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ABSTRACT

This report contains a compilation of abstracts from recently published reports and journal articles generated under the ARPA Coupling Program on Stress-Corrosion Cracking, ARPA Order 878. The abstracted reports are from work done at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory. Selected abstracts of articles from outside the ARPA program in the field of stress-corrosion cracking and a diary of events are also included.

STATUS

This is a progress report; work is continuing.

AUTHORIZATION

NRL Problems 61M04-08
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INTRODUCTION

In order to learn how to improve high-strength structural alloys with respect to their resistance to stress-corrosion cracking (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. Scientists prominent in the fields of surface physics and surface chemistry have been enlisted in the project in order to bring the tools of these new sub-disciplines to complement those of traditional electro-chemistry/thermodynamics in order to design new advances in the practical problem.

The reporting system has been modified as follows: Detailed technical progress from project units will be published twice each year in the winter and summer quarterly reports. Submissions for these progress reports under the headings of Titanium, Steel, or Aluminum will be forwarded to section editors who, in turn, will 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. The spring and fall quarterly reports will contain (1) abstracts of newly published reports and manuscripts of project sponsored work, (2) a chronological listing of the titles of all ARPA generated reports, and (3) selected abstracts of reports and journal articles from outside the ARPA program in the area of stress-corrosion cracking. Each quarterly will contain a diary of events section.

A. ABSTRACTS OF ARPA-GENERATED MANUSCRIPTS AND REPORTS

1. G. R. Irwin, Lead article in 2nd issue of Journal of Experimental Fracture Mechanics, Pergamon Press, to be published.

As an analysis viewpoint, fracture mechanics treats the leading edge of a crack as a line disturbance zone in a manner similar to the treatment of dislocation lines in dislocation mechanics. Linear fracture mechanics analysis is adequate for most practical applications and permits estimates of two new length factors: the approximate size of the plastic zone, $2r_Y$, and the crack border opening displacement, $\delta = \mathcal{G}/\sigma_Y$. Studies of crack extension behaviors as a function of the stress field parameters K and $\mathcal{G}$, and their interpretation with the assistance of length factors, have clarified general understanding of fracture in ways which impinge strongly on various fields of investigation such as stress corrosion cracking, fatigue, brittle transition temperature, and fracture control methods. As an example, the paper discusses interpretation of the brittle-ductile transition in terms of relative plastic zone size, and allowable-load estimates which include fracture strength in a rational way. Fracture control methods which do not rely on prior fracture failure experience are needed for new structures now under consideration. Correspondingly the need for training and experience in fracture mechanics is urgent.

2. P. C. Paris and G. R. Irwin, "Fundamental Aspects of Crack Growth and Failure," submitted to Treatise on Fracture ed. by Liebowitz, Pergamon Press.

The analytical aspects of linear fracture mechanics are complete relative to basic formulation and two-dimensional static problems.

Extensions of current analysis techniques are needed for certain three-dimensional and dynamic problems. The terminology of linear crack stress field analysis permits descriptive characterization of a wide range of macroscopic crack extension behaviors.

Plasticity analysis aspects of cracks are less advanced. However, simple aspects can be treated in ways which permit an understanding of the brittle-ductile fracture mode transition and provide essential guidance for studies of the relationship of crack toughness to plastic flow properties. Attempts to provide general characterization factors for crack extension in terms of plasticity analysis (rather than linear analysis) have been only partially successful. Although advancement in certain fields of fracture behavior may be delayed pending clarification of factors dependent upon non-linear analysis, applications of the linear fracture mechanics treatment to fatigue and stress corrosion cracking, as well as to other fields, have become established and these provide ample scope for continued growth of the fracture mechanics movement.

3. W. A. Spitzig, P. M. Talda, and R. P. Wei, "Fracture-Crack Propagation and Fractographic Analysis of 18Ni(250) Maraging Steel Tested in Argon and Hydrogen Environments," Journal of Engineering Fracture Mechanics, January 1968.

Fatigue-crack propagation studies on an 18Ni(250) maraging steel were performed at room temperature in dry and humid argon and hydrogen environments (atmospheric pressure) to examine the effects of moisture and hydrogen on the rates of fatigue-crack propagation and on the fracture path through the microstructure. The results showed that the rate of fatigue-crack propagation in the 18Ni(250) maraging steel was insensitive to moisture in the test environment. Nearly the same rates of crack propagation were observed in dry argon, humid argon, and humid hydrogen. The influence of dry hydrogen was, however, pronounced, the rate of fatigue-crack propagation in dry hydrogen was nearly three times that observed in the other environments.

Analyses of the fracture surfaces by electron fractography showed that similar surface characteristics existed for the specimens tested in dry argon, humid argon, and humid hydrogen. The fracture paths appeared to be transgranular, at least with respect to the prior austenite grain boundaries, and the fracture surfaces consisted largely of ductile fatigue striations. Specimens tested in dry hydrogen, on the other hand, exhibited numerous regions with a cleavage type of surface structure.

Relationships between the observed fracture-surface topography and measured crack-propagation rates are considered. The role of hydrogen and water vapor in promoting crack growth are also discussed.

4. A. P. Popichak and J. D. Wood, "Plane Strain Stress Corrosion Crack Propagation in 7075-T6 Aluminum," presented at the 97th Annual Meeting of the Metallurgical Society of AIME, to be submitted to the Journal of Metals.

Stress corrosion crack propagation has been studied in pre-cracked short transverse specimens of 7075-T6 aluminum alloy under plane strain stress conditions and in aqueous 3-1/2% NaCl solution. The propagation rates decrease as the crack extends (the stress intensity increases). In addition, the growth rates are significantly affected by agitation of the solution. The results of this stress corrosion investigation will be discussed in relation to fracture mechanics and electrochemical concepts.

5. M. Codell, H. Gisser, J. Weisberg, and R. D. Iyengar, "Electron Spin Resonance Study of Hydroperoxide on Zinc Oxide," submitted to J. Phy. Chem.

The ESR signal observed on zinc oxide (g = 1.961) following oxygen treatment at 500° decreases in intensity on exposing the degassed sample to tertiary butyl hydroperoxide (TBHP) vapors. However, with samples vacuum outgassed at 500°, the adsorption of TBHP leads to the formation of two signals (g = 1.965 and 1.961) in place of the original signal. No spectra of free radicals resulting from decomposition of TBHP have been observed. When vacuum outgassed ZnO is treated with oxygen at 700 torr, reoutgassed at 25° and left in vacuum for more than 24 hours, two signals are again observed which correspond to the two signals observed earlier on the TBHP treatment. The formation of the two signals and variation in their intensities have been discussed in terms of oxygen ion vacancies and interstitial Zn^{+} ions.

6. R. D. Iyengar and V. V. Subba Rao, "Electron Spin Resonance of Nitrogen Dioxide (NO_2) Adsorbed on Zinc Oxide," submitted to J. Am. Chem. Soc.

The electron spin resonance spectra of NO_2 adsorbed on zinc oxide have been investigated. The signal at g = 1.96 observed with outgassed ZnO is reduced about 80% by the addition of excess NO_2 and a new signal at g = 2.015, the intensity of which decreases with increasing temperature above -196°, is produced. Outgassing at room temperature caused the formation of a complex spectrum due to NO_2 strongly adsorbed on ZnO. The species responsible for the sharp signal at g = 2.015 will be further investigated.

7. R. D. Iyengar, M. Codell, and J. Turkevich, "An ESR Study of the Nature of the Surface Oxygen During Oxidation of a Nonstoichiometric Rutile Surface with Oxides of Nitrogen," J. of Catalysis, Vol. 9, 1967, p. 305.

Nitrogen dioxide restores the oxygen deficiency at the surface of outgassed rutile, and produces a signal which has been attributed to O_2^+. Similarly, nitrous oxide also reacts with vacuum outgassed samples of rutile to produce the signal attributed to O_2^+. Neither oxide of nitrogen produces O_2^- on interaction with vacuum-outgassed high area TiO_2.

8. A. J. Solomon, R. D. Iyengar, and A. C. Zettlemoyer, "On the Use of a Quadrupole Residual Gas Analyzer for a Continuous Scan of the Products in a Low Pressure Catalytic Flow Reactor," submitted to J. of Catalysis.

During a flow study of the catalytic decomposition of nitrous oxide, erroneous results were obtained if large net pumping speeds were not provided at the mouth of the mass spectrometer (Quadrupole Residual Gas Analyzer, Varian) used for product analysis. The introduction of a VacIon pump close to the outlet of the mass spectrometer eliminated the decomposition of nitrous oxide to oxygen on the Quadrupole filament.

9. R. F. Hochman and B. G. LeFevre, "Field Ion Microscopy Studies of the Structure and Properties of Metal and Alloys," presented at the AICHE Materials Conference, Philadelphia, Pennsylvania, April 3, 1968; to be published in the AICHE Proceedings.

A brief review of the principles of field emission and field ion microscopy are presented. Confirmation of defect structure and grain boundaries characteristics on an atomic scale are discussed. Studies of alloy properties, order-disorder oxidation are covered. A brief review is presented of the application of field ion microscopy to solids other than metals, and to biological studies.

10. B. G. LeFevre, H. Grenga, and B. Ralph, "Field Ion Images from Ordered Ni_4Mo," submitted to Philosophical Magazine.

Field ion images from ordered Ni_4Mo with He-Ne are very stable and contain a variety of interesting crystallographic features. Translational antiphase boundaries are readily identified because of the layered structure of Ni_4Mo and the prominence of the Mo atoms in the images. Although the Ni atoms do not image readily they are faintly visible on certain superlattice planes where they occur in layers. A dark zone pattern which is asymmetric with respect to the overall crystallographic pattern is shown to be related to the orientation of the ordered β structure with respect to the disordered face-centered cubic α structure.

11. S. Schuldiner, "Passivation of Anodic Reactions," submitted to J. Electrochem. Soc.

It is shown that passivation of a Pt electrode for the hydrogen oxidation reaction can be explained by small amounts (fraction of a monolayer) of adsorbed anions. Anion adsorption can effectively reduce the active electrode area, but the major passivation effect is the poisoning of catalytic sites which retard the oxidation reaction so that in most of the region where passivation occurs the reaction rate is controlled by the increased free energy of activation with increased potential. Dermasorbed oxygen atoms in addition to sulfate ions can have a strong effect on the catalytic activity of Pt for the hydrogen oxidation reaction.

12. S. Schuldiner and C. M. Shepherd, "Anodic Oxidation of Hydrogen on Iron and Platinum in Sodium Hydroxide Solution," submitted to J. Electrochem. Soc.

In a rigorously controlled high-purity, closed system, the electrochemical behavior of Fe and Pt electrodes for the hydrogen oxidation reaction showed marked differences both in the active and passive regions. The catalytic behavior of the two metals reflect the differences in metallic properties and anion adsorption. Iron was found to be a far better catalyst with a much less pronounced passive region. Iron corrosion was insignificant. Small amounts of Pt on Fe strongly retarded hydrogen oxidation. Significant Pt dissolution and deposition on the iron working electrode was not found.

13. J. M. Krafft and J. H. Mulherin, "Tensile-Ligament Stability and the Slow Growth of Cracks in Alloys of Iron, Aluminum, Copper and Titanium," prepared for the ASTM Committee on Fracture Testing of Metals, meeting at Illinois Institute of Technology, Chicago, March 12-15, 1968; also to be offered to ASM.

A model which attributes stress corrosion crack growth to erosive surface attack of d_T-size ligaments is re-examined by comparing the lifetime of cracked bend specimens in fresh and salt water with bulk plastic flow properties. The results suggest that the ligament stability model is applicable if it is restated in terms of a uniaxial tensile instability criterion. In all alloys the behavior of the moving crack is closely predicted. In iron-base alloys, the strength threshold of stress corrosion cracking K_{Iscc} is identified with the uniaxial elastic limit as a threshold of elastic stability. In two aluminums and a brass, this elastic threshold appears to be elevated by the necessity to establish the ligaments, by yielding across them the distance d_T, in the triaxial stress field of the plane strain crack. In titanium alloys the elastic anisotropy appears to affect this constraint, and thus K_{Iscc}, in a complex manner. The coherency of the precipitate phase in the non-ferrous alloys may prevent the ready ligament formation of the ferrous alloys. The surface attack rate V_S is very high in the martensitic steels of low tempering temperature. If the consequent depression in K_{Ic} is neglected the process zone size d_T can be taken as independent of tempering temperature. On the other hand V_S remains constant with differing crack orientation in a maraging steel.

B. CHRONOLOGICAL LISTING OF ARPA-GENERATED REPORTS NOTICED IN PREVIOUS QUARTERLIES

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. D. A. Howe, "Effects of Heat-Treatment Environmental Conditions on Stress-Corrosion Cracking Resistance of Several Titanium Alloys," Report of NRL Progress, February 1967, pp. 32-35

5. 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

6. G. Sandoz, "Effects of Some Organics on the Stress-Corrosion Susceptibility of Some Titanium Alloys," article in DMIC Memorandum 228 (entitled "Accelerated Crack Propagation of Titanium by Methanol, Halogenated Hydrocarbons, and other Solutions"), Battelle Memorial Institute, March 6, 1967

7. George Sandoz and R. L. Newbegin, "Some Environmental Effects on Titanium Alloys," Report of NRL Progress, March 1967, pp. 28-30

8. J. M. Krafft, "Role of Local Dissolution in Corrosion-Assisted Cracking of Titanium Alloys," Report of NRL Progress, March 1967, pp. 6-18

9. G. Sandoz, "Stress-Corrosion Cracking Susceptibility of a Titanium Alloy in a Non-electrolyte," Nature, Vol. 214, April 8, 1967, pp. 166-167

10. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Second Quarterly Report)," NRL Memorandum Report 1775, April 1967

11. A. M. Sullivan, "Dissolution Velocities of Different Organic Media," Report of NRL Progress, April 1967, pp. 18-19

12. E. P. Dahlberg, "Thin Foil Electron Microscopy," Report of NRL Progress, April 1967, pp. 19-21

13. G. Sandoz, "Delayed Fracture Characteristics of Ti-8Al-1Mo-1V Alloy," Report of NRL Progress, May 1967, pp. 31-32

14. 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, The Boeing Company, May 1967

15. C. O. Timmons, R. L. Patterson, Jr. and L. B. Lockhart, Jr., "A Study of the Adsorption of Carbon-14 Labeled Stearic Acid on Iron," NRL Report 6553, June 2, 1967; also published in Journal of Colloid and Interface Science 26, January 1968, pp. 120-127

16. H. R. Smith, D. E. Piper and F. K. Downey, "A Study of Stress-Corrosion Cracking by Wedge-Force Loading," Document D6-19768, The Boeing Company, June 1967

17. 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

18. R. W. Judy, Jr. and R. J. Goode, "Stress-Corrosion-Cracking Behavior in Titanium Alloys," Report of NRL Progress, July 1967, pp. 38-40

19. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Third Quarterly)," NRL Memorandum Report 1812, August 1967

20. G. Sandoz and R. L. Newbegin, "Effect of Specimen Breadth on Susceptibility to Stress-Corrosion Cracking of Ti-8Al-1Mo-1V Alloy in Salt Water," Report of NRL Progress, August 1967, pp. 45-46

21. J. C. Williams, "Some Observations on the Stress-Corrosion Cracking of Three Commercial Titanium Alloys," Document D6-19553, The Boeing Company, September 1967

22. D. G. Howe, "Effects of Heat Treatment on the Stress-Corrosion-Cracking Resistance of the Alloy Ti-6Al-6V-2.5Sn," Report of NRL Progress, September 1967, pp. 51-52

23. D. N. Fager and W. F. Spurr, "Some Characteristics of Aqueous Stress Corrosion in Titanium Alloys," Document D6-60083, The Boeing Company, September 1967

24. M. J. Blackburn and J. C. Williams, "Metallurgical Aspects of the Stress-Corrosion Cracking of Titanium Alloys," Presented at "Fundamental Aspects of Stress-Corrosion Cracking," Ohio State University, September 11-15, 1967; to be published in Proceedings.

25. D. A. Meyn, "Effect of Crack Tip Stress Intensity on the Mechanism of Stress-Corrosion Cracking of Titanium-6Al-4V in Methanol," Corrosion Science, Vol. 7, No. 10, October 1967, pp. 721-723

26. E. P. Dahlberg, "Stress-Corrosion-Cracking Test Methods," Report of NRL Progress, October 1967, pp. 41-42

27. R. W. Huber, R. J. Goode, and R. W. Judy, Jr., "Fracture Toughness and Stress-Corrosion Cracking of Some Titanium Alloy Weldments," Welding Journal Research Supplement, October 1967, pp. 1-9

28. R. W. Huber, R. J. Goode, and R. W. Judy, Jr., "Fracture Toughness and Salt-Water Stress-Corrosion-Cracking Resistance of Titanium Alloy Weldments," Report of NRL Progress, November 1967, pp. 1-11

29. D. A. Meyn, "Delayed Failure of Ti-7Al-2Cb-1Ta Under Mode III Loading in Air, Salt Water, and Methanol," Report of NRL Progress, November 1967, pp. 33-34

30. R. W. Judy, Jr., and R. J. Goode, "Study of Notch Acuity on the SCC Characteristics of Titanium Alloys," Report of NRL Progress, November 1967, pp. 34-35

31. G. Sandoz and R. L. Newbegin, "Effect of Hydrogen Content on Subcritical Crack Growth in Ti-8Al-1Mo-1V Alloy," Report of NRL Progress, November 1967, pp. 35-36

32. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Fourth Quarterly," NRL Memorandum Report 1834, November 1967

33. M. Creager and P. Paris, "Elastic Equations for Blunt Cracks with Reference to Stress Corrosion Cracking," International Journal of Fracture Mechanics, Vol. 3, No. 4, December 1967, pp. 247-252

34. H. W. Paxton and R. P. M. Procter, "The Effects of Machining and Grinding on the Stress-Corrosion Cracking Susceptibility of Metals and Alloys," Technical Paper EM 68-520, American Society of Tool and Manufacturing Engineers, Symposium on Surface Integrity in Machining and Grinding, Pittsburgh, Pa., January 24-25, 1968

35. E. P. Dahlberg, "Stress-Corrosion Cracking Characteristics of Several Aluminum Alloys by a Crack-Arrest Method," Report of NRL Progress, January 1968, pp. 23-24

36. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Fifth Quarterly)," NRL Memorandum Report 1864, February 1968

37. S. Schuldiner, "Passivation of Anodic Reactions," Report of NRL Progress, March 1968, p. 21

38. E. P. Dahlberg, "A Self-Stressed Specimen for Measuring Stress-Corrosion Cracking in Aluminum Alloys," Report of NRL Progress, April 1968, pp. 25-27

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

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

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

42. 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

43. B. F. Brown, "The Fracture Mechanics of Stress-Corrosion Cracking," submitted to Metallurgical Reviews

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

1. A. H. Roebuck and J. V. Luhan, "Anodic Corrosion Characteristics of Aluminum 7075 and 7178," Corrosion, Vol. 23, No. 9, September 1967, pp. 268-275

High-strength alloys 7075 and 7178 are widely used now in the -T6 tempers by the aerospace industry. Several more corrosion-resistant tempers have been developed recently: 7075-T73 (stress corrosion resistant) and 7075-T76 and 7178-T76 (exfoliation resistant).

Electrochemical characteristics as determined by "dynamic" (current versus potential) and "static" (current versus time) tests were found to correlate well with their performance in accelerated corrosion and natural environment marine tests. Attack on the -T6 temper was found to be localized in nature, while that on the resistant tempers (-T76 and -T73) was general, showing crystallographic form. The -T6 tempers polarized more rapidly and were less active than the -T76 or -T73 tempers. Anodic control of the corrosion process is postulated to be more important in 7075 than in the more highly alloyed 7178; the latter showing mixed anodic-cathodic control.

2. E. D. Verink, Jr., "Simplified Procedure for Constructing Pourbaix Diagrams," Corrosion, Vol. 23, No. 12, December 1967, pp. 371-373

A simplified procedure for constructing Pourbaix diagrams is presented with several examples relating to the iron system.

3. W. D. France, Jr. and N. D. Greene, "Predicting the Intergranular Corrosion of Austenitic Stainless Steels," Corrosion Science, Vol. 8, No. 1, January 1968, pp. 9-18

The precise environmental conditions necessary for the intergranular corrosion of austenitic stainless steels have been determined by potentiostatic methods. Intergranular corrosion of sensitized 18 Cr-8 Ni stainless steel only occurs in limited potential regions. These results have been used to develop a new method for rapidly predicting the intergranular corrosion tendencies of the steels in various sulphuric acid environments. It is also shown that sensitized stainless steels may be used in many media without the occurrence of intergranular attack.

4. R. F. Steigerwald, "Electrochemistry of Corrosion," Corrosion, Vol. 24, No. 1, January 1968, pp. 1-10

Principles involved in analyzing a corrosion situation according to electrochemical methods are described. The basic formulas of reactions are given, together with an explanation of their implications and use. The commonly accepted theories of inhibition and passivation are discussed in electrochemical terms.

5. J. S. Armijo, "Intergranular Corrosion of Nonsensitized Austenitic Stainless Steels," Corrosion, Vol. 24, No. 1, January 1968, pp. 24-30

The effects of alloying additions on the intergranular corrosion of nonsensitized austenitic alloys in boiling nitric acid-dichromate solutions have been determined. Controlled additions of C, N, O, Mn, S, Si and P to a high purity 14% Cr-14% Ni-bal Fe alloy and subsequent corrosion tests in boiling 5 N HNO_3-0.46 N Cr^{+6} solutions have shown that only Si and P promote severe intergranular corrosion susceptibility of nonsensitized alloys. Elimination of Si and P from austenitic alloys of otherwise commercial purity decreases susceptibility to intergranular attack by a factor of six to eight.

6. J. A. Davis and R. W. Staehle, "Local Dissolution Phenomena Occurring on Iron-Chromium-Nickel Alloys: An Electron Microscopic Study," Report No. COO-1319-66, The Ohio State University Research Foundation, 18 January 1968

The role of stress in stress corrosion cracking of iron-chromium-nickel alloys was studied. Stress causes the motion of dislocations that rupture a passive surface film or nickel rich surface. In boiling $MgCl_2$, the unprotected metal exposed by slip is preferentially dissolved. This is probably the first step in the initiation of stress corrosion cracking. If the walls of the microtrench are cathodically polarized by precipitation of a noble constituent, stress corrosion cracking will occur. Otherwise, the microtrench is repassivated and no further attack occurs until another slip event happens.

Preferential dissolution along slip traces as observed by electron microscopy is not a criterion for stress corrosion cracking. Preferential dissolution along slip traces occurs in alloys that do not stress corrode and in environments that do not cause stress corrosion cracking.

Crystallographic pitting was observed on several alloys exposed to boiling $MgCl_2$. The formation of crystallographic pits is believed to result from the adsorption of impurity atoms at kink sites with the result that the rate of lateral dissolution is restricted.

7. R. S. Treseder and T. M. Swanson, "Factors in Sulfide Corrosion Cracking of High Strength Steels," Corrosion, Vol. 24, No. 2, February 1968, pp. 31-37

Results of laboratory sulfide corrosion cracking tests on commercial steel alloys are presented. Emphasis is placed on effects of environmental factors, alloy composition and metallurgical variables. Environmental factors studied include pH in the range of 2 to 5, H_2S partial pressures in the range 0.001 to 1.0 atmosphere and addition of sodium chloride. Twelve percent chromium stainless steels and low alloy steels containing more than 1 percent nickel, were found to have lower resistance to cracking at the same hardness level than low alloy steels normally used for oil field equipment. Plastic deformation of low alloy steels by cold rolling decreased the resistance to cracking.

8. J. D. Boyd, F. H. Haynie, W. K. Boyd, R. A. Wood, D. N. Williams, and R. I. Jaffee, "The Effect of Composition on the Mechanism of Stress-Corrosion Cracking of Titanium Alloys in N_2O_4, and Aqueous and Hot-Salt Environments," Contract No. NASr-100(09), Battelle Memorial Institute, 29 February 1968

A series of α and α-β titanium alloys have been heat treated to produce comparable microstructures and evaluated for susceptibility to stress-corrosion cracking in an aqueous environment. The aluminum content appears to be the most critical compositional variable in determining susceptibility. The effect of β-stabilizing content is being investigated. Room-temperature tensile data and strain-rate-sensitivity parameters for all the α and α-β alloys have also been obtained. Preliminary creep tests have been conducted to determine suitable stress levels for the hot-salt stress-corrosion experiments.

Work on the stress-corrosion-cracking mechanism has concentrated on determining the effects of dissolved hydrogen on the deformation properties of α-β alloys. It has been found that a total hydrogen content of 800 ppm is required for spontaneous nucleation of hydrides in Ti-8Al-1Mo-1V when the hydrogen is charged at an elevated temperature. However, when Ti-8Al-1Mo-1V is deformed at slow strain rate, thin hydrides form in the active $\{10\bar{1}0\}$ slip planes if the total hydrogen content is in the range 200 to 600 ppm. Calculations show that the hydrogen concentrations and strain rate around a moving stress-corrosion crack are suitable for hydride precipitation.

The electrochemical mechanism of stress-corrosion cracking N_2O_4 and methanol is being investigated by autoradiography and scanning electron microscopy. Autoradiography made by radioactive chlorine ions failed to show a significant adsorption of Cl by titanium during exposure, under stress, to red N_2O_4. Preliminary tests on α and α-β alloys indicate that both Ti-4Al base alloys and Ti-8Al base alloys are susceptible to stress-corrosion cracking in methanol, but the cracking modes are different for the two groups of alloys.

9. H. R. Copson and G. Economy, "Effect of Some Environmental Conditions on Stress Corrosion Behavior of Ni-Cr-Fe Alloys in Pressurized Water," Corrosion, Vol. 24, No. 3, March 1968, pp. 55-65

Stress corrosion tests have been run in pressurized water at 600 F (316 C) using double U-bends and double bent beam specimens. The tests were conducted in autoclaves for up to 3000 hours. The composition of the gas phase above the water and the pH were controlled. The materials tested were commercial heats of Inconel 600, Inconel 625, Incoloy 800 and stainless steel Types 304, 304L and 347; some Inconel alloy 600 weldments; and some experimental laboratory compositions. Several heat treatments were included.

10. J. A. S. Green and R. N. Parkins, "Electrochemical Properties of Ferrite and Cementite in Relation to Stress Corrosion of Mild Steels in Nitrate Solutions," Corrosion, Vol. 24, No. 3, March 1968, pp. 66-69

Polarization studies were carried out both at an iron electrode and an iron electrode having a surface layer of cementite. Anodic and cathodic polarization curves were compared in nitrate and chloride solutions and the effect of temperature and the addition of acid was examined also. The Fe_3C electrode was found to undergo relatively little cathodic polarization at low current densities and the cementite was thought to be acting as an efficient site for cathodic discharge during the corrosion reaction.

11. G. Sanderson and J. C. Scully, "Stress Corrosion of Titanium Alloys in Aqueous Magnesium Chloride Solution at 154 C," Corrosion, Vol. 24, No. 3, March 1968, pp. 75-82

Titanium alloys have been found susceptible to slow intergranular stress corrosion cracking in $MgCl_2$ solutions boiling at 154 C (309 F). Titanium metal suffers from pitting but not from cracking in the same solution. Experiments on Ti-Al alloys have shown that as aluminium is added there is a transition from pits linked by wide fissures to narrow cracking. The effect of chemical polishing of specimens, which creates a surface layer of hydride phase, is to change the mode of cracking in the richer alloys from predominantly intergranular to predominantly transgranular. This is explained by the formation of reactive dislocations in these alloys particularly at the hydride/matrix interfaces where corrosion attack is initiated. Formation of a hydride phase at the bases of pits during corrosion also will create reactive interfaces. Intergranular cracking arises from segregation to the grain boundaries of solute and possibly impurity atoms.

12. A. J. Sedriks, J. A. S. Green and P. W. Slattery, "Stress-Corrosion Cracking of Titanium and Ti-Al Alloys in Methanol-Iodine Solutions," RIAS, Special Technical Report No. 1, Contract No. DAAG46-67-C-0138(X), Martin Marietta Corporation, March 1968

Studies of the mechanical behavior of unalloyed titanium in methanol-halogen solutions have led to the suggestion that stress-corrosion cracking (SCC) in these environments occurs by localized anodic dissolution at the crack tip. The validity and generality of this model for SCC has been examined by means of comparative studies of the corrosion characteristics and susceptibility to SCC of pure titanium and Ti-Al binary alloys in methanol-iodine solutions.

Evidence is presented which indicates that two distinct SCC mechanisms may be operative, namely (i) stress accelerated intergranular corrosion involving dissolution of metal at a crack tip, and (ii) a transgranular cracking process which has the characteristics of mechanical failure. The characteristics of SCC failures of pure titanium and the Ti-2.1 w/o Al alloy appear to be consistent with the dissolution model. In the higher alloys (> 5 w/o Al), however, dissolution appears to be responsible only for the crack initiation stage, propagation involving transgranular cracking. Stress-corrosion failure in the higher alloys may therefore be prevented by inhibiting the initiation process via cathodic polarization or the introduction of passivators (i.e. water) into the testing environment.

13. J. C. Griess, Jr., "Crevice Corrosion of Titanium in Aqueous Salt Solutions," Corrosion, Vol. 24, No. 4, April 1968, pp. 96-109

Crevice corrosion of titanium in high temperature sodium chloride solutions was investigated. Corrosion occurred only in very restricted crevices and attack was greater the higher the salt concentration. It was shown that crevice corrosion occurs because of the development of a low (~ 1) pH in the solution within the crevice and is not specific to chloride solutions. Crevice attack was demonstrated in iodide, bromide and sulfate solutions.

An electrochemical polarization technique was used to determine the effect of temperature and hydrogen and chloride ion concentrations on the corrosion of titanium and to determine the corrosion characteristics of several titanium alloys. Results indicate that titanium alloys containing sufficient molybdenum, nickel, or palladium are more resistant to nonoxidizing acid solutions than commercially pure titanium and, therefore, should be more resistant to crevice corrosion.

14. J. J. DeLuccia, I. S. Shaffer, "Evaluation and Comparison of the Corrosion Susceptibilities of 7178 Aluminum Plate Material of Various Tempers," Report No. NADC-MA-6716, 16 April 1968

Plate material of 7178 aluminum alloy in the -T651 and -T7651 tempers was evaluated for resistance to exfoliation and stress corrosion. Stress corrosion susceptibility was determined using tuning fork specimens stressed in the short transverse direction and exposed to alternate immersion in 3-1/2% NaCl solution. Susceptibility to intergranular and exfoliation corrosion was determined by exposure in both acetic acid salt spray and NaCl-SO_2 environments. The -T651 temper was found to be acutely susceptible to intergranular corrosion and hence exfoliation and stress corrosion cracking. The -T7651 temper is less susceptible to intergranular attack and more resistant to exfoliation and stress corrosion cracking than the -T651 temper.

D. DIARY OF EVENTS

A Structures and Materials Forum was held at the Commercial Airplane Division of The Boeing Company on December 18 and 19, 1967. The structure, objectives, and progress of the ARPA Coupling Program on Corrosion were presented to an audience of educators selected from the universities of North America.

An ARPA Seminar on Physical Metallurgy and Stress-Corrosion Cracking of Titanium Alloys was conducted at the Boeing Scientific Research Laboratories on February 12 and 13, 1968 in conjunction with the ARPA winter executive committee meeting. The program included presentations on processing, usage, joining and phase transformations in titanium alloys. A short tour of the production facilities of the Commercial Airplane Division was arranged for students, staff and visitors attending the meeting.

On March 26, 1968, Professor Marcel Pourbaix of CEBELCOR and The Free University of Brussels, Belgium, presented a seminar at the Naval Research Laboratory on the Ti-H Potential pH Diagram.

Dr. J. A. Feeney participated in a Graduate Seminar on Development Research in Materials at Stanford University on April 5, 1968. He presented some of the research conducted as part of Boeing's ARPA Coupling Program and discussed the overall objectives of the program.

Dr. D. E. Piper presented a preliminary report on stress-corrosion testing techniques to the Working Party on Stress Corrosion of the Structures and Materials Panel of AGARD in Lisbon, Portugal, on April 2, 1968. Dr. Piper is Coordinator to the Working Party.

The Annual Review meeting of the ARPA Coupling Program on Stress-Corrosion Cracking was held at the Georgia Institute of Technology in Atlanta on May 14, 1968. Presentations were made by each coupling partner covering the whole program in a general way and recent progress more specifically.

In connection with the Annual Review Meeting Symposium on Field Ion Microscopy in Physical Metallurgy and Corrosion was held on May 15-17, 1968 in Atlanta, Georgia. All the principal research workers in this field were in attendance.

An executive meeting was held at the Naval Research Laboratory in Washington, D. C. on June 14, 1968, where program plans were discussed and evaluated.

A one-day meeting - "Discussion on Stress-Corrosion Cracking of High Strength Aluminum Alloys" - was held at Lehigh University, Bethlehem, Pennsylvania, on June 20, 1968. The meeting brought together research workers both within and outside the ARPA program for an informal and frank discussion of recent research activities in the field of stress corrosion of aluminum.

Mr. R. A. Davis has assumed the duties of project director for the ARPA program at The Boeing Company. Dr. Henry Leidheiser, Jr., Director, Center for Surface and Coatings Research, will direct the ARPA program at Lehigh University.

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13. ABSTRACT

This report contains a compilation of abstracts from recently published reports and journal articles generated under the ARPA Coupling Program on Stress-Corrosion Cracking, ARPA Order 878. The abstracted reports are from work done at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory. Selected abstracts of articles from outside the ARPA program in the field of stress-corrosion cracking and a diary of events are also included.

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