on Stress Corrosion Cracking Rates," by S. Mostovoy, H. R. Smith, R. G. Lingwall and E. J. Ripling, to be published in Engineering Fracture Mechanics

Presentations

"A Note on Stress Corrosion Cracking Rates," by S. Mostovoy, H. R. Smith, R. G. Lingwall and E. J. Ripling, presented at the National Symposium on Fracture Mechanics, Lehigh University, August 25, 1969

The Boeing Company

DEVELOPMENT OF TEST SPECIMENS AND PROCEDURES FOR MEASURING THE STRESS-CORROSION CRACKING CHARACTERISTICS OF TITANIUM ALLOYS

H. R. Smith

Objective

There has been a serious inability to collate stress-corrosion data generated in different laboratories by different techniques. Precracked specimens, amenable to analysis by fracture mechanics, may provide the means by which standardization can be achieved. The objective of this program was to investigate the variables that influence the determination of the threshold stress intensity factor for (K_{Isc}) of titanium alloys.

Approach

- a) To establish that the fracture mechanics parameter, K_I , was more suitable in describing SCC than was net- or gross-section stresses.
- b) To optimize specimen design and testing procedures by investigating the variables which affect the determination of the threshold stress intensity factor, K_{Isc} .

The environment was aqueous 3.5% sodium chloride solution.

Achievements

Center cracked panels were subjected to sustained wedge force loading and exposed to an aqueous corrosive environment. This type of experiment provides a unique resolution of whether stress-corrosion cracking depends on K_I or net-section stress, because crack extension causes a decrease in K_I , but an increase in net-section stress at the crack tip. Dependency on K_I was proved when changes in crack growth rate followed similar changes in K_I .

The effect of thickness on K_{Isc} of a Ti-6Al-4V alloy was determined from sets of specimens varying in thickness from 0.010 in. to 0.750 in. obtained by machining to size. Over this range, K_{Isc} was insensitive to thickness. K_{Isc} was determined from sets of mill annealed Ti-8Al-1Mo-1V and Ti-6Al-4V specimens which had been precracked at different stress levels varying from 15 to 80% of K_{Ic} . The pre-cracking stress level caused changes in K_{Isc} that were no greater than those usually attributed to scatter.

A successful comparison of data generated at two different laboratories has also been achieved (3). Single-edge cracked specimens of Ti-8Al-1Mo-1V mill-annealed plate were evaluated by cantilever bending at NRL and by four-point loading at Boeing. In addition, the experiment was further varied at Boeing by adding an aqueous environment before and after loading. The K_{Isc} values obtained by NRL and Boeing were similar. The electrolyte/loading sequence was repeated for Ti-4Al-3Mo-1V, which is tougher and less susceptible than mill-annealed Ti-8Al-1Mo-1V. Again, similar K_{Isc} values were obtained. A further series of tests on commercially pure titanium, which is very tough, but susceptible to SCC, indicated lower values for K_{Isc} when the specimens were loaded in the presence of the electrolyte. Recently, a similar trend has been noticed in alpha and alpha-beta

commercial titanium alloys. Thus, it has been recommended that the specimen always be loaded in the presence of an aqueous environment.

Publications

"A Study of Stress-Corrosion Cracking by Wedge-Force Loading," H. R. Smith, D. E. Piper, and F. K. Downey, Boeing Document No. D6-19768, June 1967 (DDC Accession No. AD 661811); also Engineering Fracture Mechanics 1: 1, June 1968, pp. 123-128

"The Relationship Between Test Results and Service Experience," D. E. Piper, Symposium on the Engineering Practice to Avoid Stress-Corrosion Cracking, AGARD Conference Proceedings No. 53, Feb. 1970; Boeing Document No. D6-24473, Oct. 1969

"Stress Corrosion Testing," H. L. Craig, Jr., D. O. Sprowls, and D. E. Piper, to be published as Chapter in ECS Corrosion Monograph Series Book, Corrosion Testing, Edited by W. H. Ailor

Presentations

"Quantitative Test Techniques for Environmental Cracking," D. E. Piper, H. R. Smith, and F. K. Downey, presented by D. E. Piper at NACE 23rd Annual Conference, Los Angeles, California, March 13-17, 1967

"A Study of Stress-Corrosion Cracking by Wedge-Force Loading," presented by H. R. Smith at the National Symposium on Fracture Mechanics, Lehigh University, Bethlehem, Pa., June 19-21, 1967

"A Review of Stress Corrosion Testing Methods," presented by D. E. Piper at ASTM Fall Meeting, Atlanta, Georgia, October 1968

"The Relationship Between Test Results and Service Experience" by D. E. Piper, presented during the Symposium on the Engineering Practice to Avoid Stress Corrosion Cracking, 29th Meeting of the Structures and Materials Panel of AGARD, Istanbul, Turkey, Sept. 28, 1969

"The Selection of Pre-cracked Specimens for Characterization of Stress Corrosion," D. E. Piper and H. R. Smith, presented at WESTEC Meeting, Los Angeles, March 11-12, 1970

"Standardization of Test Techniques for Stress Corrosion Cracking," D. E. Piper, presented to Working Group on Stress Corrosion of Structures and Materials Panel of AGARD in Athens, Greece, April 1970

The Boeing Company

A METHOD OF MEASURING CRACK GROWTH RATES IN BRITTLE MATERIALS

N. M. Lowry

Objective

The rate at which a crack progresses is an important parameter which is necessary in understanding the mechanism of stress-corrosion cracking. Previous measurements of crack propagation rate in aqueous environment were tedious and subject to errors of judgment by the observer. The objective of this study was to eliminate these errors and automate the rate measurement.

Approach

There are two methods of applying grid conductors: vacuum deposition through masks and selective etching. Selective etching can produce lines as small as 0.0005 in. wide. Selective etching is accomplished by first applying a blanket coating of the resistor material, applying a coating of photoresist, and then exposing the photoresist through a master with a carbon arc to define the grid. The unexposed photoresist is soluble in xylene and the unprotected conductor can be dissolved with a suitable acid. The grid is placed on the surface of the specimen across the anticipated crack path, electrically insulated by oxide films from both metal and corrodent. Electrical resistance of the grid is monitored and indicates the severing of individual elements.

Achievements

An accurate network of resistors can be prepared with a suitable combination of materials that will provide a reproducible method of measuring the propagation rate of brittle-type fractures in small specimens.

Publications

"A Method of Measuring Crack Propagation Rates in Brittle Materials," N. M. Lowry, O. K. Mulkey, J. M. Kuronen, and J. W. Bieber, Boeing Document D6-60072, May 1967 (DDC Accession No. AD 661814)

The Boeing Company

TERMINAL FRACTURE OF TITANIUM ALLOYS CONTAINING STRESS-CORROSION CRACKS

C. S. Carter

Objective

To confirm that rapid brittle fracture occurred under plane strain conditions when the stress intensity at the tip of a propagating stress-corrosion crack was equal to K_{Ic} .

Approach

Approximately one-hundred precracked single-edge notch specimens of Ti-6Al-4V and Ti-4Al-3Mo-1V previously sustain loaded in 3.5% aqueous sodium chloride solution were examined. The stress intensity at which stress-corrosion was terminated by rapid fracture was established for each specimen and compared with the fracture toughness K_{Ic} determined by a conventional rising load test.

Achievements

Rapid brittle fracture occurred when the stress intensity at the stress-corrosion crack tip was equal to K_{Ic} . The fatigue precrack in specimens loaded to stress intensities below K_{Isc} was not affected by the environment. The results provide a justification for estimating K_{Ic} from broken specimens by this technique.

Publications

"Terminal Fracture of Titanium Alloys Containing Stress Corrosion Cracks,"
C. S. Carter, Boeing Document D6-19771, 1968

The Boeing Company

THE STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

M. J. Blackburn and J. C. Williams

Achievements

The metallurgical and mechanical factors which influence the stress-corrosion cracking (SCC) of titanium alloys in aqueous solutions are considered. It is shown that failures of alpha phase in Ti-Al alloys and in commercial alloy Ti-8Al-1Mo-1V under SCC conditions occur by cleavage on the $\{10\bar{1}8\} - \{10\bar{1}7\}$ plane of the hexagonal phase. The general phase structure of these alloys is described and it is shown that the $\alpha - \alpha + \alpha_2$ (Ti₃Al) transformation is of considerable importance in determining susceptibility. In the commercial alloy, the presence of the beta phase and the martensitic phases reduce susceptibility. Results on the binary Ti-Al alloys indicate that the onset of susceptibility to SCC occurs between 4-5% aluminum which correlates with a change from homogeneous to planar dislocation arrangements. The influence of stress on the nucleation and propagation of a crack has been analyzed for precracked specimens using the methods of linear elastic mechanics. From these results several factors which influence the nucleation stage are discussed. It is proposed that for a propagating crack there are two components of fracture, i. e., electrochemical and mechanical. At low alpha phase strength levels or aluminum contents the electrochemical component predominates while at higher strength levels or aluminum contents the mechanical component increases. Some qualitative correlations are made between mechanical properties, deformation structures, fracture mode, and susceptibility to SCC.

Publications

"Metallurgical Aspects of Stress Corrosion Cracking of Titanium Alloys," by M. J. Blackburn and J. C. Williams, presented at Conference on Fundamental Aspects of Stress-Corrosion Cracking, Ohio State University, September 11-15, 1967; published in Proceedings of Conference, NACE, (1969) p. 620

The Boeing Company

RELATIONSHIP BETWEEN COMPOSITION, MICROSTRUCTURE, AND STRESS-CORROSION CRACKING (IN SALT SOLUTION) IN TITANIUM ALLOYS

R. E. Curtis

Objective

To determine the influence of composition and microstructure on the stress-corrosion cracking (SCC) behavior of titanium and its alloys.

Approach

Four alpha titanium alloys and nine alpha-plus-beta titanium alloys were characterized to relate phase composition and associated microstructure to SCC in 3.5% aqueous sodium chloride solution. The effect of alpha stabilizers such as oxygen and aluminum, and neutral strengtheners such as tin and zirconium on SCC was determined using commercial alpha alloys. These alloys were also used to examine the influence of grain size, grain morphology, degree of order, and dislocation structure on SCC. The effect of beta stabilizing additions was also investigated using commercial or near-commercial alpha-plus-beta alloys. Both isomorphous stabilizers (Mo and V) and eutectoid stabilizers (Fe, Cu, and Si) were investigated. Microstructural changes were achieved in these alloys by varying heat-treatment conditions and by thermomechanical treatment.

Achievements

The resistance to SCC was found to be dependent on microstructure for a wide range of titanium alloy compositions and thermomechanical treatments. Alloys that exhibited planar slip in the alpha phase also showed pronounced susceptibility to SCC. Planar slip is characteristic of alloys containing: (1) high oxygen (3800 ppm, Ti-707); (2) aluminum in excess of approximately 6 wt-% (e. g. Ti-6Al-4V, Ti-7Al-2.5Mo, and Ti-8Al-1Mo-1V); or 5 wt-% or greater aluminum and 2.5 wt-% or greater tin (Ti-5Al-2.5Sn and Ti-5Al-5Sn-5Zr). A low oxygen, commercially pure titanium alloy (Ti-50A) deformed more homogeneously and was immune to SCC under the conditions of these tests.

Formation of ordered domains of Ti_3Al or $Ti_3(Al, Sn)$ in the alpha phase further restricted slip and increased stress-corrosion susceptibility.

Relative stress-corrosion resistance improved with an increased volume percent beta-phase stabilized by isomorphous-type elements Mo or V or both. This has been attributed to the ability of the beta-phase to arrest stress-corrosion cracks that propagate readily through the alpha phase. However, decomposition of the beta-phase may mitigate the ductile behavior of the phase and markedly reduce the stress-corrosion cracking resistance. For example, precipitation of the omega-phase in the beta phase of the alloy Ti-70 is thought to be responsible for reducing $K_{I_{SCC}}$ from 70 ksi $\sqrt{in.}$ to 54 ksi $\sqrt{in.}$ A large volume fracture of alpha-phase in a beta-phase matrix resulted in similar low threshold values. In alloys containing Cu, or Si, low stress-corrosion properties were attributed to precipitation of alpha-phase and intermetallic compounds Ti_2Cu or Ti_5Si_3 in the beta-phase.

Publications

"Relationship Between Composition, Microstructure, and Stress-Corrosion Cracking in Titanium Alloys," R. E. Curtis, Boeing Document No. D6-23716, October 1968 (DDC Accession No. AD 685380); also published by R. E. Curtis, R. R. Boyer and J. C. Williams in ASM Transactions Quarterly 62, June 1969, p. 457

The Boeing Company

TITANIUM ALLOY DEVELOPMENT

R. E. Curtis and P. T. Finden

Objective

To develop high strength titanium alloys with improved resistance to stress-corrosion cracking (SCC) in neutral aqueous solutions.

Approach

Previous work on commercial and near-commercial titanium alloys has shown that both composition and microstructure have a pronounced effect on stress-corrosion susceptibility. In this program, composition changes which have been shown to be consistent with improved resistance to SCC and improved fracture toughness were studied. Twenty-three experimental compositions have been selected to determine the contribution of individual alloying elements and to establish optimum compositions. The alloys are characterized by reduced Al, added Zr, and a relatively large volume percent beta phase compared to most commercial alpha-beta alloys. The aluminum-zirconium combination has been balanced to maintain alloy strength and avoid formation of the α_2 (Ti₃Al) phase. Molybdenum and vanadium have been added to stabilize up to 25 volume percent beta. In addition, four beta eutectoid stabilizers, silicon, copper, nickel, and iron, have been added to investigate the conditions of intermetallic compound formation and to determine their effects on mechanical properties. The alloys were cast in 8-lb. ingots and fabricated to 0.5-in.-thick plate.

Achievements

Experimental alpha-beta alloys have been developed which have improved stress-corrosion resistance and toughness compared with commercial titanium alloys of similar strength. These improvements have been achieved over a ultimate tensile strength range from 140 to 200 ksi. For example, at 150 ksi the experimental alloys were approximately 80% more resistant to SCC and 46% tougher than beta processed Ti-6Al-4V. The most promising alloys contain relatively low aluminum, added zirconium, molybdenum, vanadium and/or iron and limited amounts of silicon or nickel. Small zirconium additions were found to increase strength without reducing either resistance to SCC or fracture toughness. Molybdenum and/or vanadium additions also increased strength, but caused small reductions in SCC resistance and toughness.

The influence of beta eutectoid stabilizers on SCC was dependent on both the amount added and on the kinetics of intermetallic compound formation. Silicon additions within the solubility limit of silicon in beta titanium resulted in maximum fracture properties at a tensile strength of 200 ksi. Similarly, small nickel additions resulted in optimum fracture properties at an intermediate tensile strength level of about 175 ksi. Additions of greater amounts of nickel caused pronounced embrittlement. In thin foil and optical metallographic studies, Ti₂Ni particles were detected in the higher nickel alloys ranging in diameter from 0.05 μ to 2 μ . In contrast to nickel, iron additions exceeding the solubility limit of iron in beta titanium did not cause either compound precipitation or embrittlement. Apparently, the kinetics in this system are sufficiently sluggish to preclude Ti-Fe formation even during a slow furnace cool and subsequent 550°F/25ksi/1000 hr. exposure.

ARPA funds have been limited to the stress-corrosion testing phase of this total titanium alloy development program. Further development of these alloys (i. e., new compositions, scaling-up of ingot size for promising experimental alloys, etc.) is being continued wholly under Commercial Airplane Group funding.

The Boeing Company

INFLUENCE OF MICROSTRUCTURE ON THE FRACTURE MODE OF
TITANIUM ALLOYS

J. C. Williams, R. R. Boyer, and M. J. Blackburn

Objective

The recent resurgence of interest in titanium has resulted in the investigation of many aspects of the mechanical, structural, and chemical behavior of titanium alloys. One area of obvious importance is the fracture behavior of titanium alloys and the factors that influence it. An attempt was made to relate observations of fracture behavior and topography to structural and environmental factors.

Approach

Information on fracture modes at ambient temperatures was obtained using standard techniques of electron fractography. All replicas were prepared by a two-stage technique using cellulose acetate for the first stage and germanium-shadowed carbon for the final stage.

Achievements

The ductile fracture of alpha, beta, and (alpha + beta) phase alloys was shown to occur predominantly by a microvoid coalescence mechanism, but some examples of more ductile behavior were observed in the relatively pure, low-strength alpha-phase.

There is a continuous change in fracture behavior of the alpha phase: alternating shear at low strengths, microvoid coalescence at intermediate strengths (decreasing dimple size with increasing strength), and cleavage fracture at high strengths. Cleavage fracture of the alpha-phase becomes more prevalent (a) at higher yield stresses, (b) at larger grain sizes, (c) in the presence of a sharp notch, and (d) if slip is localized to planar bands.

The fracture topography of macroscopically brittle beta-phase alloys differs markedly from the cleavage fractures associated with brittle fracture of the alpha-phase. Dimples which in most cases are small and shallow are observed in such alloys. The observed embrittlement is associated with formation of a high-volume fraction of small (100 to 1,000 Å) dispersed omega-phase precipitates.

It is shown that the combined action of stress and an active environment can result in brittle fracture of the alpha-phase or the beta-phase in a variety of alloys. Stress-corrosion cracking failures of the alpha-phase closely resemble cleavage fracture produced in air; furthermore, the various metallurgical factors that promote cleavage also increase susceptibility to stress-corrosion cracking. The structural factors that influence susceptibility of a beta-phase alloy appear to be more complicated, as these alloys are usually in their most ductile condition when susceptible to stress-corrosion cracking. There is some evidence that planar slip is observed in susceptible alloys, which may be one structural parameter of importance. It is suggested, however, that the electrochemical properties of the beta-phase may also be an important factor in determining susceptibility.

Publications

"The Influence of Microstructure on the Fracture Topography of Titanium Alloys,"
J. C. Williams, R. R. Boyer, M. J. Blackburn, Boeing Document No. D6-23622,
June 1968 (DDC Accession No. AD 685379); also ASTM STP 453, Electron
Microfractography (1969)

The Boeing Company

STRESS-CORROSION CRACKING OF COMMERCIAL TITANIUM ALLOYS

J. C. Williams

Objective

Stress-corrosion cracking (SCC) of titanium alloys in salt water environments has recently been the subject of intensive investigations. As a result, the relative susceptibility of many of the commercial alloys has been catalogued, although no attempt has been made to explain the observed differences in susceptibility. Alloys that are susceptible to SCC fail by slow growth of a crack under sustained load, followed by fast fracture when the critical crack length is reached. In this study, attention was focused on explaining the occurrence of cleavage fracture of some titanium alloys in salt water environments in terms of metallurgical factors.

Approach

Electron fractography, electron metallography, and thin-foil electron microscopy were employed to study three commercial titanium alloys. Of these alloys, Ti-8Al-1Mo-1V was shown to be the most susceptible, Ti-6Al-4V to be less susceptible, and Ti-4Al-3Mo-1V to be highly resistant to SCC.

Achievements

The SCC of Ti-8Al-1Mo-1V and Ti-6Al-4V were shown to occur by cleavage of the alpha-phase and by ductile rupture of the beta-phase.

Evidence was presented to show that the beta-phase or transformed beta-phase act as crack arrestors.

Planar dislocation arrangements were shown to exist in Ti-6Al-4V and Ti-8Al-1Mo-1V, but not in Ti-4Al-3Mo-1V. Variations in susceptibility were qualitatively shown to correlate with the development of such dislocation arrangements.

Generation of large stresses normal to the fracture plane were shown to be associated with planar dislocation arrangements, and these stresses are thought to promote SCC.

Publications

"Some Observations on the Stress-Corrosion Cracking of Three Commercial Titanium Alloys," J. C. Williams, Boeing Document No. D6-19553, September 1967 (DDC Accession No. AD 661812); published in ASM Transactions Quarterly 60: 4, Dec. 1967, p. 646

The Boeing Company

AQUEOUS STRESS CORROSION IN TITANIUM ALLOYS

D. N. Fager and W. F. Spurr

Objective

The objective of this study was to determine:

- a) the effect of heat-treatment condition
- b) the necessity for precracking
- c) the tendency for cracks not to grow normal to the principal stress axis and
- d) the effect of thickness on stress-corrosion cracking of titanium alloys.

Approach

Relatively little was known about the phenomenon of aqueous SCC in titanium alloys at the start of this investigation. The approach was to test a number of alloys in different heat-treatment conditions and to examine failed specimens metallurgically to determine possible reasons for changes in susceptibility. The alloys studied were Ti-8Al-1Mo-1V, Ti-6Al-4V, Ti-4Al-3Mo-1V, Ti-5Al-2.5Sn, and Ti-13V-11Cr-3Al. The effect of specimen orientation relative to the preferred (0001) orientation in a single sheet of Ti-8Al-1Mo-1V was studied extensively. The effect of thickness on susceptibility was studied in Ti-6Al-4V. Numerous attempts were made to obtain SCC effects in smooth specimens.

Achievements

It was verified that in Ti-8Al-1Mo-1V, Ti-6Al-4V, and Ti-4Al-3Mo-1V the alpha-phase was susceptible and the beta and martensitic phase immune to SCC in aqueous sodium chloride solution. In the alpha-phase fracture must occur near the (0001) plane irrespective of specimen orientation relative to the preferred (0001) planes. It is suggested that this single fracture plane limitation resulted in the influence of stress state on the degree of susceptibility. Fracture of the beta-phase in the alloy Ti-13V-11Cr-3Al was found to occur on or near the (001). In the uniaxial stress state, the beta phase of the Ti-13V-11Cr-3Al alloy was found to be significantly more susceptible than the alpha phase of the Ti-8Al-1Mo-1V alloy.

Publications

"Some Characteristics of Aqueous Stress Corrosion in Titanium Alloys," D. N. Fager and W. F. Spurr, Boeing Document No. D6-60083, Sept. 1967 (DDC Accession No. AD 661813); published in ASM Transactions Quarterly 61: 2, June 1968, p. 283

The Boeing Company

METHANOL CRACKING OF TITANIUM-8Al-1Mo-1V

D. N. Fager

Objective

Titanium-8Al-1Mo-1V alloy is more sensitive to environmental cracking in methanol than in aqueous 3.5% sodium chloride solution. This was demonstrated when premature failures were obtained in smooth specimens of Ti-8Al-1Mo-1V in methanol, but not in salt solution (at 0.005/min. strain rates). The purpose of this study was to determine whether the greater susceptibility in methanol was due to either metallurgical effects (i. e., a susceptible beta-phase) or to the occurrence of fracture on other planes in the α phase besides the (0001) plane.

Approach

In a plate of Ti-8Al-1Mo-1V alloy, specimens of two orientations relative to the (0001) preferred orientation were tested in methanol. Specimens from these orientations (from the same plate) had been previously evaluated in 3.5% NaCl solution.

Achievements

The crack morphology was shown to be the same for methanol and 3.5% NaCl solution, i. e., in both environments the beta phase was immune and cleavage fracture in the alpha-phase was restricted to near the (0001) plane. Failure in precracked specimens occurs at a lower stress-intensity level in methanol than in salt solution. This is consistent with the difference seen in smooth specimen data. This demonstrates that a lower stress (or strain) is required for cleavage of alpha grains in methanol. An interesting observation is that crack propagation is an order of magnitude slower in methanol than in salt solution. Since the fracture characteristics are identical in both environments, the lower fracture stress in methanol must be a result of the metal-solution interface reaction.

Publications

"Methanol Cracking of Titanium-8Al-1Mo-1V," D. N. Fager, Boeing Document No. D6-23717, Oct. 1968 (DDC Accession No. AD 685381); published *Corrosion Science* 10, 1970, pp. 175-177

The Boeing Company

PREFERRED ORIENTATION IN TITANIUM-8Al-1Mo-1V

D. N. Fager

Objective

To determine variations in preferred orientation in Ti-8Al-1Mo-1V and the deformation mechanisms responsible for them.

Approach

The preferred orientation was varied by altering the processing (i. e., temperature and sequence of rolling). The possible deformation modes contributing to the preferred orientations were then analyzed.

Achievements

A processing technique for producing, in titanium sheet, the highest anisotropy possible was developed. A strain-induced transformation is offered as an explanation for the texture produced by this processing. A processing technique for significantly eliminating this high anisotropy was also developed.

The Boeing Company

AQUEOUS STRESS-CORROSION SUSCEPTIBILITY OF Ti-8Al-1Mo-1V AS INFLUENCED BY PREFERRED ORIENTATION AND NEAR PLANE STRESS CONDITIONS

D. N. Fager

Objective

Previous work on this program has shown that fracture of the alpha-phase in neutral aqueous solutions is limited to near the basal plane. Because of the anisotropy of fracture in the hcp structure, it was felt that highly textured material should be significantly influenced by the stress state. The purpose of this investigation was to determine the influence of orientation (defined as preferred basal plane orientation relative to specimen orientation) on stress-corrosion susceptibility under near plane stress conditions.

Approach

An attempt was made to obtain plane stress conditions by varying (1) specimen thickness, (2) specimen orientation relative to the preferred orientation, and (3) material heat treatment. Susceptibility to aqueous stress corrosion was determined as a function of these variables. Single-edge notched specimens were either loaded in tension or in bending.

Achievements

Soon after initiation of this program, it was learned that in thin specimens (0.020 in.) the orientation determined to a large extent whether near plane stress conditions could be approached (i. e., near plane stress could not be obtained in thin specimens independent of orientation) in an intermediate yield strength condition. The susceptibility was found to vary with the orientation such that when near plane stress conditions were approached, a significant decrease was observed. When the material was in a low yield strength condition, the same trend was noted; however, when the material was in an intermediate yield strength condition decrease in susceptibility was found in all orientations. This was consistent with the explanation that plane stress conditions tend to promote immunity.

The importance of this work is that susceptibility to aqueous stress corrosion under near plane stress conditions is much more sensitive to preferred orientation and yield strength level than susceptibility under plane strain conditions. This is shown in the following example: the effect of the ordering transformation in Ti-8Al-1Mo-1V was shown to influence susceptibility significantly in thin specimens (0.020 in.), while only a slight effect was noted in thick specimens (0.40 in.). That is, the only apparent effect of the ordering transformation was to lower the yield stress and thus allow plane stress conditions to be more nearly approached in thin specimens.

An additional complicating factor associated with thin specimens (not necessarily with plane stress conditions) was the difference in susceptibility obtained with different loading techniques. If thin specimens were loaded prior to exposure to the

salt solution environment, a lesser degree of susceptibility was found than if they were loaded after exposure. This was not noted in thick specimens of the same material and orientation.

The variables studies in this investigation can explain in large part the tremendous discrepancies in susceptibility noted among various investigators. In thin specimens, susceptibility is significantly influenced by preferred orientation, relatively small changes in yield strength level with heat treatment (~ 10 ksi), and the sequence of loading and exposing specimens to salt solution.

The Boeing Company

EFFECT OF OXYGEN ON THE MECHANICAL AND STRESS-CORROSION PROPERTIES OF BINARY TITANIUM-ALUMINUM ALLOYS

G. P. Rauscher

Objective

To determine the effect of interstitial oxygen on the phasal reactions in titanium-rich binary titanium-aluminum alloys, and to evaluate the stress-corrosion susceptibility and mechanical properties of these alloys as a function of alloy content and phasal constitution.

Approach

Nine titanium-aluminum alloys were investigated—4, 6, and 9 wt-% aluminum in titanium—each at three levels of oxygen content, nominally 0.05, 0.20, and 0.40 wt-% oxygen. Electrical resistivity measurements were utilized to determine the variation of phase transformation temperature with composition. Transmission electron microscopy was employed to determine phasal constitution as a function of heat treatment. Tensile and fracture toughness properties for selected heat treatments were determined by conventional means. Stress-corrosion susceptibility was assessed utilizing precracked single-edge notched tensile specimens in 3.5% sodium chloride solution.

Achievements

a) Phasal Reactions

No ordering reaction ($\alpha - \text{Ti}_3\text{Al}$) was observed in the 4 wt-% aluminum alloys. In the 6 wt-% aluminum alloys, short range ordering was observed at temperatures below about 600°C. The 9 wt-% aluminum alloys all exhibited long range order, the critical temperature varying from 805°C in this low-oxygen alloy to 835°C in the high oxygen alloy; oxygen was found to inhibit the rate of formation of Ti_3Al and also to distort the normal elipsoidal morphology of Ti_3Al . The alpha and beta transus temperatures of the alloys studied were elevated as much as 70°C by the addition of 0.40 wt-% oxygen.

b) Mechanical and Stress-Corrosion Properties

1. The UTS of the 4 wt-% aluminum alloy was increased from 76 ksi to 125 ksi by the addition of 0.40 wt-% oxygen, while the ductility was reduced from 22 to 15 percent elongation at fracture. Only the 0.40 wt-% oxygen alloy was found to be susceptible to stress-corrosion cracking.
2. The tensile and SCC properties of the 6 wt-% aluminum alloys were not affected by short range ordering. The low oxygen alloy was not susceptible to SCC, whereas the medium and high oxygen alloys exhibited susceptibility. UTS and elongation at fracture varied from 100 ksi and 17%, respectively, in the low oxygen alloy to 133 ksi and 8%, respectively, in the high oxygen alloy.
3. In the as-quenched condition the 9 wt-% aluminum, 0.05 wt-% oxygen alloy exhibited a UTS of 95 ksi, an elongation at fracture of 20%, and a K_{Isc} of

38 ksi $\sqrt{\text{in}}$. On aging these properties were reduced to 70 ksi, 2% elongation, and 15 ksi $\sqrt{\text{in}}$, respectively. The 0.20 wt-% oxygen alloy exhibited a UTS of 105 ksi and 57 ksi in the quenched and ordered conditions respectively. Ordering also caused the alloy to fail without yielding. Ordering enhanced the crack growth rate in salt solution, but did not alter the value of $K_{I_{sc}}$. The 0.40 wt-% oxygen alloy was found to be extremely brittle in all conditions tested.

The Boeing Company

DISLOCATION STRUCTURES IN TITANIUM-ALUMINUM-OXYGEN TERNARY ALLOYS
RESULTING FROM CYCLIC STRAINING

R. R. Boyer

Objective

To determine the effects of oxygen and aluminum contents on the dislocation behavior in titanium for the purpose of gaining an insight into the mechanisms of corrosion fatigue in this system.

Approach

Aluminum and oxygen additions to titanium are known to promote planar slip when tested in uniaxial tension. The onset of this planar slip mode of deformation has, in turn, been related to stress-corrosion cracking in titanium alloys. It was the purpose of this investigation to determine if these alloying additions had the same effect on the dislocation behavior when deformation occurs by cyclic straining. As the fracture modes of titanium alloys are similar in nature when crack propagation occurs by stress-corrosion cracking or corrosion fatigue, this program was initiated to determine if planar slip might account for, or at least play a role in corrosion fatigue.

The alloys tested had aluminum contents ranging from 0-9 wt-% and oxygen contents ranging from about 500-3000 ppm. Specimens were tested in two different ways, tension-tension and bending fatigue. The bending fatigue specimens were rather crude, making determination of the strains involved very difficult.

After testing the specimens, sections were cut out for thin foil examination and prepared using the window technique as described previously by Blackburn and Williams. They were examined on a Philips EM-200 electron microscope equipped with a goniometer lens with $\pm 45^\circ$ tilt, a decontamination device, and a precision dark-field attachment.

Achievements

Specimens of high purity titanium, Ti-2Al, Ti-5Al, and Ti-8Al, were tested in bending fatigue. Deformation in the high purity titanium occurred by slip and twinning. The twins were primarily of the $\{11\bar{2}2\}$ type while slip was rather homogeneous and $\langle 11\bar{2}0 \rangle$ in nature. The addition of 2% aluminum eliminates the twinning mode of deformation. The fatigue damage occurs by a homogeneous slip mechanism resulting in a random dislocation distribution. A cell structure is also developed in this alloy. Slip becomes more planar in 5% aluminum alloy, predominantly on prismatic and pyramidal planes. With the titanium-8% Al alloy, slip is still planar with a larger spacing between slip bands and less dislocation debris. Ordering of this alloy further enhances this trend. Heavily deformed regions of the 5% and 8% aluminum alloy show a more general deformation.

The specimens tested in tension-tension (Ti-4Al, Ti-6Al, Ti-9Al with oxygen contents between 0.06 and 0.3 wt-%) show trends similar to those observed in the bending fatigue tests. With higher aluminum and oxygen additions the slip became more planar, the slip-band spacing became wider, and decreasing amounts of dislocation debris are observed. No cell structure or twinning was observed in any of these alloys.

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ARPA Coupling Program on Stress-Corrosion Cracking

Final Technical Report: Second Edition

B. F. BROWN

*Physical Metallurgy Branch
Metallurgy Division*

Sponsored by

*Advanced Research Projects Agency
ARPA Order No. 878*

October 27, 1971



NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

The technical background, organization, and *modus operandi* of the ARPA coupling program on stress-corrosion cracking are summarized. The problem of interpreting the data from smooth stress-corrosion cracking specimens is discussed. This is followed by a summary of technical achievement highlights in narrative form treating specimen types, titanium alloys, high-strength steels, aluminum alloys, and surface sciences. An Abstracts of Achievements section (abstracts arranged by organization) is the most important part of this report, for it gives not only indications of technical contributions but also the literature citations where the interested reader can examine the detailed account of a given topical area. The Abstracts of Achievements section includes a subject index.

The program was one of multiple goals, including experimentation involving coupling NRL with academic personnel and amplifying NRL's capabilities by the addition of an industrial contractor. Since the present report is a purely technical one, it does not treat these non-technical goals. The present report represents an updating of NRL Report 7168 to include material published during the phase-out year of the program.

PROBLEM STATUS

This is a final technical report.

AUTHORIZATION

NRL Problem M04-08A
ARPA Order No. 878

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ARPA COUPLING PROGRAM ON STRESS-CORROSION CRACKING

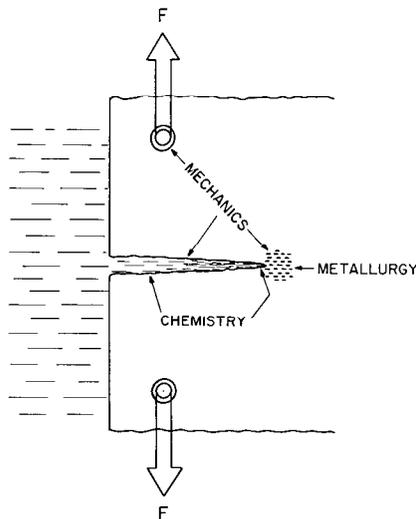
Final Technical Report

INTRODUCTION

History

By 1966 the phenomenon of SCC had affected all the military services (and NASA); had caused serious surprises to the designers of aircraft, submersibles, and rockets; and had involved all three major families of high strength structural alloys—titanium, steels, and aluminum. The Advanced Research Projects Agency (ARPA) of the Department of Defense recognized both the military importance of the problem and its technical complexity, compounding as it does the difficulties of the brittle fracture problem with chemical reactions occurring inside inaccessible cracks (Fig. 1). ARPA also was aware of new developments in surface physics and surface chemistry, some of which might be expected ultimately to afford advances in the science of metallic corrosion. ARPA therefore asked the Naval Research Laboratory to organize an intensive attack on the problem of the SCC of high-strength structural alloys with provision for coupling science to technology and also for coupling academic laboratories with an industrial laboratory and a government laboratory.

Fig. 1 - The three scientific elements of stress-corrosion cracking. Progress requires attention to all three.



Organization

The principal member institutions were NRL, The Boeing Company, Lehigh University, and Carnegie-Mellon University, to which was added Georgia Institute of Technology because of special capabilities in surface physics.

Two other universities had supplementary roles for special purposes: At a time when graduate students specializing in the electrochemistry of corrosion were almost

nil, both in the program and nationally, such students became enrolled at American University under well-qualified thesis supervision; hence, American University became a supplementary member of the program to ensure the involvement of at least a few electrochemistry graduate students, in this case studying the role of anions in corrosion reactions. At the University of Florida, Professor M. Pourbaix became available as a visiting professor and consultant to the program, and for this reason the University became a supplementary member, concentrating on experimental methods to apply Pourbaix' potential-pH method for analyzing the corrosion behavior of complex alloys (commencing with chromium steels).

There were no exclusive charters at any of the institutions, but in general the emphasis at Lehigh was on surface chemistry, that at Carnegie-Mellon was on physical metallurgy, and that at Georgia Tech was on surface physics. NRL contributed to both basic and applied research, and Boeing's role was to amplify the capabilities of NRL. Boeing and NRL filled an additional role by providing opportunities for graduate students to observe and/or participate in applied research in the course of their graduate careers.

SCC, which is caused by the conjoint action of a corrodent and a stress which may be constant, represents one of the limiting cases of corrosion fatigue (as R-1), which differs from SCC in that in corrosion fatigue the stress is necessarily fluctuating. For this reason corrosion fatigue in a limited sense was considered an appropriate subject to be included in the program, and particularly appropriate for a DoD program, since corrosion fatigue is said to be the major cause of failures in vehicles and in moving machinery. Analysis shows that there is no such thing as a simple method of generating the general engineering corrosion-fatigue characteristics of a given alloy, however, and accordingly from midprogram onward the corrosion-fatigue studies were restricted to academic research on mechanisms. Research on corrosion-fatigue mechanisms was also conducted at NRL with Navy funds but associated with the program.

The alloy families of interest were titanium, high-strength steels, and aluminum, and the relative emphasis on the three systems was set at 3:2:1. The reason for this relative emphasis was not alone the relative importance of the problem to DoD, but also the relative amount of accumulated knowledge in the three systems and the activity of producers on the problem in the area of their own products.

Modus Operandi

The program was conducted as a national one in the sense that it was fully integrated into the national technical community. Reports from the program were given unlimited distribution, and attendance at the quarterly meetings (described briefly below) was open to personnel from outside the program, subject only to the limitations of manageability. It was found that keeping the agenda of the quarterly meetings to a single narrow topic (e. g., titanium alloys) accomplished several ends: It permitted an in-depth review of the subject matter, it eased the problem of limiting outside participants, and it promoted interchange between persons working in different disciplines such as surface physics, electrochemistry, metallurgy, crystallography, and mechanics. The program profited immensely by the regular participation of outsiders.

The program was integrated into the national technological community in another manner, namely, by sharing costs. For example, in studies in which, to have technological significance, portions of large heats (batches) of alloys were required, these alloy heats were sometimes procured by other DoD interests, and the small amounts required for SCC studies were traded to the ARPA project in return for the stress-corrosion information generated. Mixed support of another type was practiced in which students whose stipends were paid from one source had the costs of their laboratory supplies and services paid by the ARPA program. These jointly supported activities

provided not only breadth of contact but also economies which in the case of large alloy heats were of important magnitude.

Also as part of the design of the program to serve the national technological community, personnel in the program were encouraged to present the output of their research at various types of technical meetings. The effectiveness of this policy is evident in the Presentations section of the Abstracts of Achievements.

Documentation

This report is primarily technical, but a brief background account is given here for the interested reader.

As another part of the final reporting sequence, there is in preparation a monograph on the state of the art of stress-corrosion cracking (SCC) of titanium alloys, high-strength steels, and aluminum alloys. That monograph is designed to be not only a summary of what has been contributed to the subject by the ARPA program, but a state-of-the-art summary without restriction as to source of contributions. The monograph will therefore be the most useful technical summary of the program for most purposes, for in it the pertinent output of the program is integrated into the entire literature on the subject.

The present report is limited to contributions from the ARPA program. Such contributions from a program as large and as productive as this one cannot be *detailed* in a manageable fashion in a single document such as the present report, but the key contributions are given herein in a consolidated narrative form. In addition, Abstracts of Achievements, modeled after the Interdisciplinary Laboratory reports, are given, together with references to the literature, so that the reader has a key directly to the technical literature of interest to him. The present report was written at the end of the program, and by the nature of the publication machinery of the technical societies many of the manuscripts generated by the program have not yet been printed. In such cases the journal or society is noted so that the interested reader can monitor the appropriate literature for the appearance of a paper of special interest. Requests for reprints should be directed to the individual authors. Qualified recipients may request from the Defense Documentation Center those reports for which accession numbers are given.

In the present report the author uses the term *stress-corrosion cracking* (SCC) to designate a cracking process caused by the conjoint action of a stress (which need not be fluctuating), and a corrodent. The term *corrosion fatigue* is used to designate a cracking process caused by the conjoint action of a fluctuating stress and a corrodent. The terms are thus based upon macrophenomenology rather than mechanisms, and the introduction of new terms such as *corrosion-assisted crack growth* and *subcritical cracking* becomes unnecessary.

The emphasis on reporting was to get contributions presented expeditiously at standard technical society meetings and published expeditiously in their journals, and the function of the quarterly reports was most importantly to notice the writing and the publication of such manuscripts in the standard literature.

THE PROBLEM OF THE MACROSCOPIC TEST

Regardless of how small the scale of events which may cause SCC, ultimately it is the macroscopic phenomenon which must be controlled. The traditional method for

characterizing SCC was to stress a specimen in a corrosive environment and report time to failure, usually meaning time for complete separation of the specimen. Although this parameter has afforded progress, particularly in the low-strength alloys, it is a defective parameter because it represents the undifferentiated *sum* of the effects of three processes, (a) incubation (usually film breakdown plus corrosion pitting), (b) SCC, and (c) terminal mechanical overload fracturing (Fig. 2). If an alloy is not susceptible to pitting, then a (smooth) specimen may give an indication of an infinite time to failure, i. e., the alloy may appear to be immune to SCC, whereas in fact it may be highly susceptible to stress-corrosion crack *propagation*. (Titanium alloys in water exemplify this behavior.) Alloys with different fracture toughness characteristics require different lengths of stress-corrosion cracks (and hence different exposure times) before the onset of overload fracturing; thus time-to-failure data could lead to grossly erroneous inferences regarding the relative SCC characteristics of these alloys. Some materials are so brittle that if they are stressed and a corrosion pit forms, the pit can initiate "brittle fracture," and an indication of high susceptibility to SCC might be inferred from a test in which in fact no SCC has occurred at all. (The 5% Cr die steel heat treated to maximum strength tends to behave in that fashion.)

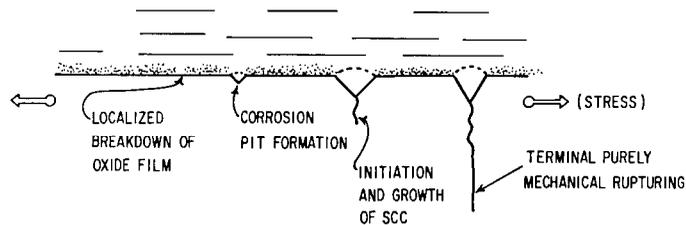


Fig. 2 - Sequence of events (left to right) by which a metal under stress with an originally smooth surface undergoes successively localized film breakdown, corrosion pitting, stress-corrosion cracking, and finally mechanical rupture

The foregoing complications are illustrated in Fig. 3, which is a plot of depth of pitting plus SCC plus mechanical fracturing on the ordinate vs time on the abscissa.

At the beginning of the program, the great bulk of data in the literature and most of that being inserted into the literature were of the undifferentiated time-to-failure type, and as has been shown above, this sort of data can be very misleading about stress-corrosion characteristics. One of the tasks of the program, therefore, was to establish the true SCC characteristics of the structural alloys of most current importance to military designers.

To do this characterization, as well as to conduct other studies both basic and applied, one or more specimen types were used containing pre-existing cracks. This tactic has three advantages: (a) It obviates waiting for a corrosion pit to grow, saving time. (b) It enables one to avoid an erroneous conclusion of immunity to SCC because of a nonpitting combination of alloy and environment. (c) It enables one to get a conservative evaluation by evaluating the material in the presence of the ultimate flaw, namely a sharp crack. There is a fourth advantage, for if the specimen meets certain criteria, the methods of fracture mechanics can be used to predict from the behavior observed in one geometry of specimen and crack what will happen in other geometries.

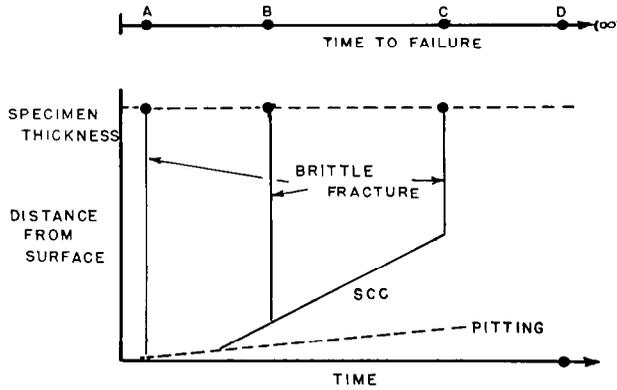


Fig. 3 - The time-to-failure information from stress-corrosion cracking tests of smooth specimens, as plotted in the line at the top, indicates an ascending order of merit with respect to stress-corrosion cracking from A through B and C to D. In point of fact, as shown schematically in the lower portion of the figure, B and C may have the same SCC characteristics but different fracture toughnesses. The SCC characteristics of A and D have not really been measured at all.

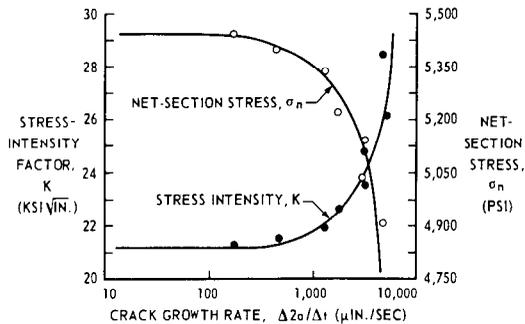
Fortunately for the program, the high level of activity in the fracture mechanics field during the decade preceding the program had produced technological information on various specimen geometries which become useful to the problem of SCC, as will be noted later in this report.

HIGHLIGHTS OF PROGRAM ACHIEVEMENTS

Specimens and Macroscopic Test Methods

During the course of the program the methods of fracture mechanics were demonstrated to afford predictability of stress-corrosion behavior from one geometry of specimen and stress configuration to another, whereas nominal stress was shown to be misleading (Fig. 4). The stress-intensity factor K thus was shown to be the most useful

Fig. 4 - Stress-corrosion cracking data for Ti-8Al-1Mo-1V in salt water. Specimen is stressed at the crack line and the crack growth rate is measured. (Chronologically the experiment proceeds from right to left in this figure.) Experiment shows that as K decreases (because of crack growth), the crack growth rate decreases, but meanwhile the nominal stress (net section stress) increases. This is an illustration of the inability of net section stress to correlate with cracking behavior. Extrapolation of data indicates a K_{ISCC} of about 21 ksi $\sqrt{in.}$.



way to quantify stress in the presence of a stress-corrosion crack. Evidence was found that for titanium alloys there is a threshold value of K below which SCC is not expected (for a given combination of alloy and corrodent), and this threshold was designated $K_{I_{SCC}}$. In the absence of positive knowledge that a true threshold exists, an arbitrarily defined $K_{I_{SCC}}$ (such as "nil crack growth in 1,000 hours") does indeed convey more information than an index of the patience of the experimenter or his skill with instrumentation; for at slightly higher K levels, one can make the positive statement that SCC will occur.

To fully characterize the SCC of a given alloy in a given K corrodent, one would like to have cracking kinetics as a function of K all the way from a threshold ($K_{I_{SCC}}$) if one exists to K_{I_C} , the stress intensity at which brittle fracture occurs. Even if one has only the value $K_{I_{SCC}}$, and even though in a given system this may not be known to be a true threshold but may represent, for example, the minimum K at which SCC is observed in 1,000 hours, the $K_{I_{SCC}}$ numbers can be plotted as a function of yield strength to produce an interesting analysis of the relative merits of various compositions or heat treatments in a given alloy family. In such a plot (Fig. 5), one can simplify the Irwin equation for a surface crack by assuming yield-strength stresses, and assuming that any surface flaw will be long compared with its depth and will lie perpendicular to the stress field, he can then draw a series of straight lines as shown in Fig. 5. Any one of these represents conditions for a given flaw depth, and the line simply means that if one may have a given flaw size as represented by the line, he must have a material with a $K_{I_{SCC}}$ lying above that line to avoid SCC.

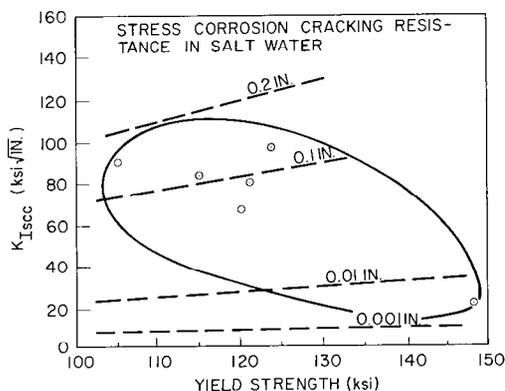


Fig. 5 - $K_{I_{SCC}}$ data in salt water for six commercial heats of Ti-6Al-4V rolled to plates 1-in. thick. All $K_{I_{SCC}}$ data for commercial heats of this alloy have been found to lie within the oval. The broken lines indicate $K_{I_{SCC}}$ values which an alloy must have (or exceed) in order to avoid SCC initiating at a long flaw of the depth shown on the line, assuming yield stresses. (Data show that no commercial alloy can tolerate a flaw as deep as 0.2 in. if the operative stress equals the yield strength.) The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

$K_{I_{SCC}}$ can be determined by a number of specimens, some set at K levels above and others below the $K_{I_{SCC}}$ level. The program showed that there are alternative ways to determine a threshold. For example, one can use the "wedge-loaded" (crack-line-loaded) sheet tensile specimen and await arrest of the stress-corrosion crack, or one can use a load-relaxing system such as an elastic ring to stress a specimen which experiences relaxation as the stress-corrosion crack advances (Fig. 6). It was shown elsewhere during the program that a specimen similar to the one of Fig. 6 can be self-stressed with a bolt and used as a stress-corrosion specimen. During the program the specimen of Fig. 6, self-stressed with a bolt instead of the elastic ring, has been shown to be extremely useful for characterizing the SCC behavior of high-strength aluminum alloys by determining the rate of crack growth as a function of K (Figs. 7, 8). Such a test has been found far more rapid and more discriminating than the traditional methods.

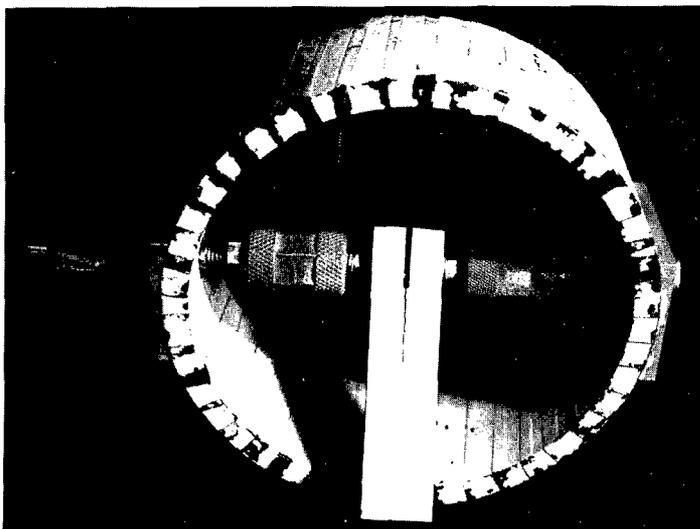


Fig. 6 - DCB aluminum alloy specimen ($1 \times 1 \times 3.5$ in.) stressed by an elastic ring which relaxes as the crack propagates. (Ring is made of high-strength steel wrapped with tape to prevent stress-corrosion cracking.) Load on ring is monitored by strain gage (not shown).

Since K has been shown to be the proper way to quantify stress around a stress-corrosion crack, and since SCC kinetics have been found to be K -dependent, specimens having the property of constant- K conditions regardless of crack length would be of obvious interest. Two such constant- K specimens were studied in the program. One of these, designated the tapered, double-cantilever beam (DCB) specimen, has given experimenters problems with the arms breaking off, and that was found to be true using the specimen for SCC, even though the experimenters were expert with that particular specimen. It was found possible, however, in using this specimen at a number of K levels, to extrapolate the crack rate to zero, which was found to correspond to K_{Isc} for the same steel as determined by a beam specimen. The other constant- K specimen, sometimes designated the double-torsion specimen and sometimes the Outwater specimen (after its inventor), is of additional interest because of its simplicity—it can be satisfactorily prepared from a sheet of metal using a bandsaw. For constant- K conditions the specimen can be satisfactorily stressed by a dead-weight-lever system, and it appears to be well behaved in stress-corrosion tests, at least for high-strength steel.

A small inexpensive self-stressed specimen was developed for possible use as a quality-control specimen for sheet materials.

The newcomer seeing all the various specimens for measuring SCC characteristics might reasonably ask which one he ought to use. It might be helpful to the metallurgist or engineer to regard this selection question somewhat like the question of which *hardness* test one should use. In both cases the answer to the question depends partly on the geometry of the material of interest and partly on the answer one ultimately gets.

Titanium

The resistance to SCC of all the commercial titanium alloys and many developmental and research alloys has been determined using precracked specimens. Electrochemical

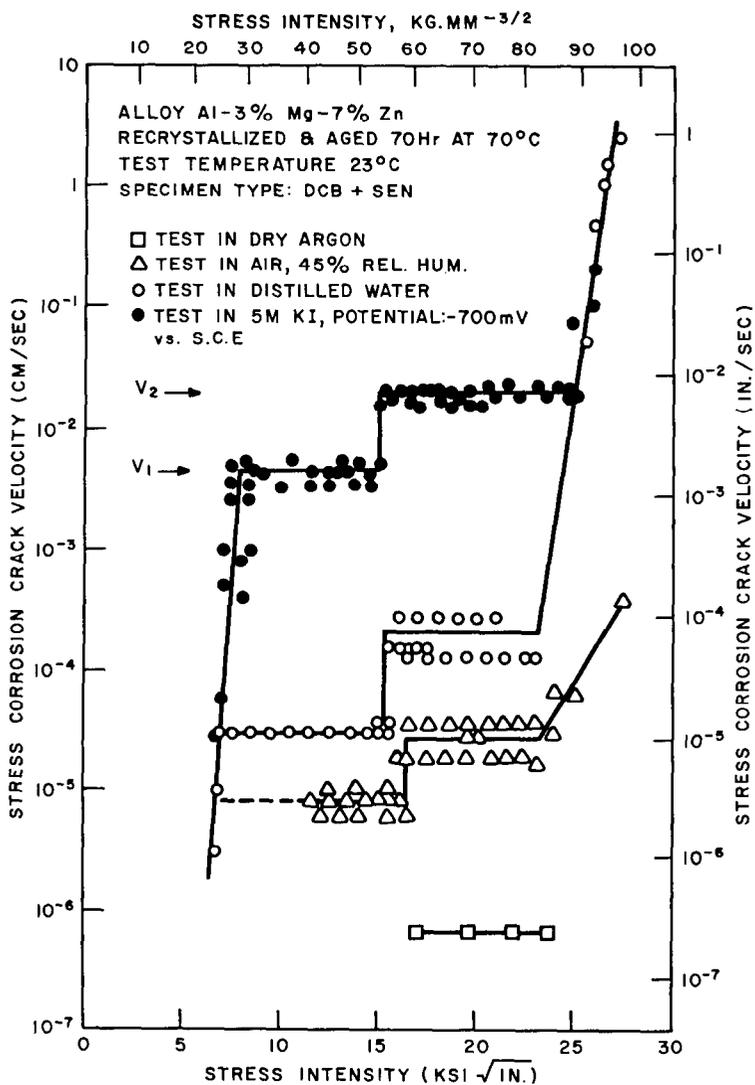


Fig. 7 - Crack-growth rate as a function of K for an aluminum alloy in several environments, illustrating the three stages of the V-K behavior

evidence was interpreted to indicate that for titanium alloys in salt water there is a genuine stress-intensity threshold below which stress-corrosion cracks do not propagate.

The resistance to SCC was found to be strongly dependent upon microstructure and dislocation substructure (Fig. 9). Alpha and alpha-beta alloys that exhibited planar slip in the alpha phase had low resistance to SCC. Beta grains in alpha-beta alloys tended to act as obstructions to the SCC fractures in the alpha phase, but with complications noted below (Fig. 10).

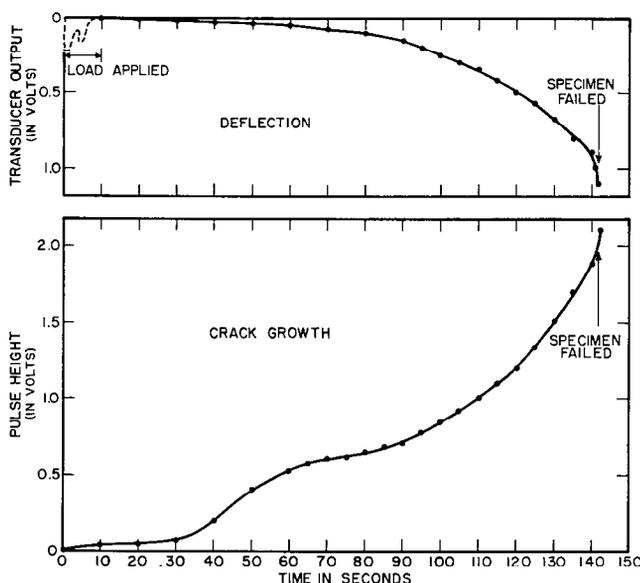


Fig. 8 - Crack-growth rate measurement continues to challenge the experimentalist. An alternative to the clip-gage technique is to monitor the reflection from an ultrasonic pulse (data shown above for a dead-weight-loaded, cantilever-bend specimen of titanium alloy).

Planar slip was found to be characteristic of alloys containing

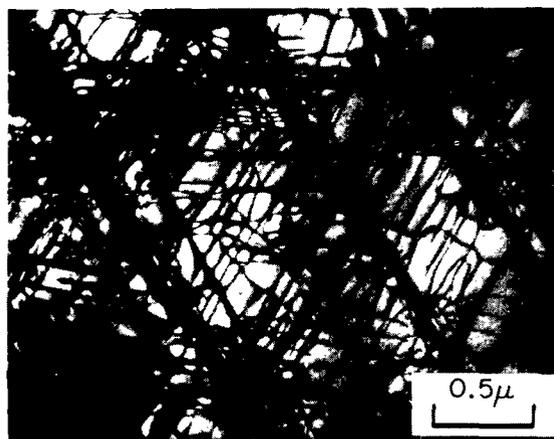
- High oxygen, or
- Aluminum in excess of about 6%, or
- Aluminum in excess of about 5% and tin content of 2.5% or more.

The formation of ordered domains of Ti_3Al or $Ti_3(Al, Sn)$ in the alpha phase further restricted slip and decreased SCC resistance.

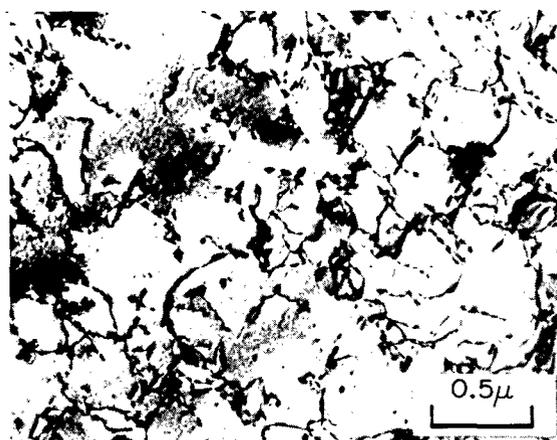
In an alpha-beta alloy, increasing the proportion of beta by increasing the amount of alloying elements such as Mo or V increased SCC resistance, perhaps by the crack-obstructing mechanism mentioned above (Fig. 11). But decomposition of the beta phase (to form omega, Ti_2Cu , or Ti_5Si_3) may embrittle the alloy and markedly lower its SCC resistance.

Of the common commercial alloys, Ti-8Al-1Mo-1V was found to be the least resistant to SCC, Ti-4Al-3Mo-1V was found to be highly resistant, and Ti-6Al-4V was found to have intermediate resistance. These observations were again observed to be correlative to the type of dislocation substructure.

In the all-beta alloy Ti-13V-11Cr-3Al, SCC fractures were observed to occur on or near the (001) plane. The crystallography of twinning of another all-beta alloy (Ti-11.5Mo-6Zr-5Sn) was found to be different from that of most other bcc metals. Mechanical fracture occurs macroscopically parallel to (001), but microscopically the fracture mechanism is not cleavage but microvoid coalescence. Unfortunately, aging this alloy to optimum strength (153 ksi yield) and toughness ($K_{Ic} = 66 \text{ ksi} \sqrt{\text{in.}}$) produced minimum resistance to SCC in halide solutions. The SCC fracture path in this alloy is intercrystalline, in contrast to the transcrystalline fracture path seen in most titanium



(a)



(b)

Fig. 9 - Coplanar dislocation arrays (above, associated with SCC-prone titanium alloys) and tangled dislocations (below, associated with SCC-resistant alloys)

alloys. The formation of omega phase during aging was observed to be an important factor reducing the ductility of the aged alloy; this phase is distributed as small particles (100 to 1,000 Å), but even so may constitute a high volume fraction of the alloy.

The SCC fractures in the alpha phase of alloys lie $15^\circ \pm 2^\circ$ from the basal plane of the hexagonal lattice. This relatively good consistency in crystallographic habit plane has led the resulting flat fracture facets to be termed cleavage (Figs. 12 & 13). The entire SCC fracture surface, however, is not cleavage, but cleavage areas are interspersed with rupture dimples (microvoids) which resemble the dimples of a purely mechanical fracture (Fig. 14). Thus, a stress-corrosion crack appears to be formed by two mechanisms, one (cleavage) involving stress plus an environmental reaction, and the other (dimples) wholly or largely of mechanical origin. The proportion of the dimple areas increases as K increases from $K_{I_{SCC}}$ to K_{I_C} , at which stress intensity the remaining ligament separates entirely by dimple rupture.

Methanol and several other organic fluid environments, including hydrocarbons, were observed to cause the SCC of titanium alloys. Carbon tetrachloride also caused

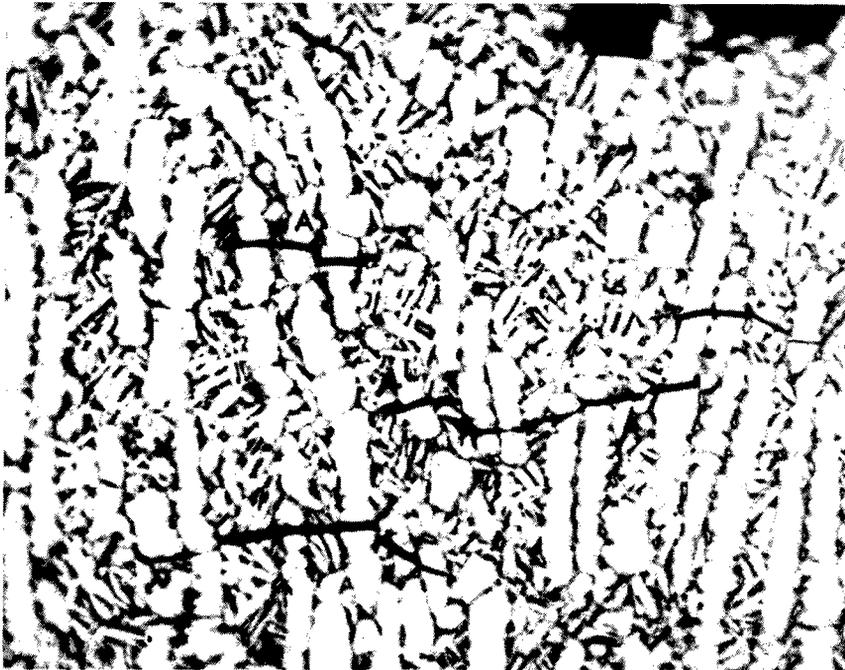
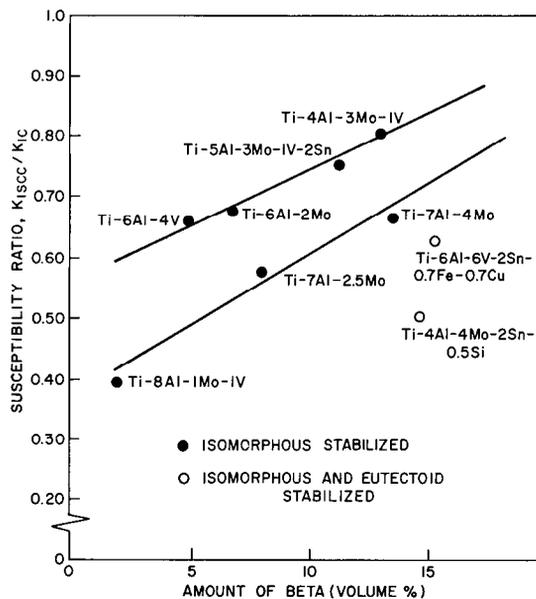


Fig. 10 - Partial stress-corrosion cracks in alpha-beta titanium alloy showing cracks in the alpha phase arrested by the beta phase. 1,000X magnification.

Fig. 11 - Increasing proportion of beta in alpha-beta titanium alloys tends to increase the ratio K_{Isc} / K_{Ic}



severe cracking. These findings have practical implications in the selection of paints and of cleaning and degreasing fluids. Except for liquid metals, carbon tetrachloride is the only environment not containing hydrogen (assuming the CCl_4 was free from HCl), which cracks titanium.



Fig. 12 - Fractograph showing cleavage surface typical of stress-corrosion cracking in titanium alloys in water at a low K level. 6,000X magnification.

Slow crack propagation was observed in titanium alloys in the absence of atmospheric moisture and also in a hard vacuum somewhat better than 10^{-7} torr. In these specimens as in those cracked in organics and in aqueous liquids, the fracture was cleavage interspersed with dimples. Heat treatment which reduced the hydrogen content of the titanium reduced its tendency to slow crack growth in vacuum (Fig. 15).

Methods were developed and applied to elucidate the nature of the corrodent near the advancing crack tip. With neutral salt water as the corrodent, the pH at the advancing crack tip was highly acid (about 1.6). The pH and the potential place the crack tip in a thermodynamic regime in which the hydride may be stable, but not an equilibrium oxide. The addition of FeCl_3 to the salt water increased the SCC resistance of the titanium, perhaps by substituting the reduction of copper for the reduction of hydrogen as the cathodic reaction.

One model which has been proposed for SCC of titanium, in accord with the observations noted above, is the hydrogen model. The reaction of a clean titanium surface with any of the hydrogen-bearing environments studied would release hydrogen which would be expected to react with or dissolve in the titanium. In aqueous salt solutions, the pH at the growing crack tip remains sufficiently acid (because of the occluding action of the SCC path) that repassivation is not possible at the crack tip, which continuously provides clean surfaces for reaction to remove more hydrogen from the corrodent. Thus the function of the precrack in specimens tested in salt water is to provide a little local straining plus the restriction to diffusion which will permit the acidity to remain high locally, whereas smooth specimens tested in salt water would repassivate because of the inability of the geometry to keep the acidity high locally. In methanol, however, the situation is different because the product of the reaction of titanium and methanol is soluble in methanol, i. e., the reaction product does not form a protective film in the

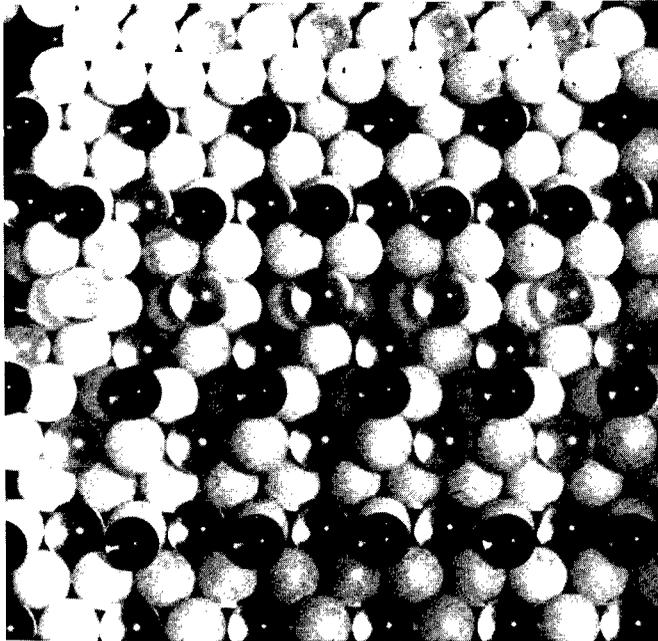


Fig. 13 - Ball model of simulated SCC fracture surface in Ti-Al alloy. Aluminum atoms on base surface are designated by clear balls and on the matching plane by dark balls. The fracture plane occurs where there is the highest concentration of Ti-Al bonds in ordered alpha.

bulk environment. This has been concluded to be the reason *smooth* specimens will initiate SCC in methanol.

Straining Ti-Al alloys in salt water was observed to cause large increases of the active range during anodic polarization, and this too is consistent with the picture of reactions occurring near the crack tip. A computer program has been developed for solving the complex electrochemical transport equations involved in SCC. The aspect ratio was found to dominate all else.

Ti-Al alloys were found to show the same precipitation of hydride at coplanar dislocations in SCC specimens as in slow strain-rate hydrogen-embrittlement specimens, again suggesting the hydrogen model.

Acceptance of the hydrogen model would require a resolution of two apparent anomalies: a) the observation of SCC in reasonably pure CCl_4 (containing traces of water), and b) the observation that increasing $[\text{Cl}^-]$ increases SCC crack-growth rates at a given K level.

Steels

The SCC characteristics of a large number of commercial and near-commercial steels were determined using salt water and natural seawater (Fig. 16). The use of pre-cracked specimens to determine SCC characteristics of alloy steels in seawater can save half a year to a year, which otherwise may be required to generate the pits which in turn initiate SCC. (A precracked specimen may, however, give erroneous data if it is



Fig. 14 - Fractograph showing flat cleavage areas plus dimpled (mechanical rupture) areas typical of SCC in titanium alloys in water at a K level much higher than that of Fig. 12

stressed to a high level before being placed in an SCC test at a lower stress level.) From the data of Fig. 16 it is apparent that the maraging steels and at least some of the precipitation-hardening steels were clearly superior to the conventional martensitic steels at the same strength level.

The following observations were made on low-alloy martensitic steels: Silicon content had no effect on $K_{I_{SCC}}$, but above about 1.5% the increased silicon greatly retarded the cracking kinetics at a given K level. Reducing the grain size also decreased the cracking kinetics, but did not affect $K_{I_{SCC}}$. Increasing the manganese or carbon content caused markedly reduced $K_{I_{SCC}}$ values (Figs. 17, 18). None of the following metallic alloying elements was observed to have a significant effect on $K_{I_{SCC}}$: nickel, cobalt, chromium, and molybdenum.

Fig. 15 - Effect of hydrogen content (varied by vacuum treatment) on fracturing of a commercial titanium alloy in various modes. The line designated K_{IH} represents the stress intensity above which a crack propagates in an inert environment, presumably due to internal hydrogen.

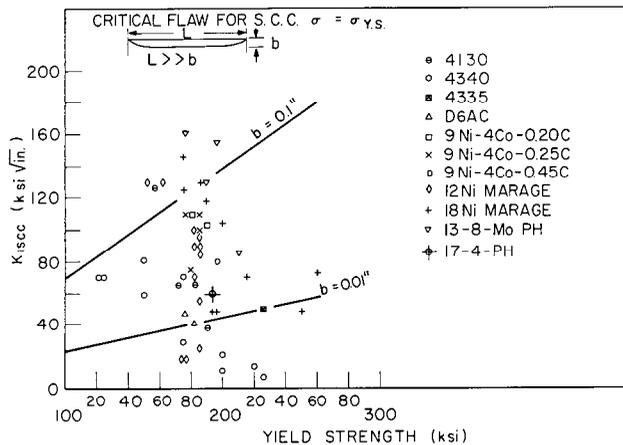
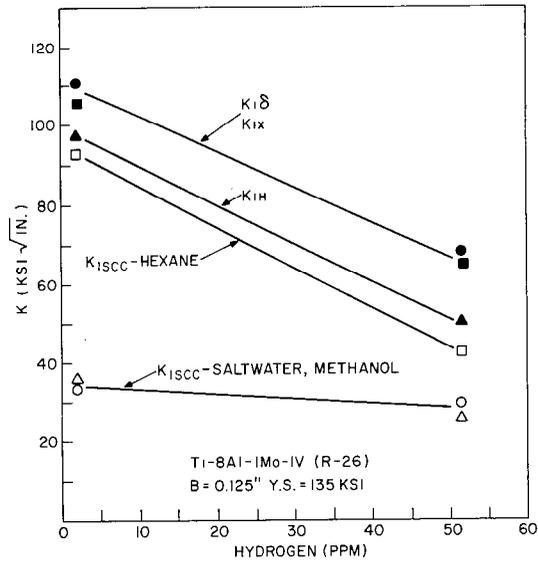


Fig. 16 - K_{ISCC} data in salt water for a number of commercial alloy steels made in production-size heats. The strength range covers strengths of interest to deep-diving submersibles, rockets, and manned aircraft. Flaws of the depth shown in a given steel would propagate stress-corrosion cracks at yield-strength stress unless the K_{ISCC} of that steel lies above the line. The ordinate is linearly proportional to load-carrying capacity in the presence of a standard flaw.

The purity of maraging steels with respect to sulfur and phosphorus was not found to have an important effect on SCC characteristics. The same was observed in low-alloy martensitic steels of the 4340 type.

Among the maraging steels, thermal history appears to have an effect above and beyond its effect on strength. Underaging the 350-grade maraging steel was found to be bad for SCC, whereas overaging was helpful. Overaging of 18%-Ni maraging steel

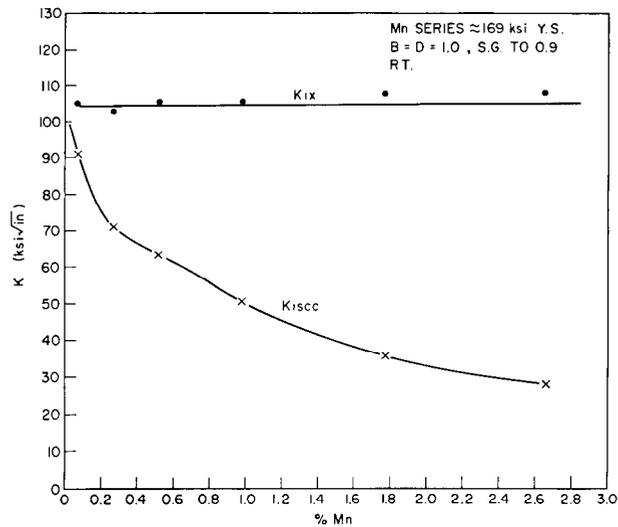


Fig. 17 - Effect of manganese content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

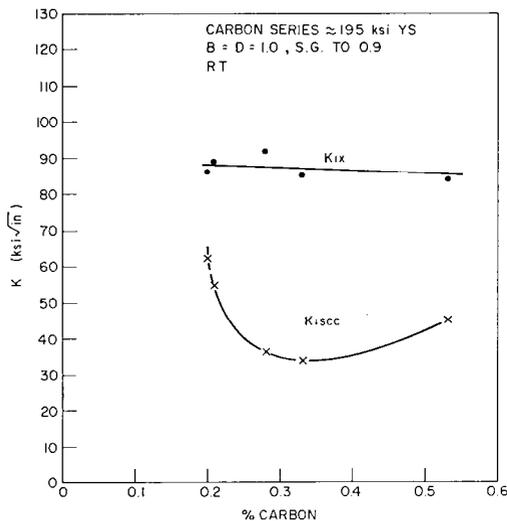


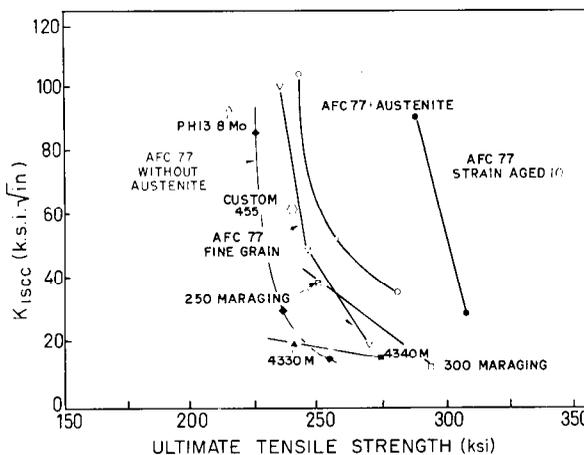
Fig. 18 - Effect of carbon content on $K_{I_{SCC}}$ and on toughness (K_{I_x}) of martensitic steel in salt water

produces reverted austenite, the primary site for which appears to be the compound $Ni_3 Mo$.

$K_{I_{SCC}}$ has a complex curvilinear dependence on strength level, but for a given martensitic steel in the 175- to 185-ksi yield-strength range, a 7% increase in yield strength (by differences in tempering treatment) caused a 20% loss in $K_{I_{SCC}}$, which is linearly proportional to the load-carrying capability of a component containing a standard flaw. The program demonstrated, however, that strengthening by strain aging (in a precipitation-hardening steel) entails a smaller penalty in SCC than the strengthening of martensitic steel by choosing the tempering temperatures, thus providing a possibly useful avenue for further advances for special needs (Fig. 19).

Stress-corrosion cracks are commonly thought to be characteristically multiply branched, because SCC was first observed in cold-worked products, which have complex

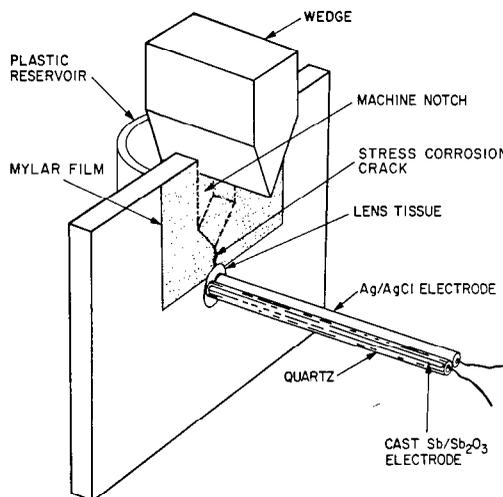
Fig. 19 - K_{Isc} for several commercial steels and one developmental steel (AFC 77) in salt water. Note, for AFC 77 in any given condition, the rapid decrease in K_{Isc} with rising ultimate tensile strength. Note also that by increasing the strength by strain aging, the strength can be increased over that of regular AFC 77 by more than 50 ksi while maintaining the same K_{Isc} .



residual stress patterns that change continuously as the article cracks. In the present program it has been found with many materials that the crack-growth rate rises sharply with increasing K until a point (K_{In}) of apparent process saturation is reached, beyond which the rate is more or less independent of K . If the material is reasonably isotropic, then at a K level of about $2K_{In}$ the crack will tend to divide or branch. This finding is useful in understanding tests in which the crack divides and thereby terminates the utility of the experiment.

During the course of the program, methods were developed which for the first time were successful in measuring the pH near the tips of growing stress-corrosion cracks in steel (Fig. 20). These methods employed successively color-change pH indicators,

Fig. 20 - One method for determining the pH at the tip of a stress-corrosion crack. The potential and pH probes rest against a small paper disk (thin to minimize the solution required to moisten it), and are connected to high-resistance recorders. They do not register a reading until the crack propagates to the disk and moistens it. (The disk does not contain solutes which affect pH.) A glass electrode designed for surface measurements can be used in place of the antimony oxide electrode.



the antimony electrode, and finally the glass electrode, and all three methods gave the same result. This work on crack-tip chemistry gave new insight on SCC (and eventually on most forms of localized corrosion, as will be discussed in a later section). It was found that regardless of the pH of the bulk solution (external to the crack) or the potential impressed upon the steel, the combination of potential and pH at the crack tip are such as to be favorable for the reduction of hydrogen (Fig. 21). This finding makes it unnecessary to postulate any mechanism for SCC in (high-strength) steel other than that commonly termed *hydrogen embrittlement*. The mechanism of hydrogen embrittlement has

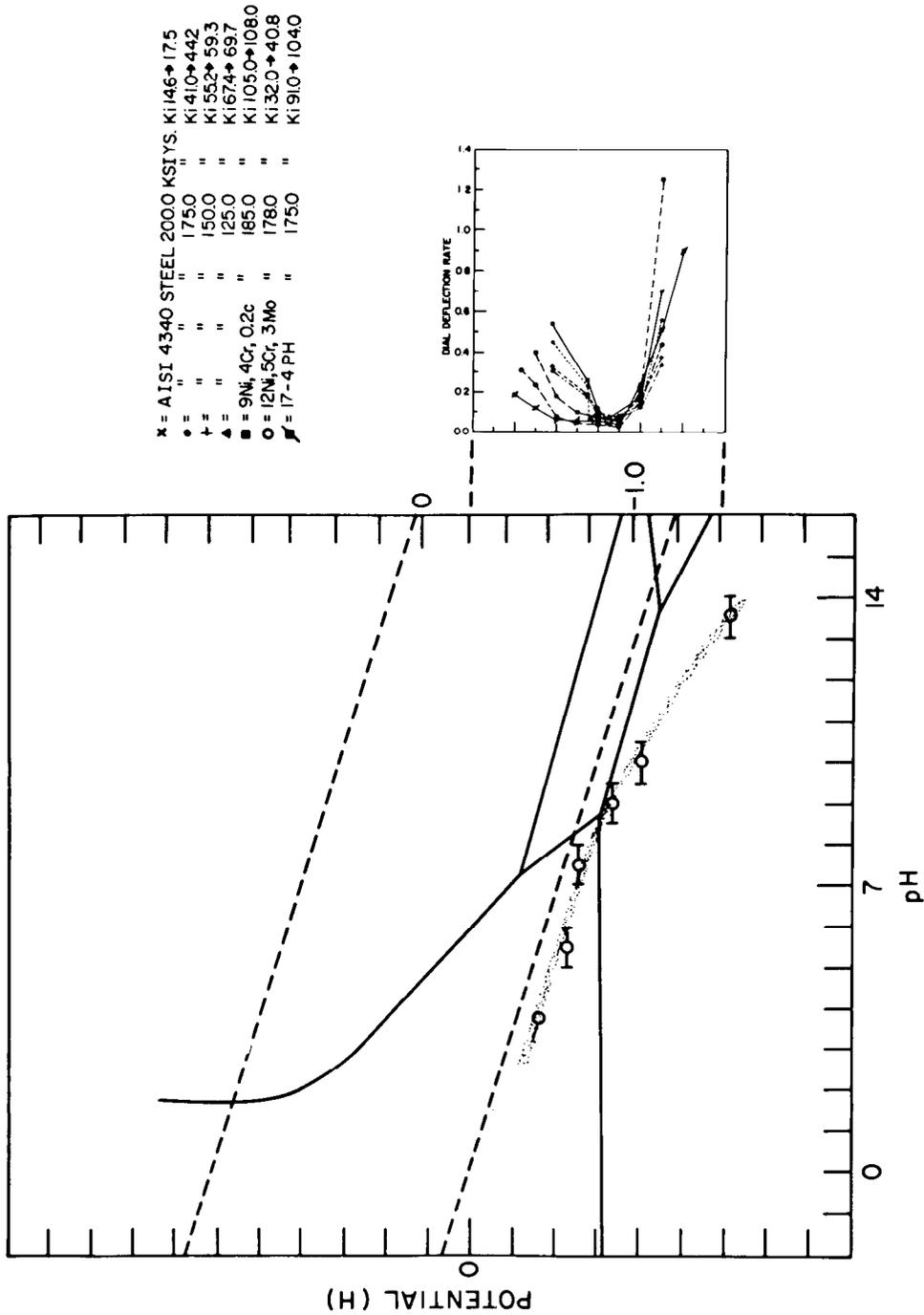


Fig. 21 - pH at the tips of growing cracks in neutral 3.5% NaCl solution, specimens potentiostatted to various levels. Curves at right indicate a function of crack-growth rate (dial deflection rate) at approximately constant K for a given steel (but different K's for different steels). These data were taken by color-change pH indicator technique but have since been confirmed by the glass electrode. Stress-corrosion cracking in steels occurs only under conditions of local pH and potential which place the crack tip under the hydrogen reduction line (lower sloping broken line).

been postulated to involve the formation of an iron hydride, thought to have been prepared and partially characterized, but work during the program has shown that the alleged iron hydride (prepared by a Grignard method) was really an organic compound of iron.

The work on crack-tip chemistry forms the basis for postulating a new role for either a corrosion pit or a pre-existing crack in initiating SCC: Formerly the pit and crack were viewed as stress concentrators, but it is now concluded that their *essential* role is to produce the local acidity which helps establish the conditions for hydrogen reduction. In the corrosion pit the acidity caused by hydrolytic reactions is retained locally by the porous cap of corrosion products, and in the stress-corrosion crack the local acidity is retained because of the long narrow diffusion path between the crack tip and the external corrodent. These observations are consistent with current findings in the program on the nature of pitting of Fe-Cr alloys (Fig. 22).

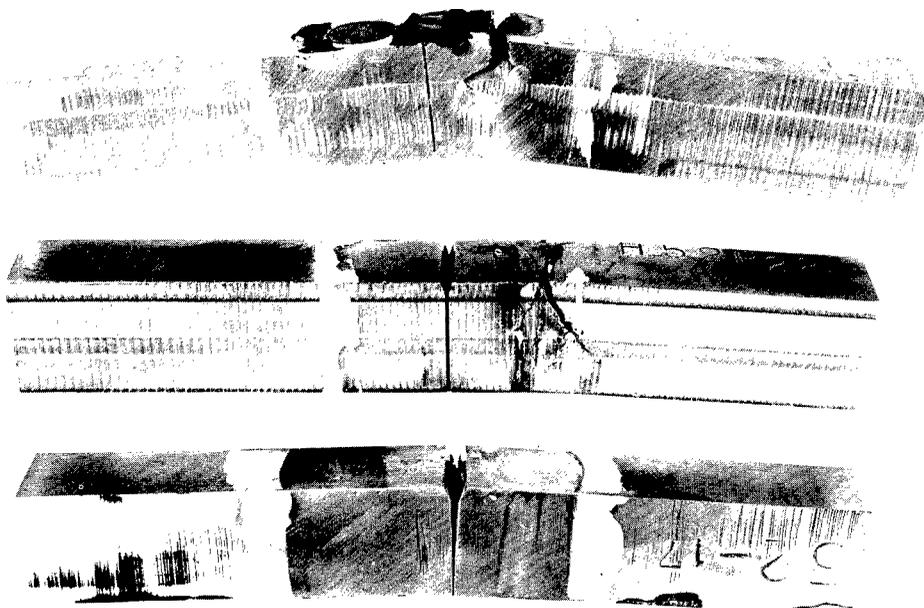


Fig. 22 - Three specimens of a 13-8Mo precipitation-hardening steel whose stress-corrosion cracking characteristics, at first puzzling, become comprehensible in the light of the experiment of Fig. 21. The lower specimen, stressed at a high K , commenced cracking at the notch. At a lower K (center specimen) there was no cracking at the notch but, after a delay of 1300 hours, there was rapid cracking under the wall of the corrodent cell. This was attributed to lowering of pH in the crevice under the wall by crevice corrosion so as to cross the hydrogen reduction curve. The upper specimen also cracked immediately at an unnotched area on which a crystal of ferric chloride had been laid to lower the pH locally.

The acidity role of the corrosion pit suggested that inhibitors and buffers which prevent the formation of the corrosion pit would be effective in preventing SCC of a smooth specimen, and this inference was confirmed experimentally. A specimen containing a precrack, however, responds only to a limited degree to inhibitors and buffers: K_{Isc} cannot be raised to K_{Ic} by such additives, doubtless because not enough of such additives are present inside the crack at the crack tip to fully control the local pH.

Cathodic protection can readily effect changes in pH deep within growing stress-corrosion cracks (contrary to a commonly held rule of cathodic protection technology to the effect that cathodic protection cannot function deeper down a crack than about eight times the crack opening dimension). [Partly because of the foregoing discrepancy, an NRL study in another program showed that the factor of 8 cited above was too pessimistic by at least a factor of 10^3 .] Cathodic protection has not appeared to be a solution to the problem of SCC in high-strength steel because, although the local hydrolytic acidification can be prevented by cathodic polarization, the conditions are still met for hydrogen evolution and cracking does continue to occur. The rate of stress-corrosion crack growth is highly dependent on potential and goes through a minimum at about -0.85 to -0.9 V (SCE) for all alloy steels which have been studied; this minimum in kinetics corresponds approximately to the potential at which iron becomes thermodynamically stable in water, suggesting that the reason for the minimum may be caused by the transfer of the anodic reaction from within the crack (when electropositive to the minimum) to outside the crack (when electronegative to the minimum). As a practical application of this information, one should be able to achieve approximately the minimum in cracking kinetics by plating with cadmium.

If one studies the details on the fracture surfaces using high-resolution replication electron fractography, one finds that regardless of potential, the fracture surface is one of smooth facets (prior austenite grain boundaries) upon which are superimposed plastic tear ridges. The tear ridges increase in number with increasing stress intensity K , until at K_{Ic} the fracture is totally tear ridges surrounding craters (purely mechanical microvoid coalescence, or dimple rupture, fracture). This identical nature of fracture details regardless of which side of the potential minimum one is on is consistent with the conclusion that only one model (hydrogen cracking) is required to account for SCC in high-strength steels.

Consistent with the hydrogen model of SCC in steels, the presence of sulfide in the corrodent (which would tend to promote the entry of hydrogen into the steel) has a strikingly adverse effect on SCC.

One can change the oxide film on the exterior of the specimen from one which is conductive (Fe_3O_4) to one which is poorly conductive ($MnFe_2O_4$), but this change does not appear to have any significant effect on SCC behavior.

The crack tip chemistry studies on *steels* in salt water or in ordinary distilled water showed that the corrodent is concentrated with respect to iron. Thus the newly formed crack surfaces do not behave like pure iron in superpure water, in which environment the iron has been shown to be as inert as platinum.

Large changes in pH locally compared with that of the bulk environment are characteristic of the corrodent in stress-corrosion cracks in all alloy families studied (Fig. 23).

One practical *caveat* appears to be provided by the finding that the behavior of pre-cracked specimens of the stainless steel designated 17-4 PH in (nearly neutral) salt water does not correlate with the poor resistance of this alloy to SCC in service. A possible explanation for this apparent discrepancy is that in service, localized hydrolytic reactions (in crevices, for example) may provide such high local acidity as to create a fundamentally different environment, perhaps also contaminated with sulfur compounds, with a different (and lower) K_{Isc} from that measured in neutral salt water.

Aluminum

The work on aluminum alloys in this program, although by design receiving the least emphasis of the three alloy families, became particularly productive in the more

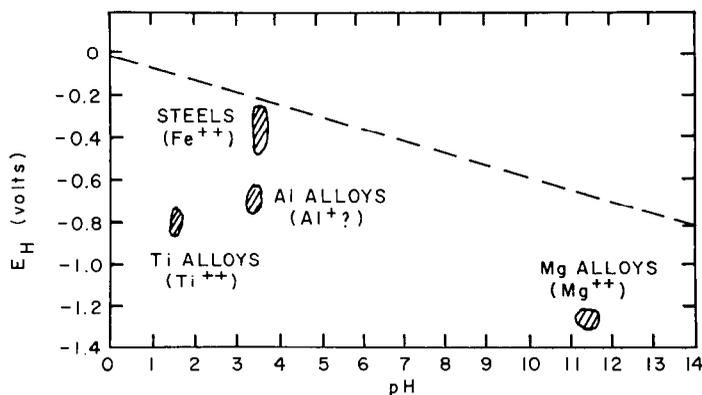


Fig. 23 - Potential and pH data for the tips of growing stress-corrosion cracks in four alloy systems in nearly neutral salt water. Data taken by color-change pH indicator paper technique. Illustrates the large differences between pH of the bulk solution and that at the occluded reaction site. (Hydrogen can be reduced from water below the broken line.)

practical aspects of the problem because of the adoption of the precracked specimen technique (Fig. 24). Wrought products of the Al-Zn-Mg group of alloys which have strengths of special interest to the DoD are highly textured, and SCC is a problem primarily only parallel to this texture. Ordinary bent-beam or tensile specimens cannot be cut in such a fashion as to test this maximum vulnerability direction unless either the plate is very thick or extensions can be welded or otherwise firmly attached to the plate material, which has never been an attractive approach.

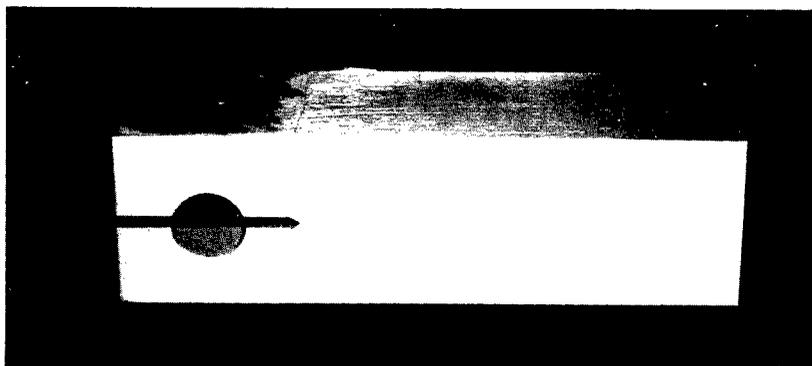


Fig. 24 - Aluminum specimen of Fig. 6 self-stressed (after the method of Novak and Rolfe) by a setscrew. Dark region is paraffin used to insulate the steel setscrew from the crack area. A stress-corrosion crack is seen emanating from the machined notch. This type of specimen was used for most of the characterization data on aluminum alloys in the program.

Early work with the specimen of Fig. 6 suggested that there was a stress intensity below which SCC stopped, but later work has indicated that, although the rate of crack growth diminishes with decreasing K at low levels of K , there does not appear to be any true threshold below which the cracking absolutely stops. Events have shown that the

best way to characterize the SCC behavior of a given alloy is to report the kinetics of crack growth as a function of K, which will be referred to here as V-K characterization.

A contribution from outside the program has been highly beneficial in using the DCB specimen of Fig. 6. This contribution was the demonstration that one could use a bolt to spread apart the two arms of the DCB specimen to stress it without the need for the proving ring, and that stressing in such fashion still permitted quantification of the stress intensity at the root of the crack. This specimen can then be described as a self-stressed DCB specimen, and it has become a most productive research tool, with demonstrated usefulness for sheet material at least as thin as 0.05 in. Among its other advantages, the self-stressed specimen has that of being suitable for wide distribution for readily assessing, say, the effect on SCC of the environment of an airport runway, or of a deep-diving submersible, or of a noxious chemical.

V-K studies have been completed on a large number of commercial and experimental alloys in various tempers (Fig. 25). These studies have shown that at low values of K, log V rises rapidly and linearly with increasing K (Stage I) until a saturation level (Stage II) is reached, after which V is nearly independent of K. In some alloys there is a third stage, near K_{Ic} , in which V is again dependent upon K. Curves of $K \log V$ yield

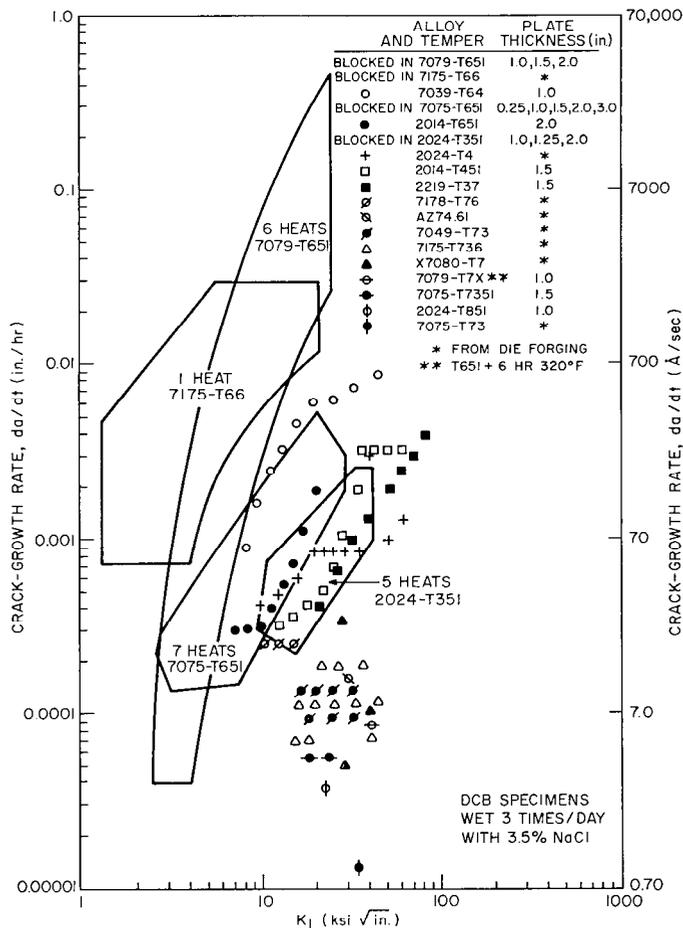


Fig. 25 - Comparison of several commercial and experimental aluminum alloys using the self-stressed DCB specimen and the crack-growth rate method

rangings which agree with established rankings using smooth specimens with two differences: The K-log V rankings are enormously more rapidly obtained, and they are more discriminating than the smooth-specimen rankings when applied to alloys having approximately the same SCC characteristics.

The DCB specimens demonstrated in a very graphic way the magnitude of the effect which quenching stresses can produce in the SCC of aluminum alloys.

The evidence to date is that in Stages I and III the rate of crack growth is little influenced by halide-ion concentration, but the velocity of Stage II apparently can be strongly affected by anion concentration.

Commercial alloys do not experience SCC except when water is present, and only the anions Cl^- , Br^- , and I^- accelerate V (in Stage II) appreciably.

New information was developed on the effects of microstructure on SCC (Fig. 26). It was shown, for example, that the microstructure controlled the cracking process through its effect on the deformation process: Specimens which were strengthened by large Guinier-Preston (G-P) zones exhibited coarse slip characteristics and proved to crack readily, while specimens hardened by small G-P zones exhibited fine slip and cracked slowly. Work on bicrystals revealed that when slip could be transferred across the grain boundary, cracking was slow, but when slip transfer was impeded by the boundary, cracking was rapid.

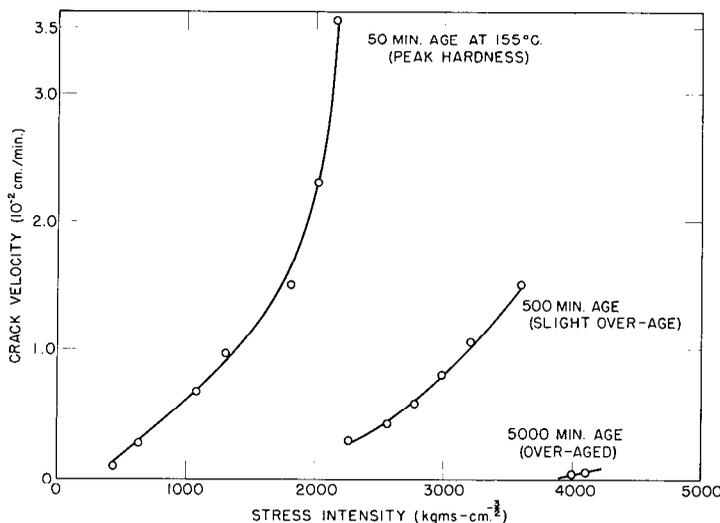


Fig. 26 - Effect of heat treatment on the stress-corrosion cracking kinetics of Al-15%Zn. Transmission electron microscopy shows that the increasing aging time at 155°C causes a progressive decrease in the volume fraction of Guinier-Preston zones.

Neither the presence nor the width of the precipitate-free zone was observed to have any effect on the stress-corrosion susceptibility of a ternary Al-Zn-Mg alloy (Fig. 27). This finding has been explained in terms of slip-band behavior.

Methods have been developed to measure the pH at the tips of growing cracks using both color-change pH indicators and the glass electrode, and in the case of 7000-series

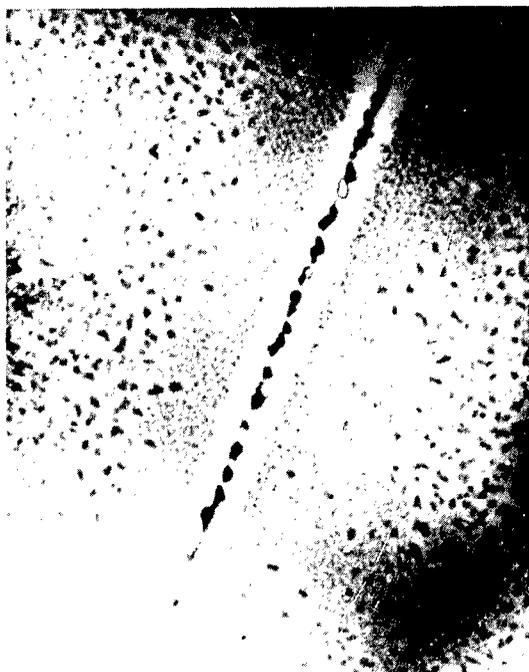


Fig. 27 - The precipitate-free zone adjoining a grain boundary in an Al-6.8% Zn-2.3% Mg alloy. There has been much controversy over the role that this zone plays in stress-corrosion cracking behavior. Studies on high-purity alloys have led to the conclusion that it is primarily the matrix precipitates, and not the grain boundary precipitate, that determine susceptibility to SCC.

aluminum alloys undergoing cracking from nearly neutral salt water, the pH at the crack tip was found to be 3.2 to 3.5. A macroscopic model was also devised to simulate the sides and the base of a stress-corrosion crack, with the simulated base electrically isolated from the simulated walls. This model has given interesting results to date and gives promise of more to come.

In addition to other basic contributions to aluminum corrosion, two reviews were written by program personnel. One of these was concerned with the aluminum-hydrogen system. A second review treated chemical effects in the corrosion of aluminum and aluminum alloys.

An academic study of the corrosion fatigue of an aluminum alloy demonstrated that hydrogen diffusion is not rate controlling (Fig. 28).

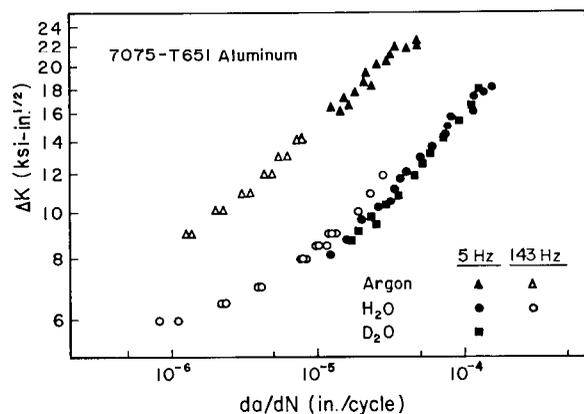


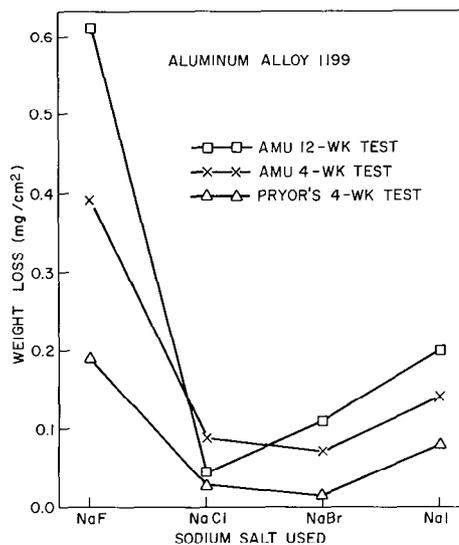
Fig. 28 - Fatigue (in argon) and corrosion fatigue (in water) crack-growth rates in an aluminum alloy. Deuterium studies indicate that hydrogen diffusion is not rate-determining.

Surface Sciences

Various entries in the Abstracts of Achievements identify contributions of some of the subdisciplines which are sometimes called collectively *surface science*. For example, techniques of Low-Energy Electron Diffraction (LEED) have been advanced by the program to enable the experimenter to study the initial reaction of any chosen gas (however corrosive) with a clean metal surface. An international conference was held in which the status of field ion microscopy and field emission microscopy were reviewed by internationally recognized experts, and the proceedings have now been published. Electron spin resonance studies were made on oxide surfaces exposed to various gaseous species.

As indicated by the foregoing, the program was instrumental in drawing to the attention of surface scientists the existence of a challenging technological problem. As a consequence many basic studies were made using various ones of the newer surface science techniques, much new and interesting information was developed, and more techniques were added to those available to the surface scientist (Figs. 29 to 31). The technique of LEED in particular made significant advances because of the program. The experimental and theoretical difficulties of the program area are such, however, that much more work is required before these newer approaches can make their contributions to corrosion technology.

Fig. 29 - Basic study of the role of the chloride ion in the corrosion of aluminum. Kinetic data show that although there are some quantitative differences between the behavior of the various halide ions, there are no qualitative differences, and the role played by chloride is due to its ubiquity rather than any uniqueness.



The electrochemical techniques and concepts, especially those developed and applied by Evans, Hoar, Pourbaix, and their students, have been shown to be of immediate value both in advancing the theory of stress-corrosion cracking and in guiding technological experimentation. Since electrochemistry is generically a surface science, the tenet that surface science would be useful to the stress-corrosion problem at an early date has thus been vindicated. As one example, it has been postulated elsewhere that hydrogen can only be reduced from aqueous solutions at a cathode, that by making a piece of steel an anode one establishes conditions incompatible with hydrogen reduction and that any SCC occurring under such conditions cannot be attributed to hydrogen. A more sophisticated analysis of the situation is as follows: A given site (electrode) can serve as an anode for the dissolution of iron and at the same time function as a cathode for the reduction of hydrogen, if the potential and pH are favorable.



Fig. 30 - Field ion micrograph Ni_4Mo . This is one of several modern techniques in surface physics which are useful to study the ultrafine-scale nature of clean metal surfaces.

The experience of the program, in summary, is that there are numerous new areas of surface science capable of yielding important scientific knowledge about metal surfaces and their reaction with environment. The more mature discipline of electrochemistry has been demonstrated to have immediate utility in the understanding of the processes of aqueous corrosion, including stress-corrosion cracking, and in the guidance of future technological advances.

ABSTRACTS OF ACHIEVEMENTS

Explanatory Notes

These abstracts were prepared by the organization performing the research as a means both of summarizing progress and giving the reader a key to the literature generated by the program. They were modeled after annual reports of Interdisciplinary Laboratories, listing task title, personnel, objective, usually the approach, the achievements, and publications and presentations.

It will be noted that a given task, represented by a single task title, may differ greatly from another in scope, staffing, and productivity. This is due in considerable measure to the broad technical nature of the program and to the fact that each organization grouped its work under a given task title as seemed most effective for conveying the output to the imagined readers.

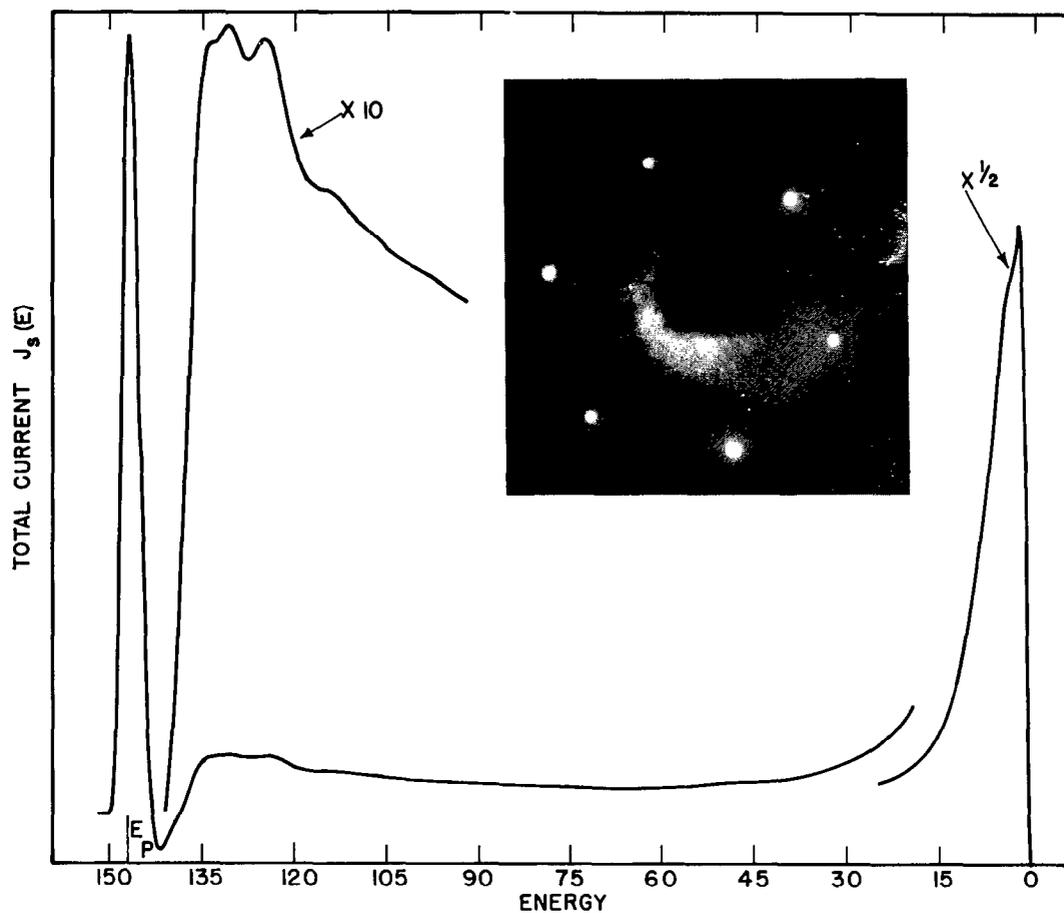


Fig. 31 - Low energy electron diffraction pattern and secondary electron energy distribution curve for an aluminum (111) surface. The curve includes a peak indicating that the elaborate steps used to prepare an entirely clean surface were not quite successful. This observation illustrates one of the many challenges of state-of-the-art surface physics and surface chemistry.

The abstracts are arranged in the following pages by institutions, commencing with The Boeing Company, followed by the universities (alphabetically), and finally the Naval Research Laboratory.

The Boeing Company

USE OF PRECRACKED SPECIMENS IN STRESS-CORROSION TESTING OF HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for several high strength commercial aluminum alloys, and to compare the rating of the alloys based on this data with the ratings established from smooth specimen time to failure data.

Approach

The V-K curves were obtained using bolt-loaded, double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Alloys and tempers tested were 7079-T651, 7079-T651 + 6 hr/325°F, 7075-T651, 7075-T7351, 7175-T66, 7175-T736, 7178-T76, AZ74.61, X7080-T7, 7039-T64, 7049-T7, 2024-T351, 2024-T4, 2024-T851, 2014-T451, 2014-T651, 2219-T37.

Achievements

The V-K curves showed a double slope behavior. At lower crack tip stress intensities the crack velocities were highly dependent on K_I , whereas at the higher K_I levels crack velocities were nearly independent of the applied crack tip stress intensity. Maximum crack velocities ranged from 4×10^{-5} in./hr for the highly susceptible 7079-T651 to 1×10^{-5} in./hr for the highly resistant 7075-T73. Although crack velocities often continued to decrease with decreasing K_I level, true K_{Isc} values (K_I levels below which growth ceases) were not observed for any alloy tested. Rankings of the various alloys based on the V-K curves agreed with established rankings based on smooth specimen time to failure data. In many cases the V-K curves provided more discriminating data than is available from smooth specimen time to failure tests. For example, at the higher K_I levels stress-corrosion crack growth rates in 7079-T651 were one to two orders of magnitude faster than in 7075-T651 even though both alloys show similar behavior in the standard smooth specimen, alternate immersion test.

A relationship between the smooth specimen stress-corrosion threshold stress from time to failure data and the V-K curves is presented.

Publications

"Use of Precracked Specimens in Stress-Corrosion Testing of High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24466, November 1969; submitted to Corrosion

The Boeing Company

USE OF PRECRACKED SPECIMENS IN SELECTING HEAT TREATMENTS FOR STRESS-CORROSION RESISTANCE IN HIGH STRENGTH ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for the alloy 7075 after various overaging heat treatments between T6 and T73.

Approach

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution. Three different techniques were employed. Two techniques used single DCB specimens containing aging gradients along their lengths. The third technique used multiple DCB specimens, each one having a different heat treatment.

Achievements

Results from each technique showed that for the 7075 alloy, overaging to an electrical conductivity of at least 38% IACS is necessary before stress-corrosion crack growth rates approach those of 7075-T73. Stress-corrosion performance was established most rapidly using multiple DCB specimens. After only a few hundred hours the crack growth characteristics were sufficiently established using this technique that the different heat treatments could be rated against the known performance of 7075 in the T6 and T73 tempers.

Publications

"Use of Precracked Specimens in Selecting Heat Treatments for Stress-Corrosion Resistance in High Strength Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-2447, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF RESIDUAL STRESSES ON STRESS-CORROSION CRACK GROWTH RATES
IN ALUMINUM ALLOYS

M. V. Hyatt

Objective

To determine the effects of quenched-in residual stresses on the behavior of pre-cracked double cantilever beam (DCB) stress-corrosion specimens of high strength aluminum alloys 7075, 7175, and 7079.

Approach

The V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were obtained using bolt loaded DCB specimens intermittently wetted with an aqueous 3.5% NaCl solution. Tests were conducted on specimens containing quenched-in residual stresses and on specimens which had been stress relieved after quenching by stretching or explosive shocking.

Achievements

Large differences in crack front profiles were observed between specimens with and without residual quenching stresses. Severe crack front bowing occurred in non-stress relieved specimens. In addition the crack opening displacement in the non-stress relieved specimens was effectively increased at the crack tip by the bowing apart of the two DCB specimen arms as the stress-corrosion crack propagated through the material. These effects result primarily from the residual compressive stresses on the surfaces of the non-stress relieved specimens. Both the crack front bowing and the bowing apart of the DCB specimen arms cause errors in the calculated K_I levels. These problems were eliminated by stress relieving DCB specimens after quenching. This work underlines the fact that residual quenching stresses in actual parts susceptible to stress-corrosion cracking not only increase chances of initiating stress-corrosion cracks, but also play an important role in increasing average growth rates. This can result from the increased crack opening displacement (and therefore K_I level) at the crack tip due to deflections caused by the residual stresses.

Publications

"Effect of Residual Stresses on Stress Corrosion Crack Growth Rates in Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24469, November 1969; submitted to Corrosion

The Boeing Company

EFFECTS OF SPECIMEN GEOMETRY AND GRAIN STRUCTURE ON STRESS-CORROSION CRACKING BEHAVIOR OF ALUMINUM ALLOYS

M. V. Hyatt

Objective

To establish the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for aluminum alloy double cantilever beam (DCB) specimens with various side grooves, grain structures, and thicknesses.

Approach

DCB specimens with various side grooves, grain structures, and thicknesses were tested in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Branch cracking and arm breakoff may occur during testing of DCB specimens of aluminum alloy materials with equiaxed grain structures. Side grooves on DCB specimens had a negligible effect on crack growth rate data. Double cantilever beam specimens from materials as thin as 0.050 in. can be successfully tested.

Publications

"Effects of Specimen Geometry and Grain Structure on Stress Corrosion Cracking Behavior of Aluminum Alloys," M. V. Hyatt, Boeing Document No. D6-24470, November 1969; submitted to Corrosion

The Boeing Company

EFFECT OF QUENCHING RATE ON STRESS-CORROSION CRACK GROWTH RATES
IN 2024-T4 ALUMINUM

M. V. Hyatt

Objective

To determine the effect of quenching rate on the V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) for 2024-T4.

Approach

Specimens of 2024 were resolution treated, quenched at two different rates, and naturally aged to the T4 temper.

The V-K curves were obtained using bolt loaded double cantilever beam (DCB) specimens intermittently wetted with an aqueous 3.5% NaCl solution.

Achievements

Actual stress-corrosion crack growth rates were higher in the more slowly quenched 2024-T4 alloy. This behavior agrees with trends observed by others based on percent loss in tensile strengths of pre-exposed specimens which have been quenched at different rates.

Publications

"Effect of Quenching Rate on Stress-Corrosion Crack Growth Rates in 2024-T4 Aluminum," M. V. Hyatt, Boeing Document No. D6-24471, November 1969; submitted to Corrosion

The Boeing Company

DEVELOPMENT OF A HIGH STRENGTH, STRESS-CORROSION RESISTANT ALUMINUM ALLOY FOR USE IN THICK SECTIONS

M. V. Hyatt and H. W. Schimmelbusch

Objective

To develop a new high strength Al-Zn-Mg-Cu alloy with a smooth specimen stress-corrosion threshold stress of 25 ksi, good toughness and fatigue properties, and a quench sensitivity such that the properties can be maintained at a high level in thick plate and forgings.

Approach

To meet the strength goals an alloy with zinc and magnesium contents intermediate between those of 7075 and 7178 was selected. To reduce quench sensitivity the copper content was reduced to about 1.0%, and zirconium and manganese were added in place of chromium which is the normal recrystallization retardant in 7075 and 7178 alloys. The amount of overaging required to meet the stress-corrosion goal was determined using both smooth specimens and precracked double cantilever beam (DCB) specimens. Finally, hand and die forgings, plate, and extrusions of the new alloy were given the selected heat treatment and evaluated to determine mechanical, fracture, fatigue, and stress-corrosion properties.

Achievements

Mechanical, fracture, and stress-corrosion properties for die forgings of the new alloy (alloy 21) and several other forging alloys are compared in the following table.

Alloy	Thickness (in.)	Minimum longitudinal properties		Longitudinal K_{Ic} range (ksi $\sqrt{\text{in.}}$)	Short-transverse stress-corrosion threshold (ksi)	
		F_{tu} (ksi)	0.2% F_{ty} (ksi)		3.5% NaCl alternate immersion	Industrial atmosphere
Alloy 21	6.75	69*	60*	30-38*	> 25*	> 25*
7049-T73	5.0	70	60	30-38*	45	?
X7080-T7	6.0	65	57	27-30	25	15
7075-T73	3.0	66	56	27-38	> 47	> 47
7075-T73	6.0	61	51	27-38	> 47	> 47
7175-T736	3.0 max	76	66	27-38	~ 35	?
7075-T6	3.0 max	75	65	25-32	7	14
7079-T6	6.0	72	62	25-32	7	6

*Estimated values

The mechanical properties of alloy 21 are comparable to those of 7049-T73. The fracture toughness of alloy 21 is as good as or better than that of the other alloys listed. The smooth-specimen short-transverse stress-corrosion threshold appears to be greater than 25 ksi. Test data also indicate that the smooth and notched axial (tension-tension) fatigue properties of alloy 21 are comparable to those of 7075-T6 and 7075-T73.

Publications

"Development of a High-Strength, Stress-Corrosion Resistant Aluminum Alloy for Use in Thick Sections," M. V. Hyatt and H. W. Schimmelbusch, Technical Report AFML-TR-70-109, May 1970, Boeing Document No. D6-60122

The Boeing Company

EFFECT OF EXPOSURE TIME AT 250°F ON STRESS-CORROSION CRACK GROWTH RATES IN 2024-T351 ALUMINUM

M. V. Hyatt and W. E. Quist

Objective

To determine the degree of sensitization to stress-corrosion cracking of 2024-T351 after exposure at 250°F (a temperature commonly used during curing of adhesively bonded assemblies).

Approach

Double cantilever beam (DCB) specimens of 2024-T351 were exposed at 250°F for times up to 300 hours. V-K curves (stress-corrosion crack velocity versus applied crack tip stress intensity) were then obtained in an environment consisting of intermittent wetting with aqueous 3.5% NaCl solution.

Achievements

Stress-corrosion crack velocities were observed to increase in specimens which had been exposed for only 2-5 hours at 250°F. Maximum crack velocity increases of about 60% occurred on specimens which had been exposed from 15 to 100 hours.

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FUNDAMENTAL ASPECTS OF STRESS-CORROSION CRACKING OF HIGH STRENGTH ALUMINUM ALLOYS

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Objective

At the Boeing Scientific Research Laboratories experimental and theoretical studies of stress-corrosion cracking in high strength aluminum alloys have three aims: (1) to identify the major influential parameters, that is, the conditions under which stress-corrosion cracks can grow; (2) to compare such conditions with those that cause stress-corrosion cracking in other alloy systems, polymers, and glasses, in an attempt to define their limits of applicability; and (3) to increase our understanding of the basic mechanisms of stress-corrosion crack propagation.

Approach

With complementary fractography and metallurgical examination, the main effort was concentrated on the measurement of stress-corrosion crack tip velocity as a function of the following parameters.

1. Mechanical parameters
 - a) applied crack tip stress intensity
 - b) specimen geometry
2. Environmental parameters
 - a) concentration of halide ions
 - b) concentration of other inorganic anions
 - c) concentration of water in the environment
 - d) presence of various gases
 - e) concentration of organic liquids
 - f) concentration of protons
 - g) presence of other cations
 - h) presence of liquid metal in the crack
 - i) temperature
 - j) viscosity of electrolyte
 - k) electrochemical potential
3. Metallurgical parameters
 - a) aging time
 - b) aging temperature
 - c) alloy concentration
 - d) recrystallization

Achievements

Crack propagation was shown to be affected by almost all the parameters listed. The first step in each case was to measure the effect of the variation of just one parameter on the velocity while keeping all the other parameters constant at some "reasonable" value. Our data showed that this can lead to quite different results,