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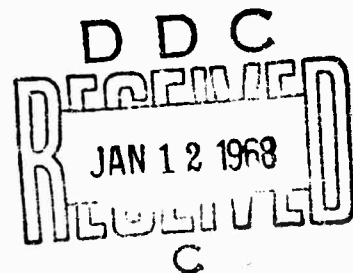
ARPA Coupling Program on Stress-Corrosion Cracking

(Fourth Quarterly Report)

Sponsored by

Advanced Research Projects Agency
ARPA Order No. 878

November 1967



NAVAL RESEARCH LABORATORY
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ABSTRACT

A progress report of the research investigations being carried out on the problem of stress-corrosion cracking of high strength materials under ARPA Order 878 is presented. Work at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory concerning physical metallurgy, surface chemistry, fracture mechanics, and characterization tests and translation related to stress-corrosion cracking is described. The materials being studied include high strength steels, titanium alloys, and aluminum alloys. Abstracts of recently published reports and a diary of events are included.

STATUS

This is a progress report; work is continuing.

AUTHORIZATION

NRL Problems 61M04-08
62M04-08
63M04-08A
63M04-08B
ARPA Order 878 and
RR 007-08-44-5512

INTRODUCTION

In order to learn how to improve high-strength structural alloys with respect to their resistance to SCC the Advanced Research Projects Agency of the Department of Defense has established under ARPA Order 878 a broadly based interdisciplinary attack upon the problem of SCC in high-strength titanium alloys, steels, and aluminum alloys. The project is composed of sectors located in The Boeing Company, Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, and the Naval Research Laboratory. In addition to having its own research activity, NRL has the responsibility for keeping the entire technical program attuned to DoD needs.

The complex phenomenon of SCC can be divided into four elements as follows: (1) the stress field, (2) the metallic phase, (3) the corrodent phase, and (4) the interface (with or without corrosion-product films) between metal and corrodent. Because of the obvious complexities of the phenomenon (and perhaps additional complexities not yet obvious), an interdisciplinary approach is essential.

The reporting system is as follows: Quarterly (commencing 1 January 1967) submissions from each unit of the project are submitted to section editors, who in turn submit the edited sections to NRL for publication as an NRL report. These sections must be kept brief to be manageable, and the project personnel are enjoined to publish the research details in the standard technical journals as a means of most effectively injecting the output of the program into the technological mainstream. When such publications are submitted to a technical journal, the abstract is included in the quarterly report, so that interested readers may contact the author if the subject matter is of immediate interest. Additionally, the abstract will again be published in the quarterly report when the paper finally is printed in the technical journal and is presumably available in reprint form. Reprints or requests for advance copies of such papers (or advance information contained in the papers) should be addressed to the

individual author or authors. Commencing with the Third Quarterly Report selected abstracts of reports and journal articles from outside the ARPA Program in the field of stress-corrosion cracking will be included as a service to readers of the Quarterly series.

The individuals responsible for directing this research at the various institutions and their participation as technical editors for the subject areas of their specialization in these progress reports are as follows:

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A. PHYSICAL METALLURGY

STEELS

Carnegie-Mellon University

The polarization characteristics of an 18Ni maraging steel (300 Grade) are being investigated by the potentiostatic method. Determination of the effects of heat treatment and chloride ion on these characteristics is the main objective.

The baseline for this study is the behavior in a de-oxygenized $\text{N H}_2\text{SO}_4$ solution. A typical anodic polarization curve obtained by the potential-step procedure is shown in fig. A. 1. The lower branch was somewhat time-dependent, but usually the current remained steady after 2 1/2 minutes. The upper branch was time independent. The potential span between the top of the lower branch and the bottom of the upper branch was not subject to potentiostatic control, i. e., no steady potential could be maintained in this region and rapid variations of both potential and current were the rule.

The only heat treatments for which polarization curves have been obtained are a 1500°F anneal for two hours followed by 700°F ages for various times. Very small shifts in the upper part of the polarization curve are the only effects of ageing the annealed material.

The effect of controlled alloy additions of selected impurities on the stress-corrosion cracking of 18Ni 300 Grade maraging steel is being investigated. 30lb. melts of the seven alloys described on page 5 of the Third Quarterly Report in this series have been successfully prepared for the contract by the P. D. Merica Research Laboratories of the International Nickel Company. After melting, the ingots were soaked for 1 hour at 2300°F., flattened twice, resoaked and then forged and rolled to bar-flats of 1/2" x 1 1/2" cross-section, suitable for further heat-treatment and eventually for use as pre-cracked cantilever-beam S. C. C. test specimens. Analysis of the alloys showed that more or less satisfactory composition and impurity concentrations had been attained. 30 lbs. of the original very high purity melting stock are still intact and will be used to prepare further alloys at a later date, as indicated by the results of the present phase of the work. Each of the alloys has a somewhat different age-hardening response due to the different impurity concentrations, and as it is most satisfactory to investigate the S. C. C. susceptibility of each alloy at the same strength

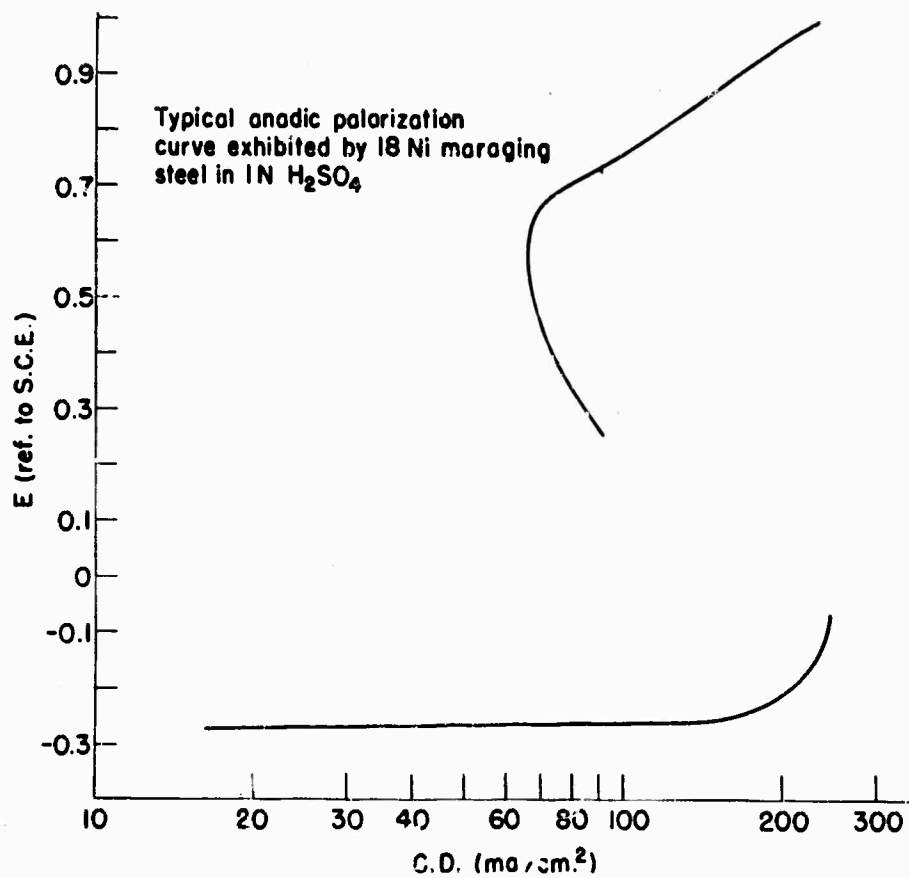


Fig. A-1 - Typical anodic polarization curve exhibited by 18Ni maraging steel in 1 N H₂SO₄

level, these ageing responses were determined for each alloy, using small samples from the large specimens. This investigation has enabled a particular combination of ageing time and temperature to be selected for each alloy so that all the S. C. C. test specimens of all the alloys will eventually have the same mechanical properties. The S. C. C. test specimen material is currently being heat-treated, as indicated by the preliminary investigation, to achieve this end. All the S. C. C. testing will thus be done on material of yield strength of 270-280 k. s. i. in 3.5% NaCl at a controlled temperature and fully aerated. The heat-treatment is also such as to result in suitably homogeneous specimens.

The diffusion of hydrogen in steel around room temperature is being studied. Apparatus for automatic abrading of steel sheet in water has been designed and built; copper gaskets were used at both sides of the steel sheet to maintain a high vacuum condition during the abrasion. The whole experimental complex consists of the automatic abrasion apparatus, a VacIon Pump (15 liter/sec, Varian Associates Co., Model 911-5011) with Control Unit (Model No. 921-0013), a Mass Spectrometer (Residual Gas Analyzer, Consolidated Electrodynamics Corporation, Type 21-615) containing an Analyzer Assembly and Control Unit, a Recorder (Honeywell Electronik 18), the glass vacuum parts (Zeolite trap [Linde Company, Type 13X] and liquid nitrogen trap) and a mechanical pump. The main parts of the experimental equipment were connected with metal Tees and Viton-sealed right-angle valves (Varian Associates Co.). The bakable experimental parts, including all the most important equipment, are surrounded by an electric oven, which is removable and has a uniform temperature distribution at the required baking temperatures. A modified connection between the Control Unit of the Mass Spectrometer and the Control Unit of the VacIon Pump has been developed to make use of the vacuum protection of the latter for the former, so that the purchase of a Cold-Cathode Vacuum-Gage was not necessary. The vacuum in the apparatus can be checked in the glass and metal systems separately, using a Viton-sealed right-angle valve. The operation and capabilities of the VacIon Pump and Mass Spectrometer are currently being tested.

The effect of prior-austenite grain-size on the stress-corrosion cracking of AISI 4340 steel is being studied. Six sets of S. C. C. test specimens with varying prior-austenite grain-sizes covering the range

A.S.T.M. 6 to 11 have been produced; the 3 coarser grain-sizes were developed by conventional heat-treatment techniques while the 3 finer grain-sizes were developed using the repeated austenising and quenching technique developed by Grange.* Currently this range is being extended to both coarser and finer grain-sizes by respectively increasing austenising times (the maximum austenising temperatures available being limited to 1700°F) and more numerous repeated austenising and quenching treatments (the minimum austenising time being limited by the specimen dimensions). It is hoped eventually to cover at least the range A.S.T.M. 3 to 13. The hardness of the specimens already heat-treated, after a 1 + 1 temper at 400°F, increases as the grain-size decreases. The yield-strengths, as estimated very approximately from the hardness and other published data for 4340 steels, cover the range 240-270 k.s.i. Furthermore, in spite of the very crude estimations, the yield strengths show a surprisingly good Hall-Petch relationship to the prior-austenite grain-size, as determined metallographically using a special etchant; this relationship was first noted for quenched and tempered steels by Grange. Unfortunately slight decarburization occurred during the heat-treatments; this has necessitated surface - grinding the heat-treated specimens, prior to fatiguing and testing, to remove the soft surface layers. A successful technique for fatigue pre-cracking the specimens in cantilever-bending according to the suggestions in A.S.T.M. STP 410 has been developed. Currently cantilever-beam S.C.C. specimens (cross-section approx. 1/2" x 3/2") of the heat-treated 4340 steel are being tested in a corrodent of circulating 3.5% NaCl, controlled at 40°C and fully aerated, to determine the usual curves of K_{Ii} against time to failure.

Georgia Institute of Technology

The various components of a Field Ion/Emission Microscope were delivered and assembled in the latter part of June. At the same time, Dr. Brian Ralph, of the University of Cambridge, England, arrived as a visiting professor at the Institute. Dr. Ralph leads the world's largest Field Ion Microscopy Group and is primarily concerned with the application of FIM to problems in physical metallurgy. With his help modifications in instrumentation and imaging techniques have resulted in early success in obtaining useful images. The effect of the ordered Ti_3Al in titanium-aluminum alloys and the effect of Ni_4Mo in stress re-

* R. A. Grange, A.S.M. Trans. Quart., 59, 1966, 26.

lieved 316 stainless were the basis for the initial studies. Alloys of Ni_4Mo and Ti_3Al were prepared for field ion microscopy. Figure A.2 is a field ion micrograph of the ordered Ni_4Mo . Better contrast and resolution are now being developed for this alloy. Ti_3Al images have also been obtained but the technique requires additional evaluation. Once the techniques have been developed for the ordered alloys, alloys of lower composition and even dilute solutions will be studied.

A symposium on the application of Field Ion Microscopy to Physical Metallurgy and Corrosion is planned for April 17 and 18, 1968. Dr. Ralph and Dr. Hochman will act as co-chairmen for the program and it will serve as the final two days of the annual ARPA meeting. Preliminary arrangements have been made to publish the program.

Studies on the effects of interstitial elements on maraging steels have begun. To date the effect of minor alloying elements on 316 and 316L stainless steels have been studied. It is planned that a complete paper and master's thesis be completed on the 316 and 316L work in the next six months. This will then serve as a basic report in this area. At present increases in mechanical properties as well as improved corrosion resistance for stress-relieved 316 have been observed.

The Boeing Company

An investigation entitled High Strength Steel Evaluation for Supersonic Aircraft, Commercial Supersonic Transport Program, Phase II-C Report, Contract FA-SS-66-5 was conducted recently to establish the crack growth resistance of several high-strength steels in 3.5-percent sodium chloride solution. Pre-cracked, single-edge-notched specimens of 300M, H11, Maraging 250, 4330V, 9Ni-4Co-0.30C, and 9Ni-4Co-0.45C (martensitic and bainitic) steels were four-point-loaded to establish K_{Isc} values. The failed specimens from this investigation were examined to determine the morphology of crack growth in salt solution.

It was found that crack extension from the tip of the fatigue precrack was either by a single crack (Type 1) propagating along the fatigue crack plane or by two divergent cracks (Type 2) that propagated at an angle to the fatigue crack plane. The 4330V, 9Ni-4Co-0.30C, and 9Ni-4Co-0.45C (bainitic) steels showed either Type 1 or Type 2 cracking, depending on the initial plane-strain stress-intensity level K_{II} . A transition from Type 1 to Type 2 cracking occurred in these steels when the ratio $K_{II}:Y$ exceeded approximately 0.25, where Y is the tensile yield strength. The



Fig. A-2 - Field ion micrograph of ordered Ni₄Mn. Several ordered domains and twinned areas are present

remaining steels - 300M, H11, Maraging 250, and 9Ni-4Co-0.45C (martensitic)-generally exhibited Type 1 cracking, and did not show the transition to Type 2 cracking. Secondary branch cracks diverged from the primary Type 1 crack propagation in 300M and 9Ni-4Co-0.45C (martensitic) steels. This branching significantly delayed the onset of rapid brittle fracture, particularly in the high-nickel steel where the apparent K_{IC} was twice as high as the known K_{IC} .

Fractographic examination of Type 1 cracks showed that initiation occurred in the region of maximum triaxiality ahead of the fatigue pre-crack border. Plastic constraint in this region raises the local tensile stress above the tensile yield stress Y . Hahn and Rosenfield* in a recent paper indicated that this stress can be estimated as $(1 + 2 \text{ in.}^{-1/2} \frac{K_I}{Y})Y$,

where K_I is the stress intensity at the crack tip. The minimum stresses for crack initiation have been determined using this expression and the experimentally determined K_{ISCC} values. These stresses were 340 ksi for Maraging 250, and ranged from 250 to 260 ksi for the other steels.

A comparison of the martensitic microstructures reported for these steels showed that the steels with the highest initiation stress have no transformation twins, whereas the steels with the lowest stress contain a high degree of transformation twins. Other investigators have shown that transformation twins have a detrimental influence on hydrogen embrittlement resistance. Moreover, the Troiano theory of hydrogen embrittlement predicts crack initiation in the region of maximum triaxiality.

The state-of-stress had a significant effect on the morphology of Type 2 cracks. Under plane-stress conditions the cracks propagated as arcs across the reduced section below the notch. Under plane-strain conditions, at a suitable ratio of K_{II} to Y , the cracks could extend along planes inclined 60 degrees to the fatigue crack line. In one specimen an inclination of 90 degrees was observed. Similar observations have been reported for the spread of plastic zones from a crack in a specimen subjected to a rising applied load. This suggests that Type 2 propagate by a repetitive process of growth through the plastic zone at the crack tip. No specific mechanism could be identified for Type 2 cracks; plans are being made to examine the influence of impressed currents on crack morphology.

Type 2 cracks extended preferentially along the side borders (plane-

* G. T. Hahn and A. R. Rosenfield, Trans. A.S.M., 59, 1966, 909

stress regions) of the specimen and lagged at the midsection. This behavior is contrary to the current hypothesis that plane-stress regions are more resistant to cracking in corrosive environments.

ALUMINUM ALLOYS

Carnegie-Mellon University

The stress-corrosion cracking of the 7075-T6 aluminum alloy in organic liquids is being investigated. As described on page 10 of the Third Quarterly Report in this series, transgranular crevice growth occurs when cantilever-beam specimens of this alloy containing an RW-type fatigue pre-crack are stressed and exposed to environments of ethanol + 1% Br; this phenomena will be investigated further at a later date. When similar specimens are exposed to reagent grade methanol, ethanol, isopropanol and ethylene glycol and stressed, the crack grows transgranularly a short distance ($1/2 - 1\ 1/2$ grains) in the RW direction but after this intergranular branching and growth of WR-type cracks occurs. This effectively blunts the RW crack so that when such specimens are fractured by overloading the "apparent fracture toughness" is raised very considerably and a flat fracture does not occur, as when a fatigue pre-cracked specimen is fractured; the two types of fracture are illustrated in figs. A-3 and A-4. The intergranular WR-type cracks grow quite considerable distances (of the order of 500 microns or more on occasion), and presumably stop when the crack opening force reaches a low enough value. There seems little doubt that these cracks are due to some "stress-corrosion" process; they are not observed in 7075-T6 precracked specimen exposed to ethanol without stress or in precracked specimen stressed in dry air for periods up to 10^4 minutes each. It is extremely difficult to obtain and maintain "dry" ethanol; however, the intergranular cracking, which was illustrated in the Third Quarterly Report, occurs when stressed specimens are surrounded by a sealed container containing fresh absolute alcohol and calcium oxide as a drying agent.

Further testing rigs to enable WOL specimens of 7075-T6 to be tested, again under plane stress conditions, have been designed and built. Specimens containing a WR-type fatigue precrack were exposed to methanol, ethanol, isopropanol and acetone for periods of 2×10^4 minutes. They were then cut along a T-type plane through the center of the specimen, the unfractured half of the specimen was examined metallographically and the other half was fractured by overloading so that the fracture surface

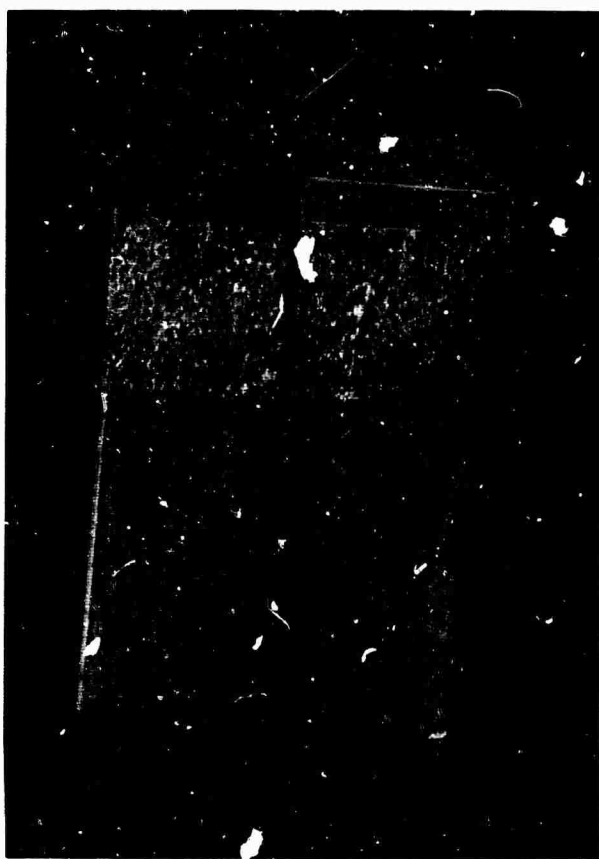


Fig. A-3 - 7075-T6 fatigue-precracked
C.B. specimen exposed to ethanol for
 10^4 min. with no stress, and then frac-
tured in air by overloading

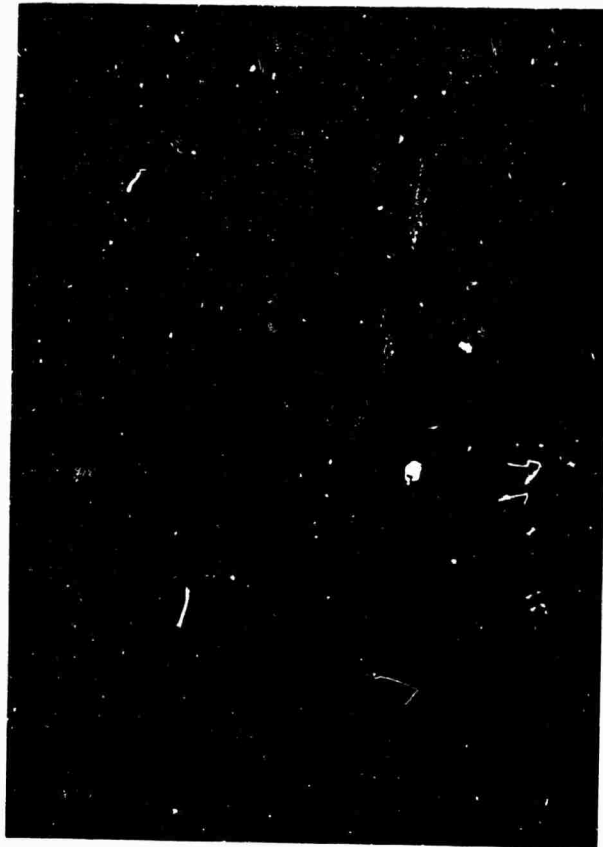


Fig. A-4 - 7075-T6 fatigue-precracked C.B. specimen exposed to ethanol for 2×10^4 min. at about 70% K_{Ic} and then fractured by overloading

could be viewed as well. In all cases typical intergranular stress-corrosion crack growth had occurred. On the metallographic specimens it was clear that the end portions of the crack were intergranular and due to S.C.C. while the earlier regions were transgranular and due to fatigue, but it was difficult to locate the precise change-over point from fatigue to stress-corrosion. On the fractured surfaces, however, this problem did not occur and the regions of fatigue, stress-corrosion and rapid fracture were immediately obvious, as shown in fig. A-5. Even when an inclined fatigue crack was put in the specimen, stress-corrosion occurred and the crack took off intergranularly at an angle to the fatigue crack, as shown in fig. A-6. A typical stress-corrosion crack tip is shown in fig. A-7. Owing to the experimental difficulties no attempt was made to keep the alcohols dry and conductivity measurements showed that the ethanol had absorbed up to 2% water over the test period; it is very probable that the other corrodents had similarly absorbed some water. The movement of the loading arm of a specimen in a dry air environment was recorded over a period of 2×10^4 min.; there was negligible deflection and subsequent examination of the specimen showed no evidence of any crack growth. A similar experiment conducted with an ethanol environment showed that the loading arm was deflecting right from the start of the test, when fresh, dry absolute alcohol was added. Although the apparent crack growth rate as determined from the curve of loading-arm-deflection against time did increase slightly as the test progressed, there is no evidence to show whether this was due to net section yielding, increasing stress intensity at the crack tip or absorption of water. To summarize, stress-corrosion cracking of aluminum 7075-T6 alloy does occur in organic alcohols; it is considered that this is not due to traces of water but this has not been conclusively proved.

Currently, similar tests are being run using corrodents which have little affinity for water and are easier to keep dry (e.g. carbon tetrachloride, benzene, heptane, etc). It is also intended to determine K_{Iscc} values for some of these organic corrodents in the near future.

The effects of solution temperature, quenching rate and aging temperature on the aging process in Al-4%Cu and Al-Zn-Mg alloys are being determined. The hardness response to aging has been similar to that reported in other work. Since the precipitate free zone (PFZ) adjacent to grain boundaries is known to be controlled by these variables it is hoped that test specimens can be produced with different PFZ widths but with

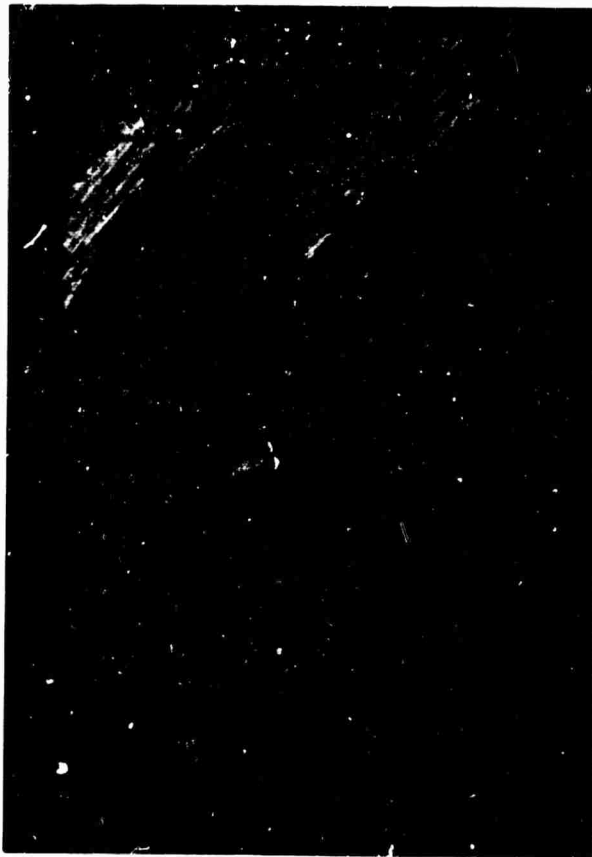


Fig. A-5 - 7075-T6 fatigue-precracked
WOL specimen exposed to methanol for
 2×10^4 min. at about 80% K_{Ic} and then
fractured by overloading



Fig. A-6 - 7075-T6 fatigue-precracked WOL specimen exposed to ethonal for 2×10^4 min. at about 75% of K_{Ic} and then fractured by overloading. Original fatigue crack inclined at 45° to R direction.

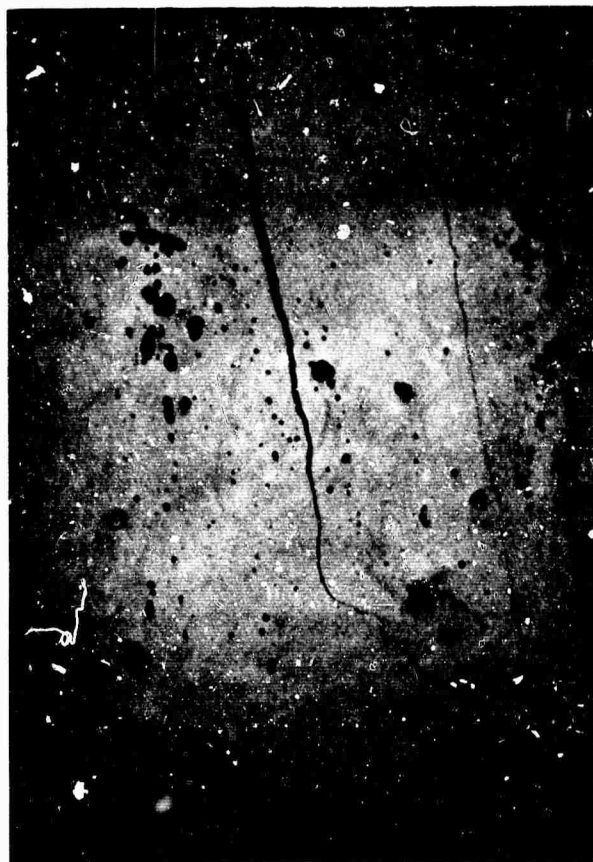


Fig. A-7 - Tip of intergranular stress-corrosion crack in WOL specimen of 7075-T6 exposed to acetone for 2×10^4 min. at about 60% K_{Ic} ; x 400.

the same macroscopic hardness and tensile properties. These will then be compared under stress-corrosion conditions.

A strain-anneal technique is also being developed to produce large (1/4" diameter) grains in thin sheet material. The purpose of this is to enable a close investigation of the cracking phenomena under highly controlled conditions to be made.

Lehigh University

Stress-corrosion crack propagation studies have been completed, in aqueous 3 1/2% NaCl, on fatigue pre-cracked 1/2" thick short transverse 7075-T6 alloy specimens. Tests with initial stress intensity values ranging from 14 k.s.i. $\sqrt{\text{in.}}$ to 22 k.s.i. $\sqrt{\text{in.}}$ exhibited crack growth rates which did not increase as the crack grew (i.e., the crack tip stress intensity increased). These results can be interpreted as indicating that corrosion (availability of corroding species) rather than the crack tip stress intensity is primarily controlling the crack growth. Additional tests are being run on thinner specimen where the distance the corroding media must diffuse is greatly reduced. (Due to the low stress intensity at which stress-corrosion cracks propagate in this alloy, the specimen thickness can be reduced to as thin as 0.100" and theoretically the crack tip should still be essentially under a plane strain stress state). All of the stress-corrosion cracks grew to a length where the stress intensity was 27 ± 1 k.s.i. $\sqrt{\text{in.}}$, at which point rapid failure occurred.

Several tests have indicated that if the stress intensity of a growing crack is reduced (i.e. the load reduced) to a value greater than the initial stress intensity, the cracks stop propagating and do not reinitiate (tests were discontinued after 100 hours). This phenomena of crack growth arrest has been observed previously in fatigue and creep studies. Further tests are planned to investigate more completely this arrest phenomenon.

TITANIUM ALLOYS

Georgia Institute of Technology

The studies in this area are concerned with three titanium-aluminum binary (alpha phase) alloys. Large alpha grain size is produced through the established technique of solution heat treatment at 1400°C for 6 to 8 hours followed by quenching to approximately 100°C below the alpha transition and holding there for 4 to 6 hours. Because of the large temperature

range during heat treatment, and the requirement of a controlled atmosphere, a special high temperature vertical quench furnace has been constructed. Techniques have been established for fractography, x-ray diffraction, transmission electron microscopy, grain orientation determination by polarized light, and dislocation characteristics at the fracture site. A graduate student on this program spent one month at the NRL this summer working in areas related to the studies on this program; this visit resulted in a broadening of his background which will do much to amplify this graduate research program.

The Boeing Company

The relation between the stress-corrosion fracture path and microstructural features in several titanium alloys has been studied by means of optical microscopy and x-ray diffraction. The alloys studied were Ti-3Al-1Mo-1V, Ti-6Al-4V, Ti-4Al-3Mo-1V, Ti-5Al-2.5Sn, and Ti-13V-11Cr-3Al. Some of the metallurgical variables shown to influence the stress-corrosion susceptibility of titanium alloys are the crystalline structure of the susceptible phase (h.c.p. or b.c.c.), preferred grain orientation, and relative phase content where one phase is immune.

Stress-corrosion cracking occurs on or near the {100} planes in the b.c.c. beta phase, but can only occur near the single (0001) plane in the h.c.p. alpha phase. This restriction on cracking in the alpha phase results in the significant influence of preferred orientation, and also partly explains the dependence of susceptibility on the state-of-stress in the high-alpha alloys.

The apparent lack of correlation between the stress-corrosion susceptibilities of the phases and their structures indicates that the basic mechanism is surface-controlled rather than structurally controlled.

B. SURFACE CHEMISTRY

ELECTROCHEMISTRY

Carnegie Institute of Technology

With the shielded reference electrode system used for the measurement of steady state anode polarization voltage, the rate of polarization is too fast to be measured with our present recorder, if saturated aqueous ferrous chloride solutions are the electrolytes. Considerable time has been devoted to the construction and trial of new electrode systems with as low electrical resistance between anode and reference electrode as possible. The electrode system now in use consists of a hollow cylinder with a solid cylindrical cap electrode which serves as the reference electrode and is separated from the main (anode) electrode by a 2 mil polyethylene film washer.

The anodes and caps used so far have been made from Armco 1308 iron. When first assembled the voltage difference between cap and anode with no current flow is of the order of 25 to 50 millivolts but drops with time. The aging process can be greatly accelerated by passing one milliampere for several hours using the cap electrode as an anode, and after the electrolysis treatment the potential difference between cap and main electrode was less than two millivolts.

Experimental behavior is shown in Figure B-1. In part A of the curve the anode overvoltage increases to a plateau. With continued flow the plateau slowly shifts, part B, to a new and lower level at which the system will continue for an indefinite period of time. If the current is turned off, the overvoltage decreases as in part C. Part A is first order, part C is between first and second order and closer to second with calcium chloride-ferrous chloride solution than with saturated ferrous chloride solution.

Apparently during electrolysis, in the immediate vicinity of the electrode, concentrations of ferrous ion are somewhat greater than the equilibrium values imposed by the presence of solid ferrous chloride. Attempts to relate this concentration gradient to the overvoltage have not been successful as yet. Part B must be affected by one or more of: the diffusion of ferrous ions into the bulk solution, diffusion of chloride ions to the vicinity of the anode,

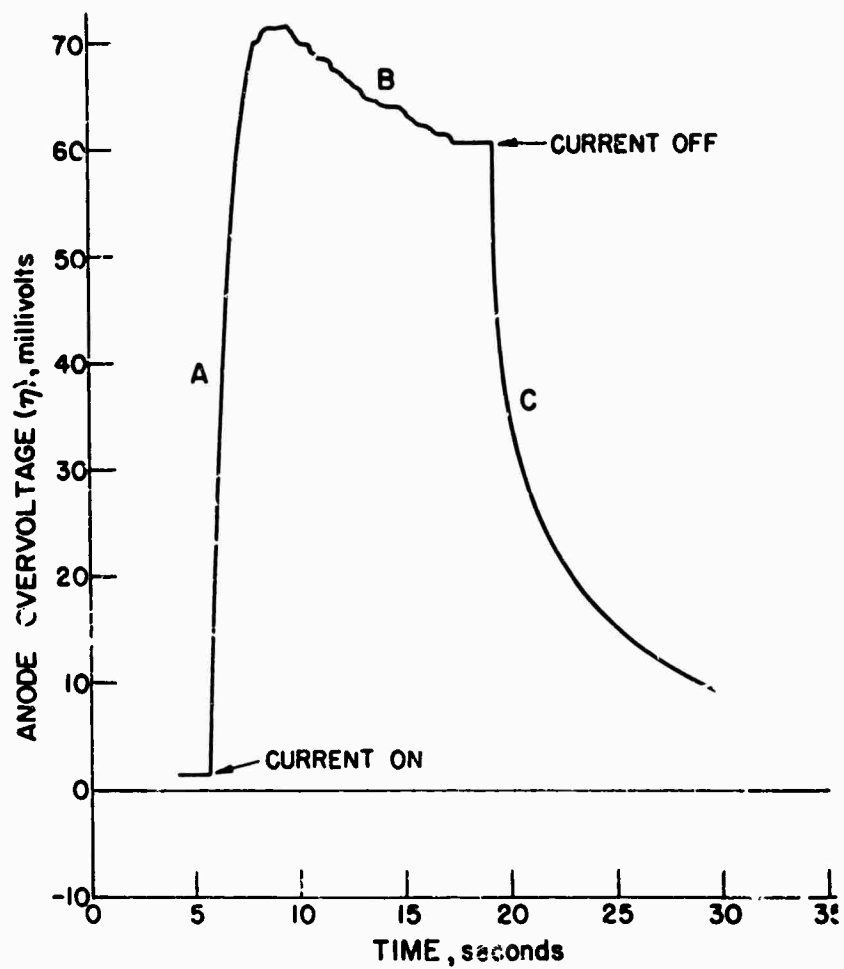


Fig. B-1 - Plot of anode overvoltage vs. time

electrical transport of ferrous and chloride ions, nucleation and precipitation of solid ferrous chloride. Part C involves the same complexity of mechanism as part B although electrical transport of ferrous and chloride ions is no longer involved. By their interference with electrical transport and diffusion processes electrolytes such as calcium chloride and non-electrolytes such as urea should permit the mechanism to be elucidated.

Naval Research Laboratory

Electrochemical investigation of the passivity of pure iron is continuing in the NRL high-purity, closed electrochemical system. Measurements were made in sodium and lithium hydroxide solutions of various concentrations and effects of trace impurities are being determined. Results have indicated several regions with different passivity. The passive films do not appear to be bulk oxides, and depending on the potential region, the currents obtained are associated with either the reduction of water to hydrogen or its oxidation to oxygen. Steady state potential vs. current density measurements require very long times (hours or even days) which is interpreted as meaning that sorbed species, primarily oxygen and hydrogen atoms, in the top atomic layers of the iron can have marked effects on its behavior.

MACROSCOPIC SURFACE MEASUREMENTS

Georgia Institute of Technology

The mechanical properties of many materials have been found by numerous investigators to be sensitive to the environmental conditions at the surface. Mechanical measurements on thin metal foils and oxide films were initiated at Georgia Tech to isolate for detailed study the material volume most directly affected by the surface. An apparatus (Figure B-2) was developed which has the sensitivity and precision necessary for measurements on very thin samples in both air and liquid environments. An air bearing torque dynamometer is employed for small force measurements and a differential transformer is currently being used for displacement measurements.

Measurements have been made on unsupported anodized aluminum oxide films in air, on pure aluminum and on pure titanium foils. Titanium foils with both the normal oxide and thermally oxidized surfaces are now being

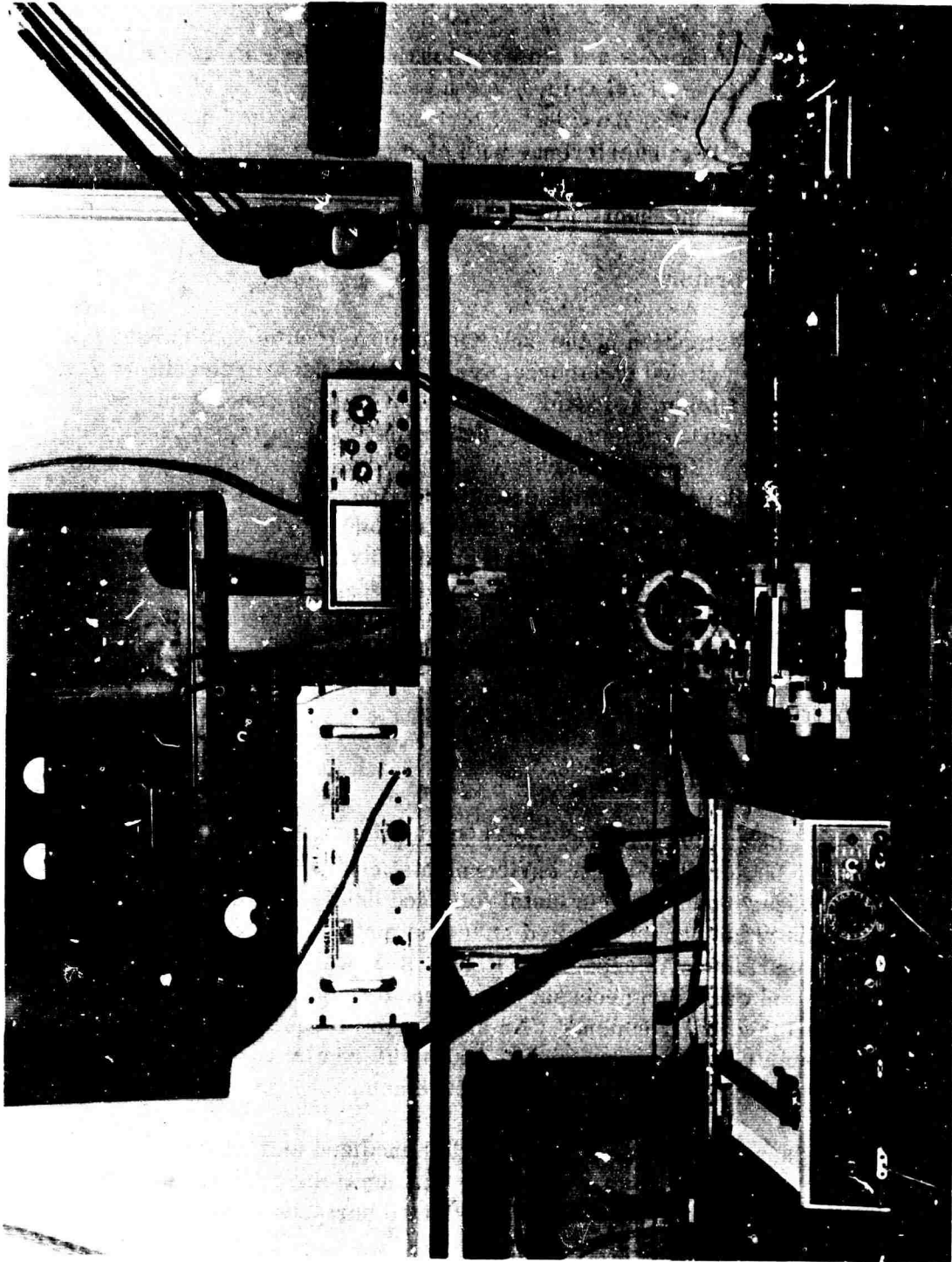


Fig. B-2 -Apparatus for making microtensile measurements on thin foils and films

bent in air, distilled water, salt water, methanol, and acetone environments. Transverse force vs. transverse displacement data for a 2.5×10^{-4} inch thick titanium foil in three liquid environments are shown in Figure B-3. Each of these curves was obtained from three point bending measurements in the elastic stress region of the material. An evaluation of these data as well as data obtained from several other pure titanium foils indicates that the elastic modulus is lowered significantly for a foil in methanol but little or not at all for a foil in either acetone or distilled water. These measurements are being continued. In addition, thin samples of three high strength titanium alloys are being prepared from material stock obtained from and evaluated at NRL. Both bending and tensile experiments will be carried out on the very thin alloy samples to determine how these measurements relate to bulk stress corrosion cracking data.

Lehigh University

Preliminary experiments using the apparatus for flash desorption studies of interactions between hydrogen and titanium have been completed. Adsorption-desorption spectra of nitrogen on tungsten have been recorded and will be analyzed using a computer program which is now being written. Comparison of this work with data in the literature will establish working parameters and techniques for the titanium experiments.

An apparatus for the deposition of variously stressed nickel films in UHV is now being constructed. Adsorption of gases on the films will be investigated by ferromagnetic resonance measurements.

Samples of six copper-gold alloys have been received and are being heated for two weeks at 850°C before quenching in cold water. Immersion tests in a 2% ferric chloride solution at 25° and 100° on stressed and unstressed, homogenized and as cast alloys will follow.

In continuing studies of the interaction of oxygen with metal oxides, ESR spectra from low area rutile (TiO_2) were investigated as a function of oxygen pressure. Two signals were observed: one was possibly O_2^- ; the other has not yet been identified. Variations with oxygen treatment temperature of these two signals on high area rutile have yielded more clues concerning the nature of the adsorbed species.

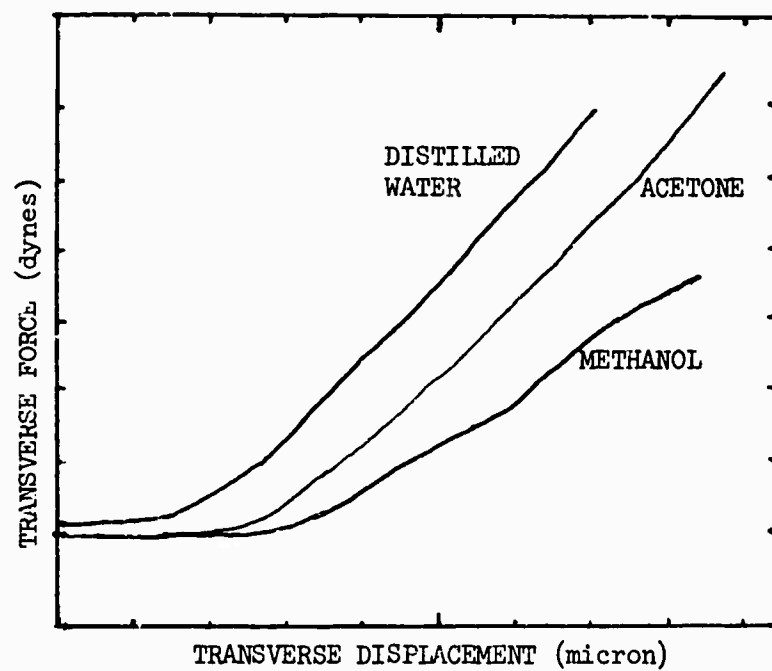


Fig. B-3 - Transverse force vs. transverse displacement curves obtained for titanium foils in different environments

Zinc oxide is also being studied. As an aid to the identification of the species adsorbed on its surface the effect of oxidation of oxygen-deficient zinc oxide by the nitrogen oxides is being studied by ESR techniques. That reaction with nitrogen dioxide eliminated Zn^+ was demonstrated by the decrease in the signal at $g = 1.96$, and formation of a sharp and symmetrical signal (4 gauss peak to peak) at $g = 2.015$. The latter signal is probably due to O^- on the surface although one would have expected a triplet, not a singlet from this species on the ZnO lattice. Nitrous oxide interaction with similar zinc oxide samples seems to confirm O^- formation. Both ESR projects are continuing.

Naval Research Laboratory

Procedures have been developed for the preparation of adsorbed monomolecular films of carbon-14 tagged stearic acid on iron and nickel, and on 304 and 416 steel alloys. The packing density of the stearic acid appears to be greater on Armco iron than on the other metals studied which may be related to the high reactivity of iron (or iron oxide) surfaces. Thermal desorption studies of the films have been started.

In the study of oxide films formed on iron in aqueous media, experiments have been initiated for determining the effect on corrosion, if any, of incorporation of cobalt or manganese in the spinel protective film generated on a steel specimen in alkaline water solutions. Investigations are being made of changes in the rate of hydrogen evolution in a Bloom hydrogen effusion apparatus at 300°C caused by the addition of cobaltous ions. Information gained from these measurements will be applied to treatment of high strength steel alloy specimens for stress corrosion cracking tests using the Brown cantilever beam technique.

C. CHARACTERIZATION TESTS AND TRANSLATION

TEST TECHNIQUES

Stress-corrosion cracking properties of a 7079-T6 high-strength aluminum alloy in the TR orientation (crack running parallel to rolling plane and direction) have been measured at NRL using a uniform double-cantilever beam (DCB) specimen. Figure C-1 shows the DCB specimen together with the load application apparatus used in these experiments. The specimens are 1 in. by 1 in. by 4 in. and contain a 1-in. machined notch. This notch may be further sharpened by fatigue cracking, but with this particular alloy it was not necessary. The load is applied with a stiff tensile proving ring, and the specimens can be immersed in an aqueous environment in a way that wets only the crack tip and unbroken ligament.

The test results are shown in Table C-1. Initially, only specimen F contained a prefatigue crack and, therefore, the values of K_{Ii} are only indicative of the initial stress intensity. Compliance measurements for this loading configuration are being conducted. The K_I levels have been determined through use of the approximate formula:

$$K_I = \frac{2P}{b} \left[\frac{3(a+0.6h)^2 + h^2}{(1-\nu^2)h^3} \right]^{1/2}$$

where P is the load; h , the specimen half height; b , the specimen width; a , the crack length; and ν , Poisson's ratio.

These results indicate the salt water $K_{I_{SCC}}$ of this material is approximately 7 ksi $\sqrt{\text{in.}}$.

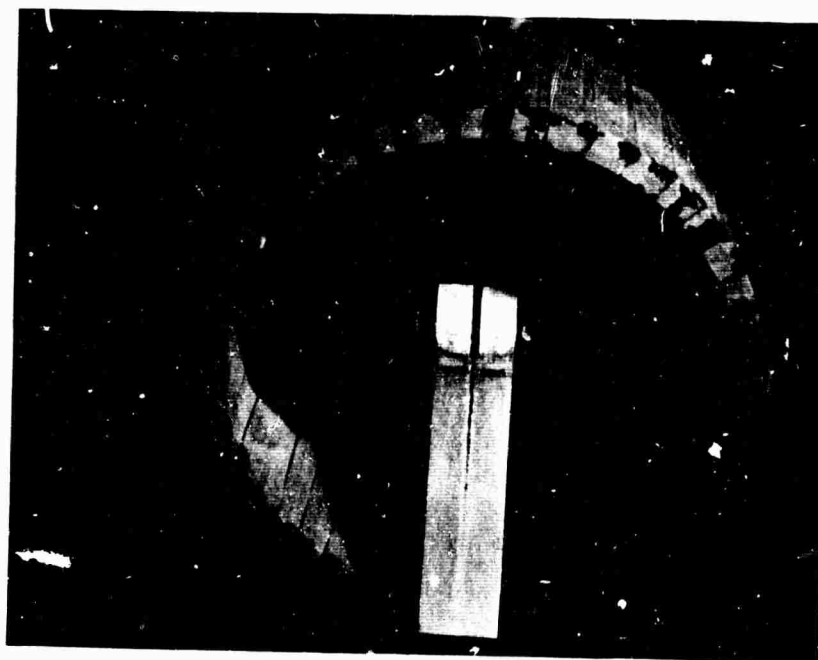


Fig. C-1 - DCB specimen and loading device

TABLE C-1

Specimen	Remarks	K_I (ksi $\sqrt{\text{in.}}$)	$K_{I \text{ SCC}}$ (ksi $\sqrt{\text{in.}}$)	K_{I_x} (ksi $\sqrt{\text{in.}}$)	Time (hours)
B	3.5% NaCl	16.0	7.2	15.6	24
E	3.5% NaCl	15.0	7.1		50
E	3.5% NaCl (reload)	10.0	7.8	16.2	22
F	3.5% NaCl (prefatigue crack)	11.7	6.3		32
F	3.5% NaCl (reload)	10.0	7.0		23
F	3.5% NaCl (reload)	10.0	7.8		17
G	Distilled H ₂ O	10	9.2		28
G	3.5% NaCl	9.2	7.3		24

GENERAL CHARACTERIZATION STUDIES

The effects of variations in heat treatment on the mechanical properties and stress-corrosion susceptibility of Hylite 50 have been determined at Boeing and are tabulated below. Hylite 50 is a British commercial titanium alloy containing 4 percent Al, 4 percent Mo, 2 percent Sn, and 0.5 percent Si.

TABLE C-2

Heat Treatment	Tensile Properties				Fracture Properties	
	UTS (ksi)	0.2% YS (ksi)	R A (%)	Elongation in 1 in. (%)	K _{IC} (ksi√in.)	K _{ISCC} (ksi√in.)
1650°F/30 min/WQ	169.5	136.1	47	17	54	45
1800°F/30 min/WQ	212.1	182.4	6	4	46	42
1650°F/30 min/AC +932°F/24 hrs/AC	168.6	157.5	46	14	52	30
1650°F/30 min/AC +1100°F/24 hr/AC	162.9	153.8	44	14	43	23
1650°F/30 min/AC +1300°F/24 hrs/AC	150.7	145.6	43	15	42	23
1500°F/30 min/WQ +1100°F/24 hrs/AC	157.2	150.5	44	14	45	20
1650°F/30 min/WQ +1100°F/24 hrs/AC	175.7	164.7	39	12	31	19
1800°F/30 min/AC +1650°F/30 min/WQ +1100°F/24 hr/AC	172.6	156.8	8	5	57	31

D. FRACTURE MECHANICS

Lehigh University

Fatigue crack propagation experiments were carried out within the framework of linear elastic fracture mechanics to examine the effect of water and its constituents on the rate of crack growth in a high strength aluminum alloy over a range of test temperature from 295 to 380°K. Dehumidified high purity argon was used as an inert reference environment.

The results indicate that fatigue crack propagation itself is controlled by a thermally activated process, the apparent activation energy being strongly dependent on the crack-tip stress intensity parameter.

The results also showed that water accelerated the rate of fatigue crack growth by about a factor of 10 in this temperature range, whereas dry oxygen and dry hydrogen had a negligible effect on the rate of crack growth. They tend to confirm the findings of Hartman, and Bradshaw and Wheeler, that the cause for the large increase in the rate of crack growth by water is the formation of hydrogen gas with high pressure in the region ahead of the crack tip, driven in by the reaction of water with the freshly created aluminum crack surfaces, as suggested by Broom and Nicholson.

Fatigue crack propagation in water is again controlled by thermally activated processes. The rate controlling step, for the range of crack growth rates 10^{-6} to 10^{-5} in./cycle, appears to be that associated with the creation of new crack surfaces.

The strong dependence of the apparent activation energy on ΔK suggests that a careful study of the kinetics of crack growth and a reexamination of the crack propagation laws are in order. Complete theories of fatigue crack propagation must incorporate both the mechanical and environmental variables.

Naval Research Laboratory

The effect of notch acuity on the initiation of stress-corrosion cracking in cantilever-beam bend test specimens was investigated using four titanium specimens with machined notch flaws having varying root radii. The results of these studies were compared with results from precracked specimens.

Notches with root radii of 0.002 in., 0.005 in., 0.010 in., and 0.015 in. were machined into specimens of four alloys with K_{ISCC} threshold levels as follows:

Ti-7Al-2Cb-1Ta (31 ksi $\sqrt{\text{in}}$)
Ti-6Al-4V (68 ksi $\sqrt{\text{in}}$)
Ti-6Al-4V-2Sn (88 ksi $\sqrt{\text{in}}$)
Ti-5Al-2Mo-2V-2Sn (100 ksi $\sqrt{\text{in}}$)

The specimens were tested in the cantilever bend test in 3-1/2 percent salt water solution.

The highly sensitive Ti-7Al-2Cb-1Ta alloy did not show any effect of the notch root radius; the threshold value for this alloy increased to only 35 ksi $\sqrt{\text{in}}$ for the 0.015 in. radius. However, the threshold value for the other three alloys were highly dependent on the radius of the notch. The threshold values increased quite rapidly with increasing root radius. It appears that a fatigue crack is required to initiate stress-corrosion cracks in titanium alloys at the lowest possible stress intensity level.

Continuously monitored load-deflection curves amplified at appropriate time intervals have provided crack velocity (V_C) data for two titanium alloys (Ti-8Al-1Mo-1V and Ti-7Al-2Mo-1V). The specimens were beams loaded in three-point bending. Examination of the beam characteristics revealed that the constant K curve of load against displacement was so nearly a straight line in the region of interest that with suitable adjustment of machine stiffness, the specimen would unload along the machine stiffness curve with K constant to less than 5 per cent. Therefore, loading to a predetermined

value, then locking the head (constant displacement), provides several data points at constant K . The load can then be either increased or decreased to provide data at other levels of K . An as yet unanswered question, however, is the effect on crack growth of the enlarged plastic zone necessarily present when going from a high to a low K value.

Further, it has become obvious that as the crack grows, a point is reached where the detecting gage is no longer indicating crack growth but a hinge-type yielding in the unbroken part of the beam, and that this is dominant rather than beam thickness in determining test validity. Therefore, only those points are considered valid where $\beta^1 < 0.5$

$$\beta^1 = \frac{1}{W-a} \left(\frac{K}{\sigma_{YS}} \right)^2$$

When these selected points are plotted as K vs $\ln V_C$, a discrimination between the two alloys is attained. However, the curves have an apparently steeper rise than that predicted by Krafft's dissolution model analysis, though of the correct order of magnitude; approaching K_{IC} , the 7-2-1 alloy has a V_C of 0.9×10^{-3} in./sec, whereas the 8-1-1 is faster, 4.4 in./sec.

The dynamic mechanical behavior at the tip of a plane strain crack has been further examined for two ferritic steels¹. Although the stress intensity around the crack is continuously varying in an elastic singularity, in real materials the pattern breaks down at the tip across discretely sized regions of stress relaxation. Within these regions, conditions of stress, strain, and strain rate can be characterized as uniform and equal to the point value in the singularity at a distance equal to the region size. High strain rate within this zone can be attained by crack movement or by rapid loading of a stationary crack. Fracture strength is largely governed by the triaxial plastic stability and size of these regions. Determinations of plastic stability from dynamic compression tests correspond nicely to speed variations and temperature-wise trends in fracture strength. For the two steels discussed, speed spectrum effects are very marked. Representing as they do, enormous variations in fracture strength, they are of great practical significance.

Torsion tests of circumferentially notched-and-fatigue pre-cracked specimens of Ti-7Al-2Cb-1Ta have shown what appears to be stable crack growth in water and in methanol under mode III conditions. A specimen loaded to a K_{III} of 35,000 psi/ $\sqrt{\text{in}}$ failed in water after 30 minutes while one loaded to a K_{III} of 37,000 psi/ $\sqrt{\text{in}}$ broke after 14 minutes in methanol. The fracture surfaces have not yet been examined in detail.

Carnegie-Mellon University

The phenomenon termed stress corrosion in metals is more commonly known as delayed fracture or static fatigue when it occurs in non-metals. The existence of static fatigue, long observed in glass, is now well established in single and polycrystalline Al_2O_3 in the presence of water where it manifests itself by an increase in fracture strength with strain rate and a decrease in strength with time under constant load.

There is some question as to whether MgO exhibits behavior which may be correctly called static fatigue. In an effort to resolve this question, a different testing technique, that of the double cantilever beam,^{3,4,5} has been used on single crystal specimens of MgO. Dynamic tests in which the fracture strengths for a number of crack lengths in a given specimen were determined at pulling speeds from 0.0002 to 0.0500 in./min. gave little evidence of static fatigue even when tested in water. Static tests whereby similar specimens were dead loaded in water to 75 to 90 percent of the anticipated fracture load accordingly have also shown little effect to date.

Results thus far are inconclusive but seem to indicate that either the MgO-water couple is not susceptible to static fatigue, or at best that the effect is a subtle one.

References

1. J. M. Krafft, "Dynamic Mechanical Behavior of Metal at the Tip of a Plane Strain Crack", Southwest Research Institute Symposium on the Mechanical Behavior of Materials Under Dynamic Loads, San Antonio, Texas, September 1967.

2. R. J. Charles, "Static Fatigue: Delayed Fracture", Studies of the Brittle Behavior of Ceramic Materials, Tech. Doc. Report ASD-TR-61-628, Part II, 467-519, April (1963).
3. J. J. Gilman, "Direct Measurements of Surface Energies of Crystals", J. Appl. Phys., 31, 2208-18 (1960).
4. S. M. Wiederhorn, "Effect of Environment on The Fracture of Glass", Environment - Sensitive Mechanical Behavior, ed. Westwood and Stoloff, Gordon and Breach Science Publishers, New York, (1966).
5. D. A. Shockey and G. W. Groves, to be published, J. Am. Ceramic Soc.

E. ABSTRACTS OF MANUSCRIPTS AND REPORTS

1. M. Creager and P. Paris, "Elastic Equations for Blunt Cracks with Reference to Stress Corrosion Cracking," to be published in International Journal of Fracture Mechanics, December 1967.

The elastic stress field equations for blunt cracks are derived and presented in a form equivalent to the usual sharp crack tip stress fields. These stress field equations are employed in analyzing a dissolution model for the arrest of stress corrosion cracking by crack tip blunting, which is often observed with the arrest of stress corrosion cracks.

2. R. P. Wei, "Fracture-Crack Propagation in a High-Strength Aluminum Alloy," to be published in Journal of Fracture Mechanics.

Fatigue-crack propagation experiments were carried out within the framework of linear-elastic fracture mechanics to examine the effect of water and its constituents on the rate of crack growth in a high-strength aluminum alloy over a range of test temperatures from 295 to 380°K. Dehumidified high-purity (99.9995 percent purity) argon was used as an inert reference environment. The results showed that water accelerated the rate of fatigue-crack propagation by about a factor of 10 in this temperature range, whereas dry oxygen and dry hydrogen had a negligible effect. They confirm the findings of Hartman and Bradshaw and Wheeler that the cause for the large increase in the rate of crack growth is the formation of hydrogen gas at high pressure in the region ahead of the crack tip, driven in by the reaction of water with the freshly created aluminum crack surfaces, as suggested by Broom and Nicholson. The results showed further that fatigue-crack propagation in water, as well as in the dry environments, is controlled by thermally activated processes, with apparent

activation energies that depend strongly on the crack-tip stress-intensity parameter, ΔK . The rate controlling process appears to be that associated with the creation of new crack surfaces in the range of crack growth rates 10^{-6} to 10^{-5} inch per cycle. The strong dependence of the apparent activation energy on ΔK suggests that a careful study of the kinetics of fatigue-crack growth and of the crack growth laws is in order. Such a study should incorporate both the mechanical and chemical variables involved.

3. R. P. Wei, "Application of Fracture Mechanics to Stress Corrosion Studies," to be published in Proceedings — International Conference on Corrosion, Ohio State, September 1967.

The successful application of linear-elastic fracture mechanics analyses to describe the fracture behavior of high-strength materials under monotonically increasing loads has led to a logical extension of these same concepts to the study of slow crack growth under both static and fatigue loads, commonly termed subcritical-crack growth. The use of the crack-tip stress-intensity parameter (K), which governs the intensity or magnitude of the local stresses, to characterize the crack-driving force has met with considerable experimental success.

With the increasing interest in applying the fracture mechanics approach to stress corrosion cracking studies in high-strength materials, a brief review of the basic justification and limitations in using linear-elastic fracture mechanics analyses to describe crack growth and fracture seems appropriate. Some practical considerations in the design of experiments and test specimens are given. Recent results on water-enhanced fatigue crack growth in a high-strength aluminum alloy are discussed.

4. G. W. Graves and D. A. Shockey, "Effect of Water on the Toughness of MgO Crystals," submitted to Journal of American Ceramic Society.

It was found possible to drive plastically blunted cleavage cracks through double cantilever beam specimens of impure MgO monocrystals in a series of small propagations. The forces required to propagate the cracks often defined a fairly constant apparent surface energy and provided an environment-sensitive measure of toughness.

Widely scattered apparent surface energies within the range 2000 to 3500 ergs/cm² were obtained on different MgO crystals tested in air. Some of this variation arose from non-central cracks. Values of apparent surface energy obtained from crystals tested in a water-free environment agreed well with values from similar specimens tested in air, suggesting that water vapor present in laboratory air does not significantly affect the toughness of MgO. Specimens tested while immersed in water were approximately 30% tougher than when tested in air, and exhibited a faceted fracture surface, in contrast to the relatively smooth fracture surface produced in air.

5. George Sandoz, "Subcritical Crack Propagation in Ti-8Al-1Mo-1V Alloy in Organic Environments, Salt Water, and Inert Environments," to be published in Proceedings — International Conference on Corrosion, Ohio State, September 1967.

A comparative study of the stress-corrosion susceptibility of a Ti-8Al-1Mo-1V alloy in salt water, alcohols, and alkanes was made utilizing precracked specimens and cantilever loading. All of these environments were found to cause crack propagation at values of stress intensity less than required to produce fracture in dry air. In dry air, however, the stress intensity

required to produce crack growth and fracture was found to be time and section size dependent and lower than K_{IC} .

The long-chain alcohols and the alkanes appear to cause crack propagation at about the same stress intensity level. Similarly, salt water, methanol, and ethylene glycol are of a class, but produce crack propagation at lower levels of stress intensity.

The environments studied, except for dry air, appear to cause crack propagation at about the same stress intensity level whether the specimens meet the requirements for plane strain conditions or not.

F. TITLES OF PREVIOUS REPORTS

1. Matthew Creager, "The Elastic Stress Field Near the Tip of a Blunt Crack," (Master's Thesis) Lehigh University October 1966
2. E. P. Dahlberg, "An Annotated Bibliography of Recent Papers and Reports on the Subject of Ambient Temperature Aqueous Stress-Corrosion Cracking of Titanium and Titanium Alloys," NRL Bibliography Report 29, October 1966
3. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Corrosion (First Quarterly Report)," NRL Memorandum Report 1739, December 1966
4. G. Sandoz and R. L. Newbegin, "Stress-Corrosion Cracking Resistance of an 18Ni 200 Grade Maraging Steel Base Plate and Weld," NRL Memorandum Report 1772, March 1967
5. George Sandoz and R. L. Newbegin, "Stress and Corrosive Environments (Some Environmental Effects on Titanium Alloys)," Report of NRL Progress, March 1967, pp. 28-30
6. G. Sandoz, "Stress-Corrosion Cracking Susceptibility of a Titanium Alloy in a Non-electrolyte," Nature, Vol. 214, April 8, 1967, p. 6
7. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Second Quarterly Report)," NRL Memorandum Report 1775, April 1967
8. A. M. Sullivan, "Dissolution Velocities of Different Organic Media," Report on NRL Progress, April 1967, pp. 18-19
9. E. P. Dahlberg, "Thin Foil Electron Microscopy," report of NRL Progress, April 1967, pp. 19-21

10. G. Sandoz, "Delayed Fracture Characteristics of Ti-8Al-1Mo-1V Alloy," Report of NRL Progress, May 1967, pp. 31-32
11. N. M. Lowry, O. R. Mulkey, J. M. Kuronen, and J. W. Bieber, "A Method of Measuring Crack Propagation Rates in Brittle Materials," Document D6-60072, May 1967, The Boeing Company
12. C. O. Timmons, R. L. Patterson, and L. B. Lockhart, Jr., "The Adsorption of C-41 Labeled Stearic Acid on Iron," NRL Report 6553, June 2, 1967
13. H. R. Smith, D. E. Piper and F. K. Downey, "A Study of Stress-Corrosion Cracking by Wedge-Force Loading," Document D6-19768, June 1967, The Boeing Company
14. R. W. Judy, Jr. and R. J. Goode, "Stress-Corrosion Cracking Characteristics of Alloys of Titanium in Salt Water," NRL Report 6564, July 21, 1967
15. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Third Quarterly Report)," NRL Memorandum Report 1812, August 1967
16. G. Sandoz, "Effects of Some Organics on the Stress-Corrosion Susceptibility of Some Titanium Alloys," to be published in Battelle DMIC Conference Summary
17. D. A. Meyn, "Effect of Crack Tip Stress Intensity on the Mechanism of Stress-Corrosion Cracking of Titanium-6Al-4V in Methanol," to be published in Corrosion Science
18. B. F. Brown, "The Fracture Mechanics of Stress-Corrosion Cracking," submitted to Metallurgical Reviews

G. ABSTRACTS OF SOME RECENT ARTICLES ON
STRESS-CORROSION CRACKING

1. I. E. Figge and C. Michael Hudson, "Crack Propagation, Delayed Failure, and Residual Static Strength of Titanium, Aluminum, and Stainless Steel Alloys in Aqueous Environments," NASA TN D-3825, February 1967.

An investigation of crack propagation, delayed failure, and residual static strength was conducted on titanium, aluminum, and stainless steel alloys in air, in a 3-1/2 percent salt solution, and in sea water.

Fatigue cracks grew approximately 2 to 3 times faster in the aqueous environment than in air in Ti-8Al-1Mo-1V (duplex annealed) titanium alloy and 7075-T6 aluminum alloy. In the 2024-T3 aluminum alloy, the aqueous environment had a deleterious effect on the crack growth rate at the lower stress levels and a beneficial effect at the high stress levels.

In general, the delayed failure strengths of the aluminum and stainless steel alloys were essentially the same as their residual static strengths in air. The delayed failure strengths of the titanium alloys were lower than their residual static strengths by various degrees depending on the material and thickness. The residual static strength of the aluminum alloys was not affected by the aqueous environment.

2. Che-Yu Li, P. M. Talda, and R. P. Wei, "The Effect of Environments on Fatigue-Crack Propagation in an Ultra-High-Strength Steel," International Journal of Fracture Mechanics, Vol. 3, No. 1, March 1967, p. 29.

The influence of various gaseous environments on the rate of fatigue crack growth at room temperature in an 0.45 percent carbon low-alloy ultra-high-strength steel tempered at 400°F and at 800°F

has been investigated. The sensitivity of the rate of fatigue crack growth to moisture in this steel is found to be dependent on the fracture toughness of the material.

3. A. R. C. Westwood, C. M. Preece, and M. H. Kamdar, "Adsorption-Induced Brittle Fracture in Liquid Metal Environments," Technical Report, Contract No. DA-18-001-AMC-1109(X), RIAS, Baltimore, May 1967

Solid metals can be caused to behave in a brittle manner by exposure to a variety of physical or chemical environments. Perhaps the most dramatic examples of such effects, however, result from exposure to surface active liquid metals. Specimens prestressed above some critical value fail virtually instantly on being wetted by an appropriate liquid metal, and "brittle" crack propagation rates of order 100 cm per sec. have been recorded in otherwise ductile metals under such environmental conditions.

Such effects are presently considered to result from adsorption-induced reductions in the cohesive strength of atomic bonds at regions of stress concentration in the solid metal, e.g. at the tips of cracks or in the vicinity of piled up groups of dislocations. This paper describes the results of a number of recent investigations on this type of liquid-metal embrittlement, and discusses the prerequisites and possible mechanisms for its occurrence. Also discussed are the effects of such variables as chemical composition of the solid and liquid metal phases, temperature, pre-strain, rate of loading, etc., on severity of embrittlement, and such topics as the possible correlation between severity of embrittlement and electronegativity, the use of "inert carrier" liquid metals, possible means of inhibiting liquid-metal embrittlement, and criteria for brittle failure.

4. T. P. Hoar, "The Production and Breakdown of the Passivity of Metals," Corrosion Science, Vol. 7, No. 3, June 1967, p. 341.

The production of passivity is considered as the anodic process of oxide-film formation, initially as a monolayer, from the thermodynamic and kinetic points of view.

The influence of readily adsorbable anions such as Cl^- in hindering passivation and in promoting breakdown of passivity is treated in terms of the relative adsorption of anions and water at the metal-solution and oxide/solution interfaces, as influenced by anion concentration and electrode potential. A new "mechanical" mechanism for breakdown is proposed.

It is shown for that metal/electrolyte-solution systems, the occurrence at an anode of (i) crystallographic etching (ii) crystallographic pitting (iii) passivity (iv) hemispherical "bright" pitting (v) anodic brightening (vi) "imperfect" brightening can be produced by suitable variation of potential and anion/water concentration ratio. A new type of "potential/[anion]/[water]" diagram is proposed for the display of experimental data on such systems.

5. M. F. Dean, F. H. Beck, and R. W. Staehle, "Tunnel Formation in Iron-Nickel-Chromium Alloys," Corrosion, Vol. 23, No. 7, July 1967, p. 192.

Oxide films were stripped from a series of stressed Fe-Ni-Cr alloys exposed to boiling 42 percent MgCl_2 . Evidence of dissolution tunnels was found in Types 304 and 310 stainless steels and Incoloy 800. No tunnels were observed in Incoloy 825 or Inconel 600. The frequency of observed tunnels was proportional generally to the susceptibility of these alloys to stress corrosion cracking in MgCl_2 . The mechanism for

formation of the tunnels appears to be related to the interaction between dislocations and prior irregularities in initial dissolution trenches resulting from rapid dissolution at emergent slip steps. Evidence from this work suggests that the tunnels are a special case of local slip step activated dissolution. Tunneling itself appears not to be an integral part of the mechanism of stress corrosion cracking but can occur as an associated or parallel process.

6. J. H. Shively, R. F. Hehemann, and A. R. Troiano, "Hydrogen Permeability of A Stable Austenitic Stainless Steel Under Anodic Polarization," Corrosion, Vol. 23, No. 7, July 1967, p. 215.

Tests at 21 C (69 F) show hydrogen entered and penetrated Type 310 stainless steel in chloride solutions under impressed anodic currents, but not in H₂SO₄. Entry in anodic and cathodic regions was related to pit formation associated with surface irregularities and depended upon those factors which influence local attack: pH, aggressive ions and surface conditions.

7. Milton Levy, "Anodic Behavior of Titanium and Commercial Alloys in Sulfuric Acid," Corrosion, Vol. 23, No. 8, August 1968, p. 236

The anodic polarization behavior of commercially pure alpha titanium 75A (annealed), beta alloy 13V-11Cr-3Al (annealed) and alpha-beta alloy 6Al-6V-2Sn (heat treated to strength levels of 140, 160 and 180 ksi) in hydrogen saturated 5, 12 and 20 percent sulfuric acid solutions was investigated at 20, 35, 50 and 65 ± 1 C, using a potentiostatic technique.

All specimens exhibited active to passive transition at temperatures above 20 C and acid concentrations greater than 5 percent. Titanium alloy 13V-11Cr-3Al showed transpassive behavior which was attributed to the 11 percent chromium

content. Increasing acid concentration increased the critical current for passivity and shifted the critical potential for passivity in the noble direction. Increasing the temperature served only to increase the critical current for passivity.

Temperature coefficients and activation energies were the right order of magnitude for a reaction controlled by reactivity at the metal surface. For the alpha beta alloy 6Al-6V-2Sn the critical current for passivity increased as the ratio of amount of alpha to beta phase increased with increasing strength level. The dissolution is accelerated, probably, by the galvanic effects and the unfavorable area ratio. Ti 75A, a commercially pure metal and Ti 13V-11Cr-3Al, a homogeneous single phase alloy, had a smaller critical current for passivity values than did Ti 6Al-6V-2Sn, a multiphase alloy, which was expected.

The effect of Fe^{3+} , Cu^{2+} and Cl^- on polarization of Ti 6Al-6V-2Sn (180 ksi) was investigated also. Fe^{3+} and Cu^{2+} inhibited the anodic dissolution reaction and Cl^- facilitated passivation.

8. W. D. Sylwestrowicz, "Effect of Temperature on Stress-Corrosion Fracture," Corrosion, Vol. 23, No. 3, August 1967, p. 245.

Prestrained samples of copper-beryllium alloy (1.8 Be, 0.3 Co) were exposed to an ammonia atmosphere at -20, 30 and 90C (-4, 86, 194 F). It was found that the effect of temperature is related to the amount of plastic deformation. Above a critical value of plastic prestrain, temperature effect reverses; a longer exposure is needed to fracture a sample at 90 than at 30 C. This temperature dependence is explained by considering the number and distribution of dislocations.

9. S. P. Rideout, R. S. Ondrejcir, M. R. Louthan, Jr., and D. E. Rawl, "The Role of Moisture and Hydrogen in Hot-Salt Cracking of Titanium Alloys," [A report (1967) on work done at the Savannah River Laboratory for NASA under Purchase Order R-114 issued to the USAEC.] E. I. du Pont de Nemours & Co.

The role of moisture and hydrogen in the stress corrosion cracking of Ti-8Al-1Mo-1V exposed to hot chloride salts was investigated. The adsorption and retention of moisture during the application of salt deposits and subsequent heating, and the extent of HCl and hydrogen generation during corrosion were studied using radiotracer techniques and mass spectrographic analyses of volatile corrosion products. Hot-stage microscopy and cinematography were used to study crack initiation and propagation, and the characteristics of fracture surfaces were examined by electron fractography. The effects of NaCl were compared to those of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, which not only retains much more moisture but also has a much lower melting point than NaCl. These studies revealed an obvious association between the occurrence of cracking and the amounts of HCl and hydrogen generated during hot-salt corrosion. This, combined with results of supplementary experiments using sodium iodide and bromide, indicates that hydrogen, rather than the halide, plays the key role in the cracking process. The observations are consistent with a stress-sorption mechanism for cracking, in which corrosion-produced nascent hydrogen is proposed to be the sorbed species responsible for cracking. It is proposed that chloride ions are absorbed into the metal oxide film, probably occupying oxygen vacancies in the lattice. The presence of chloride ions in the oxide film should contribute to the breakdown of passivity during exposure at elevated temperatures.

10. J. L. Cavallaro, "Embrittlement of Titanium in Seawater," NSRDC, Marine Engineering Lab., Report 2483, October 1967

Sea-water stress-corrosion tests on notched cantilever-beam specimens of Alloy Ti-7Al-2Cb-1Ta (Ti-721) demonstrated that it has a transition in behavior with increasing notch sharpness. Sea-water tests on Alloy Ti-721 indicate that a threshold stress level exists below which stress corrosion does not occur.

Sea-water stress corrosion is dependent on the presence of embrittling constituents in the alloy. Alloy chemistry and heat treatment are the most significant factors which control sensitivity. The results of tests made on a series of Ti-Al binary alloys indicate that aluminum in solid solution does not cause stress corrosion, but that it is caused by a finite amount of a coherent Ti_3Al . A decrease in aluminum and oxygen contents and the addition of isomorphous beta stabilizers improve the resistance of Ti-Al alloys to sea-water stress corrosion by suppressing the formation of Ti_3Al .

A stress-sorption cracking mechanism is suggested as a general model for the embrittlement of titanium and titanium alloys in seawater.

H. DIARY OF EVENTS

On 1 July 1967 Dr. Brian Ralph arrived at Georgia Institute of Technology to serve as a visiting lecturer and researcher during the summer. Dr. Ralph spent part of his time on the ARPA program to develop Field-Ion and Field-Emission Microscopy for studying atomic characteristics of susceptible and non-susceptible alloys. During his stay Dr. Ralph presented a series of fine lectures on Field-Ion Microscopy.

A special three-day lecture series and workshop on fracture mechanics was held on 5-7 October 1967 at Georgia Institute of Technology. The lectures were presented by Professor Irwin (former Superintendent, Mechanics Division, NRL) and Professor Paris of Lehigh University.

Personnel from all segments of the Coupling Program attended a meeting at NRL on 27 September 1967 where specimen design and test techniques were discussed. The several different test specimen geometries being used by ARPA people were analyzed as a start toward the development of a proposed standard specimen, or specimens.

A number of high school science teachers and high school juniors, participants in the National Science Foundation's Research Participation Program, have been working on and assisting in some ARPA stress-corrosion projects, under supervision of contract participants at Carnegie-Mellon Univ.

Professor Pourbaix of CEBELCOR presented his lecture and demonstration course on electrochemistry of corrosion 30 October - 8 November 1967 at Carnegie-Mellon University.

Seminars were presented at NRL during the past quarter by Professor T. P. Hoar and Dr. Brian Ralph of Cambridge University, England, and Dr. J. C. Scully, The University, Leeds, England.

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A progress report of the research investigations being carried out on the problem of stress-corrosion cracking of high strength materials under ARPA Order 878 is presented. Work at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory concerning physical metallurgy, surface chemistry, fracture mechanics, and characterization tests and translation related to stress-corrosion cracking is described. The materials being studied include high strength steels, titanium alloys, and aluminum alloys. Abstracts of recently published reports and a diary of events are included.			

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