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NRL Memorandum Report 1775

**ARPA Coupling Program on  
Stress-Corrosion Cracking  
(Second Quarterly Report)**

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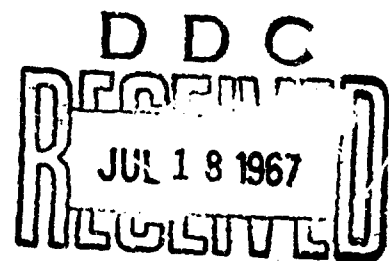
Advanced Research Projects Agency  
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## CONTENTS

Sponsor Acknowledgment .....	ii
Abstract .....	iii
Status .....	iii
Authorization .....	iii
INTRODUCTION .....	1
PHYSICAL METALLURGY .....	5
STEELS .....	5
Carnegie Institute of Technology .....	5
Georgia Institute of Technology .....	6
The Boeing Company .....	7
ALUMINUM ALLOYS .....	8
Carnegie Institute of Technology .....	8
Lehigh University .....	9
TITANIUM ALLOYS .....	10
Carnegie Institute of Technology .....	10
Georgia Institute of Technology .....	10
The Boeing Company .....	11
Lehigh University .....	14
OTHER SYSTEMS .....	15
Georgia Institute of Technology .....	15

<b>SURFACE CHEMISTRY .....</b>	<b>17</b>
<b>ELECTROCHEMISTRY .....</b>	<b>17</b>
The Boeing Company .....	17
Carnegie Institute of Technology .....	18
<b>LEED, FIELD ELECTRON AND FIELD ION MICROSCOPY ...</b>	<b>20</b>
Georgia Institute of Technology .....	20
<b>MACROSCOPIC SURFACE MEASUREMENTS .....</b>	<b>21</b>
Georgia Institute of Technology .....	21
Lehigh University .....	21
Naval Research Laboratory .....	22
<b>FRACTURE MECHANICS .....</b>	<b>24</b>
The Boeing Company .....	24
Naval Research Laboratory .....	24
<b>CHARACTERIZATION TESTS AND TRANSLATION .....</b>	<b>26</b>
<b>ABSTRACTS OF MANUSCRIPTS AND REPORTS .....</b>	<b>33</b>
<b>TITLES OF PREVIOUS REPORTS AND PAPERS .....</b>	<b>37</b>
<b>DIARY OF EVENTS .....</b>	<b>38</b>

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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 Institute of Technology, 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  
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ARPA Order 878 and  
RR 007-08-44-5512

## INTRODUCTION

The increasing use of high-strength metals for complex and highly stressed structural applications has made the problem of stress-corrosion cracking (SCC) one of critical and immediate concern. Not only do corrosion cracks often grow more readily in materials of high tensile strength, but also the ability of such a material to contain a corrosion crack of a given size without catastrophic "brittle fracture" is much impaired compared with materials of lower strength (and higher toughness).

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 876 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 Institute of Technology, Lehigh University, and the Naval Research Laboratory. An associated sector supported by Navy funds is located at the Georgia Institute of Technology. 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.

Regardless of the experimental method, essentially all SCC experiments include crack propagation as an essential part of the investigation. The stress field important to this cracking process cannot be adequately described by conventional methods ("nominal stress"), but at least as a useful approximation the stress field can be described by existing fracture mechanics analysis. Additionally,

fracture technology in general (including fracture mechanics) is useful in selecting specimen dimensions for macroscopic measurements and in understanding the meaning of these measurements. Also, fracture mechanics analysis may give important clues to fundamental processes, just as macroscopic measurements gave the first clues to the existence of dislocations in crystalline materials. Finally, it appears important to extend existing macroscopic fracture mechanics to treat the tips of corrosion cracks, especially to better understand the important phenomenon of SCC blunting. Hence our attention to element (1), the stress field.

We know that the same titanium or aluminum alloy heat treated one way may be highly susceptible to stress corrosion, whereas the same alloy with a slightly different heat treatment (and without gross changes in other mechanical properties) may be largely immune to stress corrosion. This is one of many indications of the importance of microstructural features of the metallic phase to the SCC problem. Hence our interest in element (2), physical metallurgy.

One of the most baffling questions in SCC, both to the theorist and to the engineer, is the reason that in many cases only a few corrodents will cause SCC in a given alloy. Hence our interest in element (3), solution chemistry of the corrodent.

Corrosion phenomena in themselves are typically complex, even in the absence of stress. They involve at one stage active-site reaction, and in many systems they involve the nucleation and growth of solid corrosion-product films which may tend to isolate the metal from the corrodent phase. Hence our interest in element (4), the interface zone.

If we knew precisely those features in the complex structures of high-strength alloys which control SCC behavior, our physical metallurgy studies could be greatly narrowed. Likewise if we knew the critical corrodent species with certainty or if we knew the identity of the interface process(es) controlling the corrosion reaction, our task would be much simpler. But we do not know precisely where we should be concentrating our efforts in these areas. Much of the more fundamental work may therefore turn out to develop information which may be of little direct

utility to the practical problem of the SCC of high-strength alloys. But these endeavors will not even then lose their value to DoD interests, which include advancing the physical metallurgy of these terribly complex (but terribly necessary) alloys, as well as advancing the science of metallic corrosion of the same alloys.

Additionally, work is continuing to further develop the cheapest, most meaningful test procedure possible, and to use the cheapest reliable one available at any given moment to characterize the stress-corrosion properties of commercial and near-commercial high-strength alloys. These macroscopic characterization data serve several purposes. They inform DoD contractors and program managers how good and how poor various alloys can be, and they provide an "analog computer" to test theories and also to suggest theories.

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.

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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## PHYSICAL METALLURGY

The overall objective of the physical metallurgy groups is to investigate the relations between metallurgical variables and stress corrosion cracking behavior. Initially, the study has largely been confined to materials of current engineering interest. The individual research projects and their current status are described in the following paragraphs.

### STEELS

#### Carnegie Institute of Technology

Bar stock of an 18Ni maraging steel has been obtained. It has the following composition:

C	Si	Mn	S	P	Ni	Mo
.005	.01	.01	.006	.004	18.23	5.08
Co	Al	Ti	Zr	B		
8.99	.08	.67	.027	.0025		

A superficial study was undertaken to determine the approximate response of this alloy to heat treatment. The results indicate that time-temp. combinations for solution treatment are not very critical, for maximum strength (measured by hardness) is easily obtained on lower temperature aging and maintained at this level for long aging times.

Differences in stress-corrosion cracking susceptibility due to heat treating procedure will be determined by using the pre-cracked cantilever test. At the present time, Sonntag SF-J-U fatigue testing machine is being modified to pre-crack the cantilever specimens.

Also, the polarization characteristics of this steel will be determined with the standard type set-up now being constructed. The effect of strain, strain rate and heat treatment will be considered in these studies.

It is hoped that the pre-cracked cantilever tests and the polarization studies can be related through the

structural characteristics of the maraging steel.

A series of very high purity (total substitutional impurity content less than 50 p.p.m.) melts of 18Ni 300 grade maraging steel containing separate small additions of the impurity and trace elements commonly found in the commercial steels (S, P, C, Si, Mn, Ca, Zr and B) are to be prepared. It is intended to investigate the effect of these controlled impurity additions on the environment - induced sub-critical crack growth observed in maraging steels. To date the high-purity melting stock, and other auxiliary apparatus has been ordered, and rigs for testing pre-cracked cantilever-beam specimens are being constructed.

The use of a mass spectrometer to measure the permeability of Fe, Fe - Ni and Ni with respect to hydrogen near room temperature is being explored. The apparatus has been designed and the various components have been obtained. Further progress on this project awaits the arrival of new personnel.

It is intended to investigate the effect of prior-austenite grain-size on the susceptibility of AISI 4340 steel to environment-induced sub-critical crack growth. Conventional techniques will be used to obtain as wide a range of grain-size as possible; in addition the repetitive austenising technique described by R. A. Grange will be used to develop grain sizes as small as A.S.T.M. 15. To date the basic steel and other auxiliary apparatus has been obtained, and rigs for testing precracked cantilever-beam specimens are being constructed.

#### Georgia Institute of Technology

A complete evaluation has been made of the corrosion resistance and mechanical properties of 316 and 316L stainless steel, stress relieved in the temperature range from 400 to 1000°F. Results show an increase in hardness after heat treatment reaching a flat maximum after treatment at the higher end of the temperature range. The time versus

hardness curve at 750°F indicates the possibility of two hardening processes occurring in sequence. The most marked increase in mechanical properties was found in the yield strength. Initial potentiostatic studies have been performed on the annealed, unannealed and stress relieved, and cold worked and stress relieved material. A better overall resistance to corrosion after the low temperature stress relief heat treatment has been found. The slight oxide formed during the stress relief process was removed by electropolishing.

Transmission electron microscopy has been initiated on the sub-structure of material before and after heat treatment. No major variations have been found in normal metallographic examinations. Very sensitive microhardness testing at 5 gram loads has been made on the bulk and across grain boundaries to reveal possible segregation or precipitation effects. No major variations were found. X-ray diffraction studies with a Guinier-de Wolff camera have been initiated to study any preprecipitation or precipitates in the structure. Damping capacity studies are planned to evaluate the possibility of redistribution of impurities at dislocations. Evaluation of the stress corrosion properties of stress relieved material are now being made by the cantilever beam testing method.

#### The Boeing Company

This program will evaluate the effect of silicon additions on the stress-corrosion cracking (SCC) and fracture toughness characteristics of low-alloy martensitic steel. The five heats of material required for this study have been consumable electrode melted and rolled to bar by Vanadium Alloys Steel Company. The chemical analyses of the heats are given in the table below. The bars are currently in transit to Boeing.

### Chemical analysis of experimental steels

HEAT NO.	C	Mn	Ni	Cr	Mo	S	P	Si
1	0.43	0.80	1.86	0.89	0.28	0.006	0.006	0.09
2	0.43	0.79	1.87	0.90	0.28	0.006	0.006	0.54
3	0.43	0.77	1.85	1.01	0.26	0.006	0.006	1.08
4	0.43	0.68	1.84	1.05	0.26	0.006	0.004	1.58
5	0.43	0.68	1.84	1.07	0.26	0.006	0.004	2.15

### ALUMINUM ALLOYS

#### Carnegie Institute of Technology

In contrast to titanium alloys, it became apparent at the seminar on the stress corrosion of Ti held at Boeing in February 1967, that no data is available on the stress corrosion cracking of aluminum alloys in non-aqueous solvents. It is intended to investigate the stress-corrosion susceptibility of the alloy 7075 in the T6 heat-treatment condition in various alcohols, in other organic solvents, and in selected inorganic solutions using pre-cracked cantilever-beam specimens. To date the base alloy and other supporting apparatus has been ordered, and test rigs are being constructed.

Four high purity aluminum alloys have been received from ALCOA in the form: 24" x 12" x 1/2" slabs and 24" x 12" x 0.04" sheet. These have compositions:

Al - 1.02%	Mg	6.85% Zn
Al - 2.35%	Mg	6.86% Zn
Al - 4.1%	Cu	
Al - 14.8%	Zn	

Experimental work is now being undertaken with the following aims:

- a) To modify an existing beam type, tensile stress-corrosion rig to handle sheet specimens
- b) To construct a suitable heat treating apparatus

This work should be completed in the next few weeks.

Electron microscope specimens are being prepared from high-purity Al-Zn alloys for the purpose of relating their structure to stress corrosion cracking susceptibility as measured by a double-cantilever beam specimen.

#### Lehigh University

A cantilever beam testing apparatus with a transparent corrodent chamber and circulating system has been constructed for measuring the crack propagation rate in short transverse plane strain 7075-T6 specimens in 3 1/2% NaCl solution. The crack propagation rates will be determined at various K values in a temperature range of 20°C to 100°C. In addition, the geometry of the blunting found in longitudinal 7075-T6 environmental crack study specimens is being determined and related to variation in stress intensity from the surface to the center of the specimen.

## TITANIUM ALLOYS

### Carnegie Institute of Technology

Classically, Ti Alloys, commercially pure Ti, and "pure" Ti have always contained at the very least, 300 p.p.m. oxygen. Theoretical consideration is being given to the experimental practicality and theoretical possibility of producing pure titanium with an appreciably lower oxygen content. A study of this material should yield interesting and useful results.

### Georgia Institute of Technology

Studies on the Ti-7Al-2Cb-1Ta alloy reaffirm the low angle relation of the cleavage plane in stress corrosion cracking to the basal plane of the alpha phase. A large grain size allowed relatively easy orientation of the fracture surface of a crystal perpendicular to the x-ray beam by light reflection techniques. Solution of the Laue pattern from these surfaces resulted in an average of  $14^\circ$  between the cleavage plane and the basal plane of the crystal. Fractographic studies also indicated the typical cleavage type fracture in the slow crack growth areas. A model of the system is being developed to examine the planes between  $12^\circ$  and  $18^\circ$  to basal plane in a hexagonal system. Other studies will look for concentration of interstitials, voids or precipitates on this plane. Cleavage fracture of high oxygen content titanium alloys have shown similar variations between the basal plane and the cleavage plane.

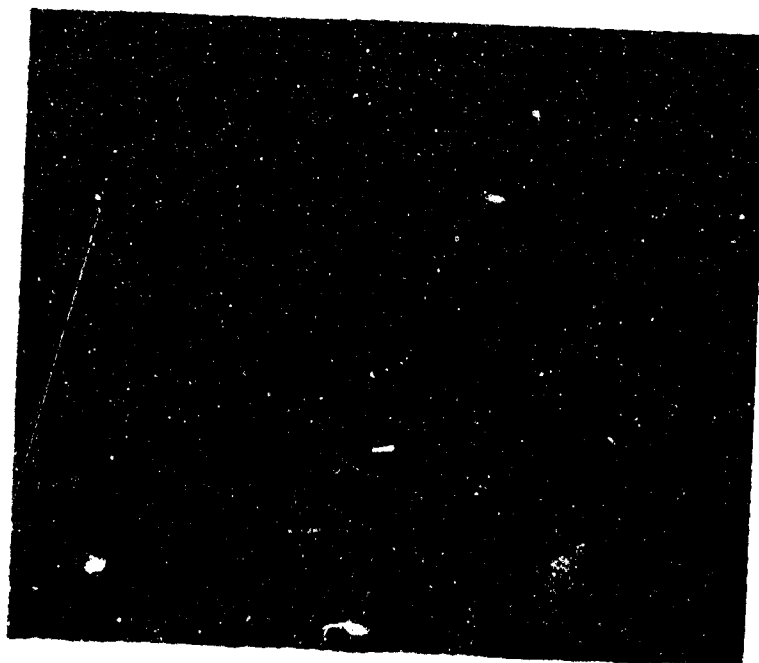
A computer program is planned in which all the information with regard to the alpha phase, plus interstitials, impurities, precipitates, and ordering of Ti<sub>3</sub>Al will be incorporated. Planes will then be cut through this structure and examined for indications of the cause of failure on this plane. The program is comparable to that of A. J. W. Moore on distribution of atoms at the tip of a field ion microscopy specimen.

### The Boeing Company

Further work has been conducted to delineate the rate-controlling step in SCC of titanium alloys. The results support the hypothesis that surface phenomena (that is, oxide film mechanism) are of primary importance. It has also been demonstrated that the grain texture of titanium alloys has a significant influence on SCC results. Mechanistic studies that neglect the affect of texturing may not be valid, thus indicating the need for single-crystal studies in SCC.

Slip-mode studies are in process in commercial titanium alloys and Ti-Al binary alloys. Preliminary work has been completed that shows qualitatively that cleavage fracture of the alpha phase in SCC correlates with the presence of coplanar dislocation arrays in this phase. Cleavage fracture has been shown to occur in both Ti-6Al-4V and Ti-8Al-1Mo-1V, while Ti-4Al-3Mo-1V fails in a ductile manner. Figure 1, (a) through (c), shows transmission electron micrographs of dislocation arrangements in the alpha phase of these alloys after 3 to 4% strain. The principal difference between Ti-6Al-4V and Ti-8Al-1Mo-1V is the reduced thickness of the slip bands in the latter. Using trace analysis it has also been shown that in the higher aluminum content alloys (>5 wt%Al) slip on the  $\{10\bar{1}0\} \langle 11\bar{2}0 \rangle$  system is preferred and that the  $\{1011\} \langle 1120 \rangle$  systems are less operative while the  $(0001) \langle 11\bar{2}0 \rangle$  systems operate only to a very limited extent at higher strains. In the lower aluminum content alloys all slip systems appear to operate with no apparent preferred slip system. This general slip behavior suggests that grain size markedly influences the mechanical properties of the higher aluminum alloys. This grain size dependence is presently being investigated in all-alpha binary titanium alloys containing 4, 6, and 8 wt% aluminum.

A series of commercial alloys containing principally Ti, Al, and Mo are being investigated to determine the effect of ordering and omega-phase formation on mechanical properties. In these alloys, omega is formed during low-temperature (approximately 500°F) decomposition of the beta



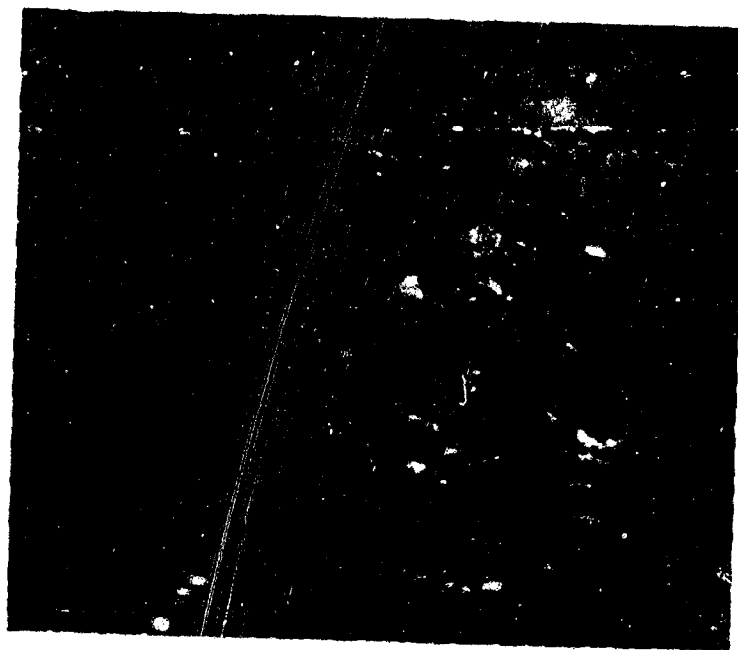
(a) Ti-8Al-1Mo-1V



(b) Ti-6Al-4V

Figure 1 - Alpha phase dislocation arrangement





(c) Ti-4Al-3Mo-1V

Figure 1 - Alpha phase dislocation arrangement

phase prior to alpha formation. Its effect on fracture properties should be most marked in the alloys containing higher percentages of molybdenum. Omega formation as well as precipitation of ordered regions of  $Ti_3Al$  in alloys containing high percentages of aluminum will be analyzed, with thin foil electron microscopy as the principal analysis technique. The results should establish the relative importance of reduced ductility in the alpha and beta phases on SCC behavior.

The influence of grain morphology on the stress corrosion properties of Ti-6Al-4V and Ti-4Al-3Mo-1V suggests that the phenomenon is sensitive to alpha platelet size. Uniquely to determine the effect, alpha platelets will be isothermally formed in Ti-6Al-4V by quenching from the beta field into a salt bath held at temperatures between 1,100 and 1,750°F. Higher bath temperatures will precipitate larger platelets, and lower temperatures will form smaller platelets. To assure constant alpha-beta ratio, phase compositions, and degree of order, all specimens will be quenched directly into a second bath held at approximately 1,150°F and aged toward equilibrium. The structures produced will be analyzed by thin foil electron microscopy, X-ray diffraction, and electron microprobe analysis. Characterization testing will be conducted by established techniques.

The University of Washington has received Ti-3Al-13V-11Cr alloy sheet from The Boeing Company. Initial studies will include the effect of heat treatment on the precipitate morphology in the beta alloy. A quenching furnace has been assembled to aid in this study. Specific heat-treatment conditions of the alloy will then be investigated further with respect to mechanical properties and SCC resistance. A literature survey is continuing. This research is being carried out by the University of Washington, sub-contractors to The Boeing Company.

#### Lehigh University

A gaseous environmental testing chamber is being constructed to determine the role of various relative humidities on the crack propagation rate of plane strain

specimens of a Ti-6Al-4V alloy. Included in this chamber are heating elements to permit determination of the activation energy of crack propagation as a function of humidity. Complete aqueous immersion crack growth rates are being determined as a function of temperature. The specific Ti-6Al-4V alloy to be used has been tested in 3 1/2% NaCl aqueous solution and found to be susceptible to stress corrosion (i.e., reduction in  $K_{IC}$  by the environment compared to air  $K_{IC}$  values).

#### OTHER SYSTEMS

##### Georgia Institute of Technology

In the search for useful parameters in the sound spectra of metals undergoing cyclic mechanical deformation, bending fatigue tests on indium specimens have been conducted and the acoustic power content of emission in various frequency ranges has been compared. This approach appears to be a novel one since in the past only total acoustic emission and sound amplitude variations have been studied in metals undergoing mechanical deformation. It should be feasible to relate the acoustic power content of various frequency bands and its change with time to metallurgical processes occurring in the material. In particular it should be possible to detect the initial crack formation and the crack propagation rate in materials which are susceptible to stress corrosion cracking. Prior to studying these materials however a certain amount of technique development has to be carried out. Materials such as indium, tin and lead are useful for the preliminary development studies.

Data obtained on one indium specimen are shown in Figure 2. The largest change in the relative acoustic level (ratio of the acoustic power in a given frequency range to the power for all frequencies) as a function of time was found to take place in the frequency range from 200 to 800 Hz.

The experiments are continuing with an extension to the higher frequency ranges. The frequency analysis technique will be applied to other metals and the relations between the observations and several factors including initial crack detection and propagation will be explored.

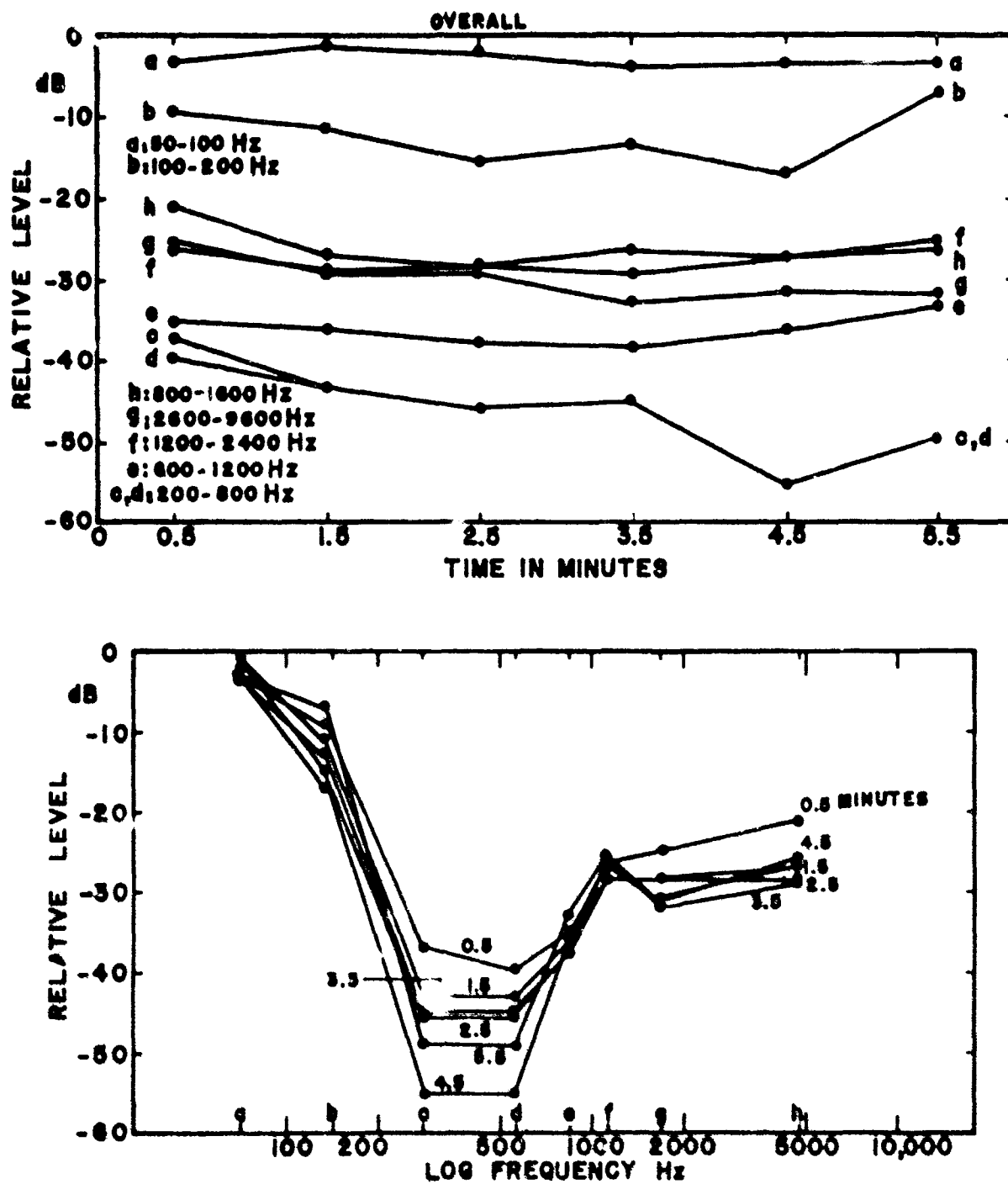


Figure 2 - Acoustic emission data for a bending fatigue test of a specimen of indium. Top: Time dependence of the relative contributions of individual frequency bands to the total sound output. Bottom: Relative acoustic output as a function of time for various frequency bands plotted at the midpoint of each band.

## SURFACE CHEMISTRY

### ELECTROCHEMISTRY

#### The Boeing Company

Electronic equipment now available at Boeing is inadequate for the study of absorption on freshly exposed bare metal samples; however, these measurements may be made by other means now under consideration. Investigations of the effects of heat treatment on the SCC susceptibility of Ti-8Al-1Mo-1V have been expanded, and measurements on one sheet of material were reproducible. A series of sheets of Ti-8Al-1Mo-1V ranging in thickness from 0.020 to 0.067 in. was examined, and thickness was shown not to be the major factor contributing to SCC in this alloy. The two extreme thicknesses tested showed no SCC, but intermediate thicknesses were susceptible. The two extremes will be examined further.

Crack propagation in Ti-8Al-1Mo-1V alloy sheet immersed in various liquids was investigated. The results are summarized in Table I.

Table I - SCC of Ti-8Al-1Mo-1V  
Alloy Sheets in Various Liquid Environments

Sheet Number	Liquid		Load (Kg.)	Velocity (cm/sec x 10 <sup>3</sup> )
2194	Methylene iodide	CH <sub>2</sub> I <sub>2</sub>	702	1.6
2194	Methylene chloride	CH <sub>2</sub> Cl <sub>2</sub> , dry	1,120	0.9
2194	Methylene chloride	CH <sub>2</sub> Cl <sub>2</sub> , water saturated	1,280	0.08
2194	Carbon tetrachloride	CCl <sub>4</sub> , dry	897	1.7
2194	Carbon tetrachloride	CCl <sub>4</sub> , water saturated	856	1.3
2194	Water	H <sub>2</sub> O, distilled	1,120	0.55
2194	Methanol	CH <sub>3</sub> OH, high purity	884	0.23
2194	Methanol + Water	CH <sub>3</sub> OH (1% H <sub>2</sub> O)	870	0.42
2283	Methanol + Water	CH <sub>3</sub> OH (2% H <sub>2</sub> O)	1,500	0.16
2283	Methanol + Water	CH <sub>3</sub> OH (10% H <sub>2</sub> O)	1,500	0.14
2283	Hexane	C <sub>6</sub> H <sub>14</sub> , high purity	2,270	0
2283	Benzene	C <sub>6</sub> H <sub>6</sub>	2,245	0
2283	Methanol	CH <sub>3</sub> OH, high purity	1,500	0.13

Hexane and benzene did not cause SCC. The effects of adding water to the organic liquids were varied and interesting; they are now being investigated.

The velocity of crack propagation during SCC in methanol containing 100 ppm NaCl solution was found to be independent of stress level.

#### Carnegie Institute of Technology

Experiments on the anodic polarization of iron alloys were carried out at 25° C. using coaxial cylindrical electrodes in a saturated aqueous FeCl<sub>2</sub> solution with solid FeCl<sub>2</sub> · 4H<sub>2</sub>O. A 100% H<sub>2</sub> gas atmosphere was employed. The reference electrode was analytical standard iron wire with 200 ppm carbon, 1000 ppm manganese, and 50, 40 and 40 ppm of phosphorus, sulfur and silicon respectively.

Experimental results were fitted to the equation,  $E = AI/(1 + BI)$ , where E is the experimental polarization voltage expressed in millivolts, I is the electrolyzing current in milliamperes, and A and B are adjustable constants obtained from a plot of 1/I vs. 1/E. It was assumed that the concentration polarization was negligible.

Three multiple component iron alloys, which show susceptibility to stress-corrosion, were studied. The compositions of these alloys are shown in Table I.

Table I - Composition of Alloys

<u>Alloy</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Mo</u>	<u>Ni</u>
4340	0.39	0.74	0.019	0.026	0.31	0.87	0.24	1.73
4140	0.39	0.83	0.017	0.033	0.26	0.93	0.20	0
RY	0.92	1.55	0.017	0.014	0.29	0	0.23	0

The experimental values of A and B are listed in Table II.

Table II - Constants for Polarization Equation

<u>Alloy</u>	<u>A (ohms)</u>	<u>B (milliamperes<sup>-1</sup>)</u>
4340	0.93	0.48
4140	12.67	0.40
RY	19.38	0.79

The experimental results listed in Table II are for electrodes which were not heat-treated. When electrodes which had been heat-treated to develop high tensile strength were used for polarization experiments reversible conditions were not obtained even after 30 days. Work on the heat-treated electrodes is continuing.

As indicated in Table II, Cr reduces the electrode polarization of

the iron (lowers A) and both Cr and Ni together greatly reduce A, assuming that the increased C and increased Mn in alloy RY have little effect. Results in the literature (Bockris and Drozic, *Electrochim Acta*, 4, 293 (1962)) suggest carbon has little effect on the anodic polarization of iron. The effect of Mn is not known.

At the suggestion of Dr. Brown, a series of Fe - Ni alloys were examined. The experimental results are given in Table III.

Table III - Fe-Ni Alloys

Electrode	Wt. % Ni	Mole % Ni	A (ohms)	B (milliamps <sup>-1</sup> )
154	25	23.8	1656.7	66.67
155	10	9.56	490.1	42.40
165	5	4.76	177.8	28.77

It was found that plots of B and A/B against weight % of Ni were straight lines the equations of which were  $B = 0.96 (\%Ni) + 1$  and  $A/B = 1.92 (\%Ni) + 20$ . In addition  $A = 1.843 (\%Ni)^2 + 21.12 (\%Ni) + 20$ . For these samples, the value of A extrapolated to 0% Ni is thus 20 ohms which is lower than the 38 ohm extrapolated value obtained with hot-rolled steel samples. The extrapolated value of B is 1 for the iron-nickel alloys and 1.4 for hot-rolled steel. Fe - Ni alloys should be further investigated.

A series of measurements were made using a pure iron electrode against a saturated aqueous solution of  $FeCl_2$  containing varying amounts of urea. The so-called pure iron electrode consists of a cage of six glass rods sealed to a half-inch glass tube. The rods are equidistant from each other and parallel to each other. About this framework analytical standard iron wire was wound as closely as possible with adjacent turns touching. The reference electrode was placed inside the wire cylinder. Experimental results are tabulated in Table IV.

Table IV  
Electrode Polarization - Saturated  $FeCl_2$  + Urea

Conc. Urea	A (ohms)	B (milliamps <sup>-1</sup> )
0 molar	66.67	0.834
1 molar	50.95	0.521
5 molar	93.47	1.52
10 molar	140.00	2.45

The values of A and B when plotted against the molarity of urea gave straight lines the equations of which are  $A = 9.95 (\text{urea}) + 41.4 (\text{urea})$  and  $B = 0.213 (\text{urea}) + 0.34$ , where (urea) indicates the molar concentration of urea. The plot for B but not for A extrapolates to the value

obtained with pure iron in the absence of urea.

Urea is a non-electrolyte ( $k_b$ , at 25° C. =  $1.5 \times 10^{-15}$ ) but its presence in solution has little effect on the solubility of  $\text{FeCl}_2$ . The experimental lines had no inflections, which indicates the solid phase remained  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  over the range of urea concentrations investigated. With solid  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  present at a constant temperature the activities of  $\text{Fe}^{++}$  and  $\text{Cl}^-$  must be constant, but the activity of the water could still have changed.

The urea molecule is probably adsorbed at sites on the surface of the iron displacing adsorbed water molecules and deactivating the sites as anodes. Current must then flow over a smaller area increasing its polarization. These results indicate that adsorbed water may be involved in the anodic dissolution of iron.

## LEED, FIELD ELECTRON AND FIELD ION MICROSCOPY

### Georgia Institute of Technology

A combined LEED and HEED system capable of handling corrosive gases was designed in association with Varian Associates of Palo Alto, California, and will be ordered in March.

A laboratory for sample preparation, which includes an acid-string saw, an acid-polishing wheel and an electropolishing apparatus, was constructed and very successfully used for the preparation of a copper sample for LEED studies. Techniques and procedures will be developed for the preparation of single crystal stainless steel samples and aluminum single crystal samples.

A stainless steel single crystal with a composition of 57% Fe, 18% Cr, and 25% Ni was purchased from Metals Research Limited of Cambridge, England. A polycrystalline sample of the same composition was also purchased, and will be used to develop sample preparation techniques. Examination of the polycrystalline sample revealed a large grain structure which will permit LEED studies of several crystallographic orientations on one sample.

Dr. F. Jona of the IBM Watson Research Center has provided a single crystal aluminum sample. All of the preliminary surface orientation and polishing was carried out by Dr. Jona, who has previously made LEED studies of aluminum. He has advised us on the cleaning procedures required in the LEED system. Results from the LEED study will be correlated with the thin film studies described below.

A system was designed for both field ion microscopy and field electron emission microscopy. The combined system will allow both characterization of surfaces by field ion microscopy and determination of surface work functions by field electron emission without removal of the sample from the UHV system. Adsorption and surface



diffusion can also be investigated. Studies of  $Ti_3Al$  and austenitic stainless steel are planned.

## MACROSCOPIC SURFACE MEASUREMENTS

### Georgia Institute of Technology

The formation and properties of metal oxide films, the interaction of the films with metals, and the properties of the interface between metals and metal oxides are being studied. Investigations of the properties of metal oxide films were continued with further stress-strain measurements of unsupported aluminum oxide films. The precision of the drive mechanisms in the original apparatus has been improved.

Interactions between oxide films and metals are being studied by applying linear and bending stresses to aluminum single crystal samples and then examining the surface slip by electron microscopy. This work is intended, in part, to define procedures for deforming a single crystal sample to produce a density of surface slip lines which is sufficient for LEED studies of the resulting exposed surfaces.

Stress-strain experiments using thin metal foils are being designed to determine the properties of metal-metal oxide interfaces. Extremely thin foils will be studied in an attempt to distinguish interface effects from bulk metal behavior.

### Lehigh University

The capacitance manometer-equipped BET apparatus described in the First Quarterly Report was found to be convenient and very sensitive. A water bath was installed around the dosing bulbs to eliminate adverse effects of ambient temperature fluctuations.

In planning are flash desorption studies of the interactions of simple diatomic gases with iron-chrome alloy filaments. For this a constant current controller is now being constructed and some modifications of the present UHV system are being made. High purity iron-chrome alloy filaments, which are already available in this laboratory, will be studied; other filaments may also be investigated.

The iron-chrome filaments are presently being used in a catalytic apparatus for the decomposition of nitrous oxide at temperatures up to  $950^{\circ}C$ . Preliminary experiments indicate that the heats of activation and the mechanism of the decomposition definitely change as a function of the chromium content of the wires. Unfortunately, at temperatures above about  $800^{\circ}C$ , the homogeneous gas phase decomposition of nitrous oxide interferes with its heterogeneous decomposition on the filaments; experiments are now in progress to determine the rates, activation energies and mechanisms of the two decompositions.

In planning are experiments using  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{16}\text{O}$  with which it should be possible to determine whether adsorbed nitrous oxide lies flat on the surface or is perpendicular to it, and whether either end is preferentially adsorbed. Consideration is also being given to altering the experimental arrangement to obtain more information concerning the initial stages of the decomposition. Oxygen uptake by the filaments during the first few minutes of contact with  $\text{N}_2\text{O}$  may be very important.

Heats of immersion measurements using  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$  samples containing various percentages of  $\text{Cr}_2\text{O}_3$  are being made. Information concerning the nature of the  $\text{Cr}_2\text{O}_3$  surface will be useful to studies of chromium-containing alloys.

A Varian V 502-15 EPR spectrometer was ordered, delivered and installed. Test spectra have been run and the apparatus appears to be in working order. An examination of the interaction of chlorine with rutile is being made while establishing experimental techniques. Later, the interactions of various gases with semiconductors, metal oxides, or supported metals will be investigated. Literature surveys and discussions with interested scientists are now in progress, and definite systems for study will soon be chosen.

#### Naval Research Laboratory

Adsorbed films of identical radioactivity and contact angle have been obtained on fire-polished soft-glass reference surfaces by retraction from nitrobenzene solutions of carbon-14 labeled stearic acid over a 25-fold concentration range. This supports the conclusion that equivalent highly compacted monolayers of stearic acid are produced on both iron and soft glass by this technique. This study will be extended to evaluate the adsorption/desorption phenomena of such ferrous metals and alloys as iron, nickel, chromium, steels, and stainless steels.

Construction of the high-purity closed electrochemical system for the electrochemical investigation of passive iron has been completed. Initial potentiostatic measurements of the current vs. potential relation in helium-saturated, sodium hydroxide solutions have shown that the entire passive region is sub-divided into several linear potential log current density regions. The slopes of these regions vary considerably, and the very low current densities vary over several orders of magnitude. These slopes can be interpreted in terms of electron-conducting or non-conducting films. All these passive films are so thin that they are invisible, and the appearance of the iron wire undergoes no apparent change.

Further work should considerably assist in elucidating the influence of these passive films, in the several potential regions, on the electrode processes occurring at the iron/solution interface.

A review of the nature of the protective films generated on iron and steel by exposure to aqueous media has revealed the following:

1. These films are usually spinels in which are incorporated some or all of the constituents of the substrate on which they have been generated.

2. Recent evidence indicates that the passive film on iron generated at ordinary temperatures contains hydrogen in its structure, and that analogous passive films on 304 stainless steel contain substantial amounts of water. When very thin these films tend to be amorphous. Pitting resistance to  $\text{FeCl}_3$  solutions has been shown to be improved by the presence of Si.

3. The incorporation of lithium in the spinel structure to produce the lithiated spinel  $\text{LiFe}_5\text{O}_8$  as a protective film gives improved resistance to high temperature aqueous attack on mild steel, and the incorporation of chromium or cobalt in spinels increases resistance to attack by  $\text{HCl}$ .

4. Recent data establishing the beneficial effect of 2 percent Cu and the corresponding deleterious effect of 2 percent Mo on the time to fracture of a 20-20 stainless steel in boiling 42 percent  $\text{MgCl}_2$  solution would seem to indicate that investigation of the structure and composition of the films generated on various alloys and their chemical resistance to chloride environments warrants attention from the standpoint of stress-corrosion cracking mechanisms.

## FRACTURE MECHANICS

The majority of tests being conducted at all of the coupled partners' sites are done using fracture mechanics analysis to characterize the stress variable in stress-corrosion cracking (SCC). Therefore, many studies using fracture mechanics are discussed in other portions of this report. Some further work toward extending the applicability of the techniques of fracture mechanics to SCC are cited here.

### The Boeing Company

Preliminary crack growth rate data, generated on 7075-T651 aluminum alloy in air and in a 3.5 percent NaCl solution, show that the stress intensity factor approach can be used to correlate fatigue crack growth rate data in corrosive environments for this alloy. This was demonstrated by the agreement in the crack growth rates of wedge-force testing and center-cracked panel testing at the same stress intensity factor. The two methods were not in agreement at very short crack lengths, although in this region the analysis for the stress intensity factor was not applicable. Two alloys, Ti-6Al-4V (mill annealed) and 2024-T3 (aluminum), will be similarly tested.

### Naval Research Laboratory

The process of plane-strain fracture instability with a tensile instability of connective ligaments at the crack tip has been examined as a model for the SCC process. In normal "dry" stressing of a crack, these ligaments contract as they are stretched so the rate of areal diminution decreases their strength. Nonetheless, for a time their overall strength rises with strain because of strain hardening. Eventually the strain hardening rate decreases until the two effects cancel. At this point the ligaments become unstable and their rupture, and instability of the crack, is inevitable. If an array of such ligaments along a crack tip is immersed in a reactive solution, a second source of areal diminution rate can be considered: the radial dissolution velocity peripheral of the ligaments. The results of this investigation show that the lifetime before fast fracture of cracked beams of various titanium alloys immersed in salt water can be estimated from this

model and related to the plastic flow properties in a way indicative of a constant dissolution velocity. The magnitude of the dissolution velocity so deduced is consistent with known rates for plastically deforming tensile rods. To achieve this correlation it was necessary to correct an earlier model of tensile instability for effects of triaxiality and local compliance. When applied to other cases of plane-strain fracture, these corrections remove several inconsistencies found in attempts to apply the earlier simple uniaxial model. The results suggest that if the dissolution velocity is inherently high, resistance to SCC is favored by a large process zone size or diameter of the ligamental cell and by a high yield strength.

## CHARACTERIZATION TESTS AND TRANSLATION

The initial goals of characterization studies at Boeing and NRL are to (1) collate test results from each laboratory, (2) demonstrate the stress-corrosion cracking (SCC) dependency on stress intensity, (3) demonstrate the validity of using linear elastic fracture mechanics for SCC testing, and (4) improve existing quantitative test techniques.

Comparison of Boeing and NRL SCC test techniques is complete. Mill-annealed Ti-8Al-1Mo-1V plate material was tested to determine fracture toughness in air,  $K_{IC}$ , and threshold stress intensity,  $K_{ISCC}$ , at Boeing and at NRL. The method of stressing involved four-point bending at Boeing and cantilever bending at NRL. At Boeing the specimens were loaded first and then a 3.5% NaCl solution was added to the container surrounding the fatigued precrack. At NRL, the precrack was immersed and then the load was applied. Neither the difference in stressing method nor the sequence of addition of solution affected the determination of  $K_{ISCC}$ . A value between 16 and 18 ksi  $\sqrt{\text{in.}}$  was indicated. Tests on Ti-4Al-3Mo-1V plate, where the order of solution and load application was reversed, were conducted at Boeing. No effect on  $K_{ISCC}$  was observed, with a value between 65 and 70 ksi  $\sqrt{\text{in.}}$  being obtained. It was concluded that the order of salt-load application does not affect  $K_{ISCC}$  since the effect was not observed in either the susceptible Ti-8Al-1Mo-1V or the relatively immune Ti-4Al-3Mo-1V alloy. It was recognized that the time period between loading the specimen and adding the aqueous environment might effect SCC susceptibility. Since the effect might depend upon the creep characteristics of the particular alloy, it has been recommended that the environment be added prior to load application during SCC characterization testing at Boeing.

Three wedge-force loaded panels were prepared at Boeing from Ti-8Al-1Mo-1V sheet (0.150 in. thick) and tested in a 3.5% NaCl solution. The first panel was loaded to a K value of 35 ksi  $\sqrt{\text{in.}}$  and exposed to environment. The crack extended and arrested at approximately 22 ksi  $\sqrt{\text{in.}}$ . The crack was then extended by fatigue-loading in air, and the panel was tested by end-loading to obtain a fracture toughness value,  $K_C$ , of 72 ksi  $\sqrt{\text{in.}}$ . The other specimens were tested so that the crack growth was started after arrest several times, and the stress-intensity value at arrest was calculated each time. A "threshold" value between 21 and 23 ksi  $\sqrt{\text{in.}}$  was indicated. The SCC dependency on stress intensity was demonstrated, and it was observed that both  $K_C$  and  $K_{ISCC}$  could

be determined by a single test specimen. Similar work on Ti-6Al-4V is planned because this alloy represents a different level of SCC susceptibility.

A successful SCC test was performed by NRL on a large tensile specimen of Ti-7Al-2Cb-1Ta alloy plate in a salt water environment. The specimen, 6 by 1 by 24 in., contained a surface fatigue crack approximately 0.6 in. long. By ultrasonic techniques, slow SCC was first observed at a nominal stress of 50,000 psi ( $\sigma_{YS} = 111,000$  psi) and a calculated stress intensity level ( $K_I$ ) of 31 ksi  $\sqrt{\text{in.}}$  at the crack tip. The specimen broke after 25 minutes at this stress. Previous cantilever bend test measurements showed the SCC threshold value ( $K_{ISCC}$ ) to be 31.5 ksi  $\sqrt{\text{in.}}$  for this material. The excellent correlation between the two types of tests is a significant demonstration of the validity of using fracture mechanics K-level testing for SCC characterization of high-strength materials.

Modification of existing SCC test techniques at Boeing includes the use of dynamic bend testing to determine  $K_{ISCC}$ . Two mill-annealed Ti-8Al-1Mo-1V specimens were four point-bend tested in a 3.5% NaCl solution, one each at stress rates of 15 and 100 psi per second. The indicated  $K_{ISCC}$  values, 28 and 29 ksi  $\sqrt{\text{in.}}$ , were higher than those obtained previously during sustained loading (approximately 18 ksi  $\sqrt{\text{in.}}$ ), but it is believed that a more sensitive deflection-measuring device now available will yield compatible threshold values.

The use of a double-cantilever-beam specimen for evaluating plane strain fracture toughness and environmental cracking behavior has been reviewed at Boeing. Work has started on the development of a specimen configuration compatible with the needs of the characterization program.

Understanding of the stress-corrosion phenomenon in titanium alloys requires analysis of a wide spectrum of compositions and associated microstructures. More than 30 alloys are being characterized at Boeing in thermal and thermomechanical conditions that vary grain morphology and size, dislocation structure, and degree of order. Commercial and near-commercial alloys representing alpha, lean alpha, alpha-beta, and beta types have been selected for evaluation.

Initial studies have been conducted on two alpha type alloys, commercially pure titanium ( $O_2 = 3,800$  ppm) and Ti-5Al-5Sn-5Zr. Of nine thermal conditions tested for the commercially pure alloy, only a 1,500°F/WQ condition was susceptible to SCC. Differences in the microstructures and fracture modes of

the susceptible and immune conditions are being investigated. Seven additional specimen blanks have been reduced 30 to 90% by rolling to more fully evaluate the role of dislocation structure, recovery processes, recrystallization, and grain growth on the SCC behavior of the alpha phase.

Ti-5Al-5Sn-5Zr is being similarly analyzed to establish the effect of composition on each metallurgical process. Six heat treatments of this alloy have been characterized, including one designed to promote order in the aluminum and tin-rich alpha phase. This heat treatment, 1,650°F/AC + 1,100°F/8-hr/AC, was noticeably more susceptible to the environment than were the other conditions. The extent of long-range order will be investigated using thin foil electron microscopy. An additional six specimen blanks will be thermomechanically processed at Wah Chang Corporation, Albany, Oregon.

Effect of heat treatment on the fracture toughness and SCC resistance of the titanium alloys 6Al-6V-2Sn, 7Al-4Mo, 6Al-2Mo, and 5Al-3Mo-1V-2Sn has been studied. Solution-treated and aged (STA), annealed, and duplex-annealed treatments were included for both the equiaxed and Widmanstätten microstructures. Although testing revealed that large differences in fracture toughness could be attained within each alloy system, heat-treatment variations produced little change in the stress corrosion susceptibility as measured by the ratio  $K_{ISCC}/K_{IC}$ . Ratio values of 0.6 for Ti-6Al-6V-2Sn, 0.65 for Ti-7Al-4Mo, 0.58 for annealed Ti-6Al-2Mo, 0.73 for STA Ti-6Al-2Mo, and 0.7 to 1.0 for Ti-5Al-3Mo-1V-2Sn were determined. Deviation from these ratios was normally less than 2% except for heat treatments producing exceptionally low fracture toughness values. Standard notch-bend specimens (7.5 by 1.5 by 0.5 in.) were tested.

Fracture toughness and stress corrosion resistance of Ti EX684 (IMI forging alloy) in the manufacturer's suggested heat-treatment condition were determined using precracked Charpy specimens. The susceptibility ratio,  $K_{ISCC}/K_{IC}$ , was less than 0.5.

Salt water (3.5%) SCC studies were conducted at NRL on recently acquired 1-inch-thick plates of several titanium alloys in as-received and heat-treated conditions. The test method used was the cantilever bend test on side-grooved specimens. Test results are shown in Table 1.



Table 1. Stress-Corrosion Cracking Characteristics  
of Some Titanium Alloys

<u>Alloy</u>	$\sigma_y$ (ksi)	DWTT (ft-lb)	$K_{Ic}$ (ksi $\sqrt{\text{in.}}$ )	$K_{ISCC}$ (ksi $\sqrt{\text{in.}}$ )	<u>Heat Treatment</u>
Ti-6Al-4V	125	2075	120	105	As received
Ti-7Al-1Mo-1V	113.7	-	118	42	1800° F/1 hr/He Cool
Ti-6Al-6V-2Sn-1Cu-1/2 Fe	120.1	-	102	78	1660° F/1 hr/He Cool
Ti-6Al-3V-1Mo	107.9	-	112	98	1850° F/1 hr/He Cool
Ti-7Al-2.5Mo	108	-	123	92	1800° F/1 hr/He Cool
Ti-6Al-4V (ELI)	115.2	-	112	84	1850° F/1 hr/He Cool
Ti-6Al-2Mo	117.6	1601	107	94	As received
Ti-6Al-4V-2Mo	126.0	1052	96	82	As received
Ti-6Al-6V-2Sn-2Mo	138.2	514	71	65	As received
Ti-6Al-6V-2Sn-2Mo	126.8	681	91	82	1660° F/2 hr/He Cool

Investigations of alpha-beta alloys received by Boeing from NRL are continuing. Titanium alloys 7Al-2.5Mo, 7Al-3Mo, 7Al-4Mo, and 6Al-4Zr-2Mo have been hot-rolled from thicknesses of 1 to 0.5 in. preliminary to heat treatment. Specimens for five thermal conditions of Ti-7Al-2.5Mo have been fabricated and are currently in test. Four titanium alloys with low oxygen — 4Al-3Mo-1V, 6Al-2Mo, 6Al-4V-2Mo, and 6Al-6V-2Sn-2Mo — have recently been received from NRL in the form of 1 by 8 by 42-in. plate. This material will be used for thermomechanical processing studies. The same alloys are on order in 5/8-in. thickness for heat-treatment studies.

Fifteen different titanium alloys for which SCC data had been previously obtained were selected for a study to determine the extent to which the "dissolution velocity" model proposed by Dr. Krafft of NRL can apply to titanium alloys. This model is reported on elsewhere in this document. The selection of alloys represents a wide range of resistance to SCC in salt water as well as a wide variety of yield strengths and fracture toughnesses. Preliminary results obtained to date by Dr. Krafft indicate that the dissolution model may apply only to those alloys that are highly sensitive to salt water SCC. A complete report on the findings of this study can be expected soon.

The fracture properties and SCC characteristics of 7075-T6 forged aluminum plate (short transverse grain direction) 4 in. thick have been eval-

uated at Boeing with extension fixtures to achieve standard specimen dimensions. A  $K_{IC}$  value of 26 ksi  $\sqrt{\text{in.}}$  and an indicated  $K_{ISCC}$  value of 22.3 ksi  $\sqrt{\text{in.}}$  (7,150 minutes for failure in a 3.5% NaCl solution) were obtained. It is recognized that the properties of 4-in. sections do not necessarily represent those of thinner plates; however, the feasibility of using extension fixtures was demonstrated. Further work is planned for short-transverse testing in thinner sections.

A modified machinability test is being investigated by Carnegie Institute of Technology as a possible way to describe the SCC susceptibility of high-strength materials. Cutting forces are recorded during crack initiation and propagation in air and under aqueous corrosive environments. Initial experiments on aluminum alloys showed that a droplet of 3.5% NaCl solution caused a substantial reduction in the peak cutting force and in the displacement, where the force fell to zero. Bubbles were observed coming from the cracks, and an electrode inserted into the droplet registered an appreciable emf. The bubbles and the emf indicated electrochemical action.

When a titanium alloy was substituted for aluminum, however, there was a reduction in the peak force and its extent, but no bubbles or emf were observed with a 3.5% NaCl solution. This suggested that the action of the NaCl on titanium was not electrochemical.

An attempt has been made to use the emf values to study specimen orientation relative to the rolling direction and to distinguish between susceptible and aluminum on titanium alloys. This has not been successful; the emf data are not reproducible. Apparently small changes in speed and electrode position in relation to the crack are extremely important.

The force traces reproduce much better from test to test; therefore they are used to study material susceptibility to stress corrosion and the influence of specimen orientation. In tests to date the speed of crack propagation has been relatively rapid (0.1 to 1 in./min). In future research this speed will be reduced to much lower values and the influence of this change studied.

In the tests that have been run to date on specimens obtained from NRL, relatively good agreement has been obtained on susceptible and immune alloys. The next work that is planned for this technique is to study the influence of compounds containing chlorine on the SCC characteristics of titanium alloys.

A computer program (TEL-138) has been developed at Boeing for analyzing and cataloging three-point-loaded and four-point-loaded, slow-bend fracture toughness and SCC data. This program can be modified to include data from other specimen configurations. Data on titanium alloys, steels, and aluminum alloys generated at Boeing by three-point loading have been cataloged with the aid of TEL-138. The documentation is complete and will be released soon.

The Apollo tankage failure caused by methanol has triggered fresh interest in the study of the SCC susceptibility of titanium alloys in nonaqueous environments. The information gathered appears to yield important clues on SCC mechanisms and provides a store of practical information.

At NRL, studies of the SCC susceptibility of Ti-8Al-1Mo-1V and Ti-6Al-4V alloys in alcohols and in alkanes have been made. It has been found that stress-corrosion cracks may be initiated in stressed smooth-specimen titanium alloys by methanol, ethylene glycol, and absolute ethyl alcohol; the aggressiveness decreases in the order given.

With precracked specimens, apparently all the alcohols degrade the threshold stress intensity level  $K_{ISCC}$  to values less than half the measured dry fracture toughness index  $K_{IC}$ . The primary alcohols of short chain degrade  $K_{ISCC}$  to a somewhat greater extent than do the long-chain alcohols or the secondary and tertiary alcohols.

The straight-chain saturated hydrocarbons — propane (gas), hexane, and heptane — degrade  $K_{ISCC}$  to about the same level as the longer-chain alcohols, which is surprising; these environments should not sustain an electrochemical process.

An explanation in terms of two reactions tentatively is proposed: The primary alcohols may initiate and propagate cracks by reacting with a fresh titanium alloy surface to yield an alkoxide and hydrogen. The tertiary alcohols and alkanes, which do not cause crack initiation, may cause cracks to propagate through a different reaction. In contact with a fresh titanium alloy surface the hydrocarbons may crack to yield unsaturated hydrocarbons and hydrogen. Both reactions are required to explain all the observations, but both entail the release of hydrogen, which is therefore suspect.

At Boeing, crack propagation caused by nonionic materials such as water and organic compounds has been examined in Ti-8Al-1Mo-1V alloy sheet. The results are summarized in Table 1 of the Surface Chemistry Section (page 17). It can be noted that of the compounds tested only those containing halogen and oxygen caused SCC. In addition, only in the case of methylene chloride did the presence of water affect SCC. The reasons for this behavior are currently under investigation. These observations may not be the same for crack initiation. The relationship of stress and velocity of crack propagation during SCC has been investigated in methanol containing 100 ppm NaCl solution. It has been demonstrated that, at least under certain conditions, velocity was independent of stress level.

Dr. Sandoz at NRL has demonstrated that certain titanium alloys will experience slow crack propagation in several inert environments (see abstract).

## ABSTRACTS OF MANUSCRIPTS AND REPORTS

1. R.W. Judy, Jr. and R.J. Goode, "Stress-Corrosion Cracking Characteristics of Alloys of Titanium in Salt Water," NRL Report 6564, February 1967

### Abstract

The salt water stress-corrosion cracking (SCC) characteristics have been determined for a large number of titanium alloys representative of commercial production as part of an NRL program directed to determining the underlying principle of SCC in metals and establishing procedures for improving the SCC resistance of these metals as well as learn how to "live" with the problem where it exists. The SCC resistance was determined using a precracked cantilever bend specimen with analysis provided by fracture mechanics techniques. Stress intensity-time curves for the occurrence of SCC are presented for all the titanium alloy materials studied to provide guideline information for programs similar in nature to the NRL program as well as for alloy development, design and materials selection, and specification and quality control.

2. 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 (in press)

### Abstract

The stress-corrosion cracking resistance in salt water of a welded 18Ni 200 grade maraging steel weldment was investigated. Unexpectedly, the weld metal was found to be more resistant to stress-corrosion cracking than the base plates.

3. G. Sandoz, "Effects of Some Organics on the Stress-Corrosion Susceptibility of Some Titanium Alloys," Conference Summary Report (Accelerated Crack Propagation of Titanium by Methanol, Halogenated Hydrocarbons, and other Solutions, March 1967), to be published by DMIC, Battelle Memorial Institute

Abstract

Some tests for stress-corrosion susceptibility of Ti-8Al-1Mo-1V and Ti-6Al-4V alloys in alcohols and hydrocarbons are described. Both smooth and precracked specimens were used to help specify the environmental effects with respect to crack initiation and crack propagation.

4. G. Sandoz, "Stress-Corrosion Cracking Susceptibility of a Titanium Alloy in a Non-electrolyte," Nature (in press)

Abstract

Stress-corrosion cracking was found to take place in n-propane, n-heptane, and n-hexane environments for Ti-8Al-1Mo-1V alloy. The stress intensity threshold level was somewhat higher than that for the same alloy tested in salt water.

5. 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

Abstract

The fracture of Ti-6Al-4V alloy by stress-corrosion cracking (SCC) in methanol demonstrates that the relative proportions of cleavage, peculiar to SCC in this alloy, and mechanical rupture depend on the crack tip stress intensity ( $K_I$ ). When  $K_I$  is low, most of the crack propagation is cleavage, with concomitant rupture of a few SCC resistant ligaments. When  $K_I$  is high, a small proportion of cleavage raises the local stress along the crack front sufficiently to trigger a large increment of mechanical rupture, leading to stable propagation with a high proportion of rupture dimples in the fracture surface.

6. George Sandoz and R.L. Newbegin, "Stress and Corrosive Environments (Some Environmental Effects on Titanium Alloys)," Report of NRL Progress, March 1967 (in press)

Abstract

Recently a relationship has been shown between the hydrogen content of certain titanium alloys and the susceptibility to stress-corrosion cracking (SCC) of these alloys in salt water. If hydrogen in the alloy is involved in the SCC process, one might also look for the "delayed fracture" type of failure which hydrogen is known to cause in certain steels.

Experiments of this type have been conducted using a Ti-8Al-1Mo-1V alloy containing 48-50 ppm hydrogen. It has been confirmed that delayed fractures in dry air and dry helium do occur at stress intensity values approximately half the values found when specimens are loaded

to fracture. Threshold stress intensity values are found below which the slow crack growth and delayed fracture do not occur. The curves of stress intensity  $K_{Ii}$  vs fracture time are similar in appearance to those obtained in water, but the rate of crack growth (time to fracture) is obviously slower and the threshold stress intensity is higher. The electron fractographic appearances of the non-environmental cracks resemble somewhat those of stress-corrosion cracks of the same alloys in salt water.



#### TITLES OF PREVIOUS REPORTS AND PAPERS

1. Matthew Creager, "The Elastic Stress Field Near the Tip of a Blunt Crack," (Master's Thesis) Lehigh University, October 1966
2. C.O. Timmons, R.L. Patterson, and L.B. Lockhart, Jr., "The Adsorption of C-14 Labeled Stearic Acid on Iron," NRL Report 6553 (in press)
3. 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

## DIARY OF EVENTS

Students associated with the ARPA Program at Lehigh University and Carnegie Institute of Technology took part in a visit and tour of The Boeing Company plant and facilities in Seattle, Washington, on 13-15 February 1967. Interesting discussions developed both within the visiting group and with Boeing personnel working in allied fields.

A one-day technical seminar on the Physical Metallurgy of Titanium Alloys was held at The Boeing Company on 16 February 1967. The seminar was attended by fifty individuals including representatives from all sectors of the ARPA Program. Investigators at Boeing, the University of Washington, and NRL discussed topics that included phase transformations, mechanical property evaluations, and SCC in aqueous, ionic, and nonionic environments. The proceedings were informal and will not be published. A further review of project work at The Boeing Company and the second quarterly executive meeting were held 17 February.

Representatives of each of the Program partners attended a one-day Coupling Program Review meeting at the Pentagon, Washington, D.C., on 28 February.

An informal one-day meeting of ARPA Program personnel was held at NRL on 1 March 1967. Dr. E.J. Scheibner of the Georgia Institute of Technology and Dr. J.M. Krafft and Dr. P.P. Puzak of the Naval Research Laboratory made presentations. A Test Methods Committee was formed for the guidance of the Program.

Mr. Ronald J. Livak, first student at the Naval Research Laboratory in the ARPA Coupling Program, was awarded the AIME student prize for the work which he did at NRL as part of the ARPA project. This is believed the first time that a Junior student has been awarded that prize. Mr. Livak is working towards his B.S. at Carnegie Institute of Technology.

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13. 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 Institute of Technology, 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 bibliography are included.		

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(PAGE 1)

39

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