UNCLASSIFIED

AD NUMBER

AD844193

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; NOV 1969. Other requests shall be referred to Air Force Materials Lab., Attn: MAAM, Wright-Patterson AFB, OH 45433.

AUTHORITY

Air Force Materials Lab ltr dtd 2 Mar 1972

THIS PAGE IS UNCLASSIFIED

AD 844193

DMIC **review** OF RECENT DEVELOPMENTS

DDC
DEC 5 1968

Corrosion and Compatibility

W. E. Berry November 29, 1968

#2 AFML(MAAM)

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFML(MAAM) WPAFB Ohio. 45433

GENERAL

Cavitation damage studies on Type 316 stainless steel, nickel 270 and 6061-T6 aluminum have been described by NASA Lewis as part of an ASTM round-robin test program.(1) A magnetostrictive transducer was used to vibrate specimens at a frequency of 25,000 hertz with a total displacement amplitude of 1.75 mils in distilled water at 75 F and 1 atmosphere pressure. The order of relative resistance of the materials to cavitation was Type 316 stainless steel > nickel 270 > 6061-T6 aluminum. The volume loss and mean depth of penetration of the 6061-T6 aluminum alloy was 45 times that of the Type 316 stainless steel after 160 minutes' exposure.

Abstracts of recent reports and papers relating to stress corrosion and generated on the ARPA Coupling Program have been listed.(2) Also identified are some related reports published by other agencies, and reports issued to date by ARPA.

Stress-corrosion-cracking studies have been included in an extensive engineering evaluation of newly developed structural materials conducted at Battelle/Columbus.(3) Seven specimens of each alloy were stressed to 80 percent of yield strength as four-point loaded bent beams, and were exposed 1000 hours in the 3.5 percent NaCl solution alternate immersion test. AFC 77, high-strength stainless steel (Fe-14Cr-14Co-5Mo-0.15C) specimens with 700 F temper failed by stress-corrosion cracking in 12 to 38 days and with 1100 F temper in 3 to 5 days. Specimens of 2021-T8E31 aluminum alloy cracked in 1 to 5 days. No cracking of TD Nickel, HP 9-4-25 (Fe-9Ni-4Co-0.25C) plate and forging, HP9-4-45 plate and forging, 62Be-38Al alloy, or 7039-T6151 aluminum plate was observed on 1000 hour's exposure.

The beneficial effects of shot peening on minimizing stress-corrosion cracking are discussed in a paper by Metal Improvement Company.(4) Examples of failures and the use of shot peening are discussed for aluminum aircraft components, high-strength steels, and titanium pressure tanks. Also discussed are process control means of evaluating shot-peening intensity.

ALUMINUM

The effect of chelating agents on passivating aluminum and increasing the adhesion of paint films has been studied at American Cyanamid.(5) Three agents appeared to be promising: bis (hydroxymethyl) phosphinic acid, acetylacetone, and 8-hydroxyquinoline. High-purity-aluminum electrodes treated with these chelating agents exhibited more noble critical corrosion potentials than those for untreated electrodes. Salt-spray tests on treated 1100-0 and Alclad 7075 alloy panels confirmed the enhanced corrosion resistance afforded by these treatments, as evidenced by fair-to-excellent resistance and the absence of pitting, after 1000 hours' exposure. Control specimens were in poor condition after 500 hours in the salt spray.

The Naval Research Laboratory has made a failure analysis of axial cracking found at the ends of several swaged 7075-T6 aluminum alloy support struts on the Apollo lunar-landing module during construction.(6) Metallography and electron microscopy revealed intergranular fractures in a short-transverse-type grain orientation indicating that failure occurred by a stress-corrosion mechanism. No mention was made as to the probable corrodent.

Boeing has developed a high-strength aluminum alloy with a short-transverse stress-corrosion threshold level greater than 25,000 psi, a yield strength of 70,000 psi, and fatigue and fracture toughness properties comparable with those of commercial alloys (7075-T6 and 7079-T6).(7) The nominal composition of the alloy is Al-6.4Zn-2.55Mg-1.0 Cu, with an allowable chemistry range of 5.9 to 6.9 Zn, 2.2 to 2.9Mg, 0.7 to 1.5Cu, 0.10 to 0.25Zr, 0.05 to 0.15Mn, 0.05 max Cr, 0.10 max Ti, 0.20 max Fe, and 0.20 max Si. Modified U-bends of the alloys were evaluated on the basis of 90 days' exposure under alternate immersion in 3.5 percent NaCl solution.

The stress-corrosion cracking susceptibility of electron-beam welded 7039-T61 aluminum alloy has been studied by Northrop/Ventura.(8) As welded, welded and aged, and welded and re-heat treated specimens were not susceptible to stress corrosion when stressed up to 100 percent of the 0.02 percent offset yield strength and exposed 500 hours (500 cycles) to alternate immersion in synthetic seawater. As-welded specimens pitted to a depth of 12 mils in the heat-affected zone, which resulted in a 26 percent loss in tensile strength in the longitudinal weld and 14 percent in the transverse weld specimens. Post-weld aged (-T61) specimens were pitted to a depth of 6 mils, but experienced no loss in strength.

The results of the second year's work on stress-corrosion-crack initiation and development in thick plates of 2219-T37, 7075-T6, 7079-T6, and 7039-T6 aluminum alloys has been reported by Alcoa.(9) Most of the tests were conducted in NaCl-$AlCl_3$ solution at pH 1. Cracks in 7075-T6, 7079-T6 and 7039-T6 alloys always initiated on "former" grain boundaries perpendicular to the stress and, in many cases, at boundaries between grains having considerably different orientation. Cracks propagated along these same paths following the straightest possible path perpendicular to the stress. Stress level affected quantity and propagation rate of cracks but had no effect on crack-initiation sites or propagation paths. There were no indications that dislocations, constituent particles, dispersoid particles, or precipitate particles had any direct effect on crack initiation.

The second annual report on the mechanism of stress corrosion of aluminum alloys has been issued by TYCO Laboratories.(10) Experiments were carried out in 1M NaCl buffered to pH 4.7 at 30 C on commercial alloys 7075 and 2219 and on pure-alloy laboratory heats. Experimentation on nonstressed specimens revealed grain boundary attack of Al-4Cu alloy in tempers both susceptible and nonsusceptible to stress corrosion, and failed to produce intergranular attack in Al-7.5Zn-2.4Mg, thus indicating that a preexisting corrodible path is not a prerequisite to cracking. Stress was shown necessary to be continuously applied to produce failure in 2219 alloy, but stress-corrosion effects were shown to account for only 20 percent of the normal life-to-failure in 7075 alloy. True corrosion accounted for the other 80 percent.

STEELS AND STAINLESS STEELS

The fatigue and stress-cracking properties of butt-welded HY-130 steel in air and in seawater are being studied at The Naval Applied Science Laboratory.(11) The results of fatigue tests of 1-inch-thick plates after the weld reinforcement was ground off under a cyclical load of zero to maximum flexure are given as follows:

	Fatigue Life, cycle	
Maximum Stress, psi	In Air	In Seawater
100,000	72,000	43,000
130,000	31,000	21,000

Grinding off the weld reinforcement improved the steel's fatigue life by 150 percent. Specimens containing fatigue cracks to a depth of up to 0.5 inch exhibited high resistance to stress-corrosion cracking in tests conducted at 100,000 and 130,000 psi stress loadings.

Straining-electrode experiments on iron-chromium-nickel alloys have been conducted at The Ohio State University to test the hypothesis that the tip of an advancing stress-corrosion crack is dynamically straining, and thereby produces sufficiently high current densities to propagate the crack by electrochemical dissolution.(12) At strain rates of up to 6 percent per minute, very little change was observed in the current density in the active region during straining. In the lower range of passive potentials, the current density of the straining electrode was not appreciably increased over that of a static electrode. At the critical potential for current increase in the passive region, the current density of the straining electrode was greatly increased over that of the static electrode. This potential is less than the pitting potential. The largest differences between the critical and pitting potentials were observed for H_2SO_4 and H_2SO_4 + KCl solutions while the smallest differences were observed for H_2SO_4 + KBr or KI. The latter two are also less prone to produce stress-corrosion cracking. Nickel in H_2SO_4 + KCl solutions did not show a significant difference in current density between the straining and static electrodes over the whole range of potentials in the passive range.

NICKEL- AND COBALT-BASE ALLOYS

Oxidation

Oxidation studies of Hastelloy X for periods of up to 12,500 hours in air at temperatures from 1200 to 2000 F have been made by Aerojet-General.(13) The primary mode of oxidation at 1600 F and lower temperatures was by thin intergranular penetration. At 1750 F and higher temperatures, internal oxidation occurred as a uniform band of small oxide particles distributed intergranularly beneath the metal-oxide interface. The oxidation produced a duplex oxide consisting of a Cr_2O_3 inner layer and a $MnCr_2O_4$ spinel outer layer. The oxidation resistance of the Hastelloy X increased as the spinel/Cr_2O_3 ratio increased and the amount of spinel formed increased with increasing manganese content in the alloy.

The oxidation of Hastelloy N is being studied at Oak Ridge.(14) The addition of silicon to the alloy markedly improved its oxidation resistance, particularly at 982 C (1800 F). There, oxidation rates decreased linearly from about 500 mg/cm^2-1000 hr at less than 0.05 percent silicon to about 15 mg/cm^2-1000 hr at 0.6 percent silicon. At 760 C, (1400 F), all rates were low at silicon contents greater than 0.05 percent, and ran less than 10mg/cm^2-1000 hr. Titanium in the range of 0 to 1 percent had little effect on the oxidation behavior of the Hastelloy N.

The oxidation behavior of nickel- and cobalt-base alloys is being studied at Savannah River in connection with encapsulating ^{60}Co heat sources.(15) Specimen performance was evaluated on total penetration which included surface-scale thickness (including that which spalled) and depth of intergranular penetration and alloy depletion. After 9400 to 10,000 hours' exposure at 1000 C (1832 F), TD Nickel-Chromium was the most resistant material, with a total affected zone of 2.4 mils. Inconel 600, Tophet C, Hastelloy C, GE2541, Haynes 25, and Hastelloy X had affected zones of 8 to 12 mils and were considered acceptable.

NASA Lewis has studied the oxidation behavior of L-605 superalloy (Co-20Cr-10Ni-15W-2Fe) in the 1000 to 1200 C (1830 to 2190 F) temperature range.(16) Both oxidation resistance and ductility were optimized by limiting the silicon and manganese contents of the alloy to the ranges of 0.1 to 0.4 and 1.4 to 1.65 percent, respectively. Alloys within this composition range exhibited parabolic reaction rates and formed scale containing chromium oxide and a spinel phase.

The oxidation behavior of Co-25Cr and Co-35 Cr alloys has been reported by Battelle/Columbus.(17) Reaction rates were parabolic in the temperature range of 900 to 1300 C (1650 to 2370 F). For the Co-25Cr alloy, the parabolic rates at high oxygen pressures(greater than 100 torr) were about two orders of magnitude higher than those at low oxygen pressure (less than 10 torr). The oxidation rates of the Co-35Cr alloy were independent of oxygen pressure over the range of 0.1 to 760 torr and were comparable with those obtained on the Co-25Cr alloy at low oxygen pressures. The oxide scale on the Co-25Cr alloy at high oxygen pressures consisted of an outer layer of CoO and an inner layer of $CoCr_2O_4$ and some CoO. The oxide scale on the Co-25Cr alloy at low oxygen pressures and on the Co-35Cr alloy at all pressures was mainly a single layer of $CoCr_2O_4$ with some Cr_2O_3. It was postualated that the initial oxidation rate was controlled by cobalt-cation diffusion through CoO. The diffusion of cobalt and chromium through the spinel then controlled the oxidation when the spinel grew to appreciable thickness.

Stress Corrosion

The cause of cracking failures of K-Monel bolt studs on autoclaves and pumps has been investigated at Petten, Holland.(18) The cracks were intergranular. Analyses indicated an increase in sulfur and copper content at the grain boundaries. The source of the sulfur was the fatty ingredient in the paste of a high-temperature lubricant that decomposed to liberate sulfides or sulfur at the vessel operating temperatures of 360 to 400 C (680 to 750 F).

TITANIUM ALLOYS

Oxidation

Experimental programs concerned with the oxidation of titanium and its alloys have been reviewed in a recent memorandum issued by DMIC; the results are compared with those predicted by theory.(19) Fifteen binary-alloy systems as well as a few ternary systems and commercial alloys were covered. The Wagner-Hauffe theory was used as the primary basis for comparison. Also included is a section on the effects of oxygen and nitrogen contamination on the mechanical properties of titanium and its alloys.

Stress-Corrosion Cracking

The stress-corrosion-cracking behavior of welded and unwelded titanium alloys in the deep ocean has been described in a report recently released by the Naval Civil Engineering Laboratory.(20) Exposure times ranged from 180 days at the surface to 402 days at 2500 feet, and 751 days at 5000 feet. Stressed specimens included welded and unwelded bent beams stressed at 35, 50, and 75 percent of yield strength, welded 9-inch-diameter rings stressed at 50 percent of yield strength, and 3-inch-diameter weld-ring deposits on flat plate. Alloys studied included Ti-0.15Pd, Ti-5Al-2.5Sn, Ti-7Al-2Cb-1Ta, Ti-6Al-4V, Ti-13V-11Cr-3Al, and unalloyed titanium. The only stress-corrosion failures observed were in the Ti-13V-11Cr-3Al alloy in the unrelieved butt-welded bent beams at the 75 percent stress level exposed at the surface and in the unrelieved 3-inch-diameter circular weld deposit at all depths studied.

McDonnell Douglas is studying the mechanism of stress-corrosion cracking of Ti-8Al-1Mo-1V alloy Precracked notched specimens are being exposed in 3 percent NaCl solution at ambient temperatures.(21) Martensitic structures containing 25 to 100 ppm hydrogen were immune to stress-corrosion cracking. The susceptibility to cracking of alpha-beta structures was dependent on the strain rate. Microautoradiography failed to detect hydrogen (tritium) diffusion into the substrate metal from the fractured face of specimens cracked in tritiated salt solutions thus suggesting that hydrogen embrittlement was not associated with stress-corrosion cracking. The fact that Ti-8Al alloy cracked while a Ti-4Al did not crack was related to the effect of aluminum content which lowered the stacking-fault energy of dislocations.

On the other hand, cracking of titanium alloys in methanol has been attributed to hydrogen embrittlement under certain conditions in research conducted in England.(22) The addition of HCl to methanol greatly shortened the failure time. It also caused a slow intergranular embrittlement that did not require any applied stress, and resulted in a total loss of strength in all alpha-phase alloys. The slow embrittlement was not found in alpha-plus-beta Ti-6Al-4V alloy. Two operative processes were suggested: transgranular hydride formation and selective dissolution from alpha-grain boundaries. The former was believed to be able to occur in any environment that discharges hydrogen in reaction with titanium and that also causes breakdown of the protective film on titanium.

The stress-corrosion behavior of Ti-6Al-4V in methanol-bromine has been investigated at Tyco Laboratories.(23) Results revealed that time to stress-corrosion cracking decreased with increasing aging time of the solution and suggested that no failures would occur in fresh (nonaged) solution. Postulated chemical reactions during aging were the formation of CO and HBr by reactions between the primary components plus further reaction of the HBr with methanol to form methyl bromide. Preexposure to the corrodent prior to applying the stress indicated that only during the last 40 percent of the normal stress-corrosion life is stress critical in causing failure.

Long-term studies on the hot-salt stress-corrosion cracking of Ti-8Al-1Mo-1V alloy have been conducted at Langley Research Center.(24) Self-stressed specimens at stress loadings of 15,000, 25,000, and 50,000 psi were dipped in 3.4 percent NaCl solution and then were exposed up to 20,000 hours at 400 to 600 F. At the 50,000 psi stress level, stress-corrosion cracking initiated after 17, 200, 1600, and 2500 hours at 600, 550, 500, and 450F, respectively. No cracking occurred after 20,000 hours' exposure at 400 F at any of the three stress levels.

MOLYBDENUM ALLOYS

The corrosion behavior of TZM (Mo-0.5Ti-0.1 Zr) and Mo-30W has been studied by the Bureau of Mines.(25) Data were obtained for a number of acid, alkali, and salt solutions. Included in the latter were results for 30-day immersion and salt-spray tests in substitute ocean water as indicated below.

Type Test	Temperature, C	Temperature, F	Penetration Rate, mils/yr Mo	Penetration Rate, mils/yr TZM	Penetration Rate, mils/yr Mo-30W	Penetration Rate, mils/yr W
Immersion	35	95	0.3	1.7	1.6	0.2
Immersion	60	140	2.1	1.7	1.4	0.3
Salt spray	60	140	0.4	1.1	0.5	0.1

Galvanic-couple tests in substitute ocean water did not produce corrosion of either member when the solution was deaerated with helium. In aerated solutions, aluminum and 4130 steel corroded sacrificially and reduced the corrosion of the TZM and Mo-30W alloys. However, both members of the couple exhibited higher corrosion rates in alloy-to-copper couples. This was explained on the basis that TZM and Mo-30W were at first the anodic members of the couples, and then copper became the anodic member.

REFERENCES

(1) Young, S. G., "Cavitation Damage of Stainless Steel, Nickel, and an Aluminum Alloy in Water for ASTM Round Robin Tests", Report TM X-1670, NASA Lewis Research Center, Cleveland, O., (October 1968).

(2) Preliminary information from ARPA and the Office of Naval Research on U. S. Navy Contracts Nonr-610(09), Nonr-760(31), N00014-66-C0365, and Nonr-991(15).

(3) Deel, O. L., and Hyler, W. S., "Engineering Data on Newly Developed Structural Materials", Final Report AFML-TR-67-418, Columbus Laboratories, Battelle Memorial Institute, Columbus, O., Contract AF 33(615)-2494 (April 1968).

(4) Milo, J. H., "Shot Peening Prevents Stress Cracking in Aircraft Equipment", Materials Protection, 7 (9), 39-42 (September 1968).

(5) Rauch, F. C., Liciw, F. W., and Murray, M. A., "Passivation of Metal Aircraft Surfaces", Final Report, American Cyanamid Company, Stamford, Conn., Contract N00019-67-C-0499 (July 1968).

(6) Dahlberg, E. P., "Analysis of Cracking in Swaged 7075-T6 Aluminum Alloy Tubing", Final Report, NRL Memorandum Report 1894, Naval Research Laboratory, Washington, D. C., (June 1968).

(7) McMillan, J. C., and Hyatt, M. V., "Development of High-Strength Aluminum Alloys with Improved Stress-Corrosion Resistance", Report AFML-TR-68-148, The Boeing Company, Kenton, Wash., Contract AF 33(615)-3697 (June 1968).

(8) Williams, L., Bleecker, E., and Greenberg, S., "Stress Corrosion Evaluation of Electron Beam Welded Aluminum Alloy 7039", Report NVR-6217, Volume II, Ventura Division, Northrop Corporation, Newbury Park, Calif., (June 1968).

(9) Hunter, M. S., and Fricke, Jr., W. G., "Study of Crack-Initiation Phenomena Associated with Stress Corrosion of Aluminum Alloys", Second Annual Report, Alcoa Research Laboratories, New Kensington, Penn., Contract NAS 8-20396 (July 15, 1968).

(10) Brummer, S. B., et al, "Study of the General Mechanism of Stress Corrosion of Aluminum Alloys and Development of Techniques for Its Detection", Second Annual Summary Report (June 2, 1967-June 1, 1968), Tyco Laboratories, Inc., Waltham, Mass., Contract NAS 8-20297.

(11) Preliminary information from Materials Sciences Division, U. S. Naval Applied Science Laboratory, Brooklyn, N. Y.

(12) Murata, T., and Staehle, R. W., "The Effect of Dynamic Straining on The Anodic Dissolution of Type 304L Stainless Steel and Nickel", Report COO-1319-71, The Ohio State University Research Foundation, Columbus, O., Contract AT(11-1)-1319 (June 3, 1968).

(13) Clarke, Jr., W. L., and Titus, G. W., "Evaluation Study of Hastelloy X as a Nuclear Cladding". Final Report AGN-8289 Nuclear Division, Aerojet-General Corp., San Ramon, Calif., Contract AT(04-3)-368 (June 1968).

(14) Rosenthal, M. W., Briggs, R.B., and Kasten, P. R., "Molten-Salt Reactor Program Semi Annual Progress Report for Period Ending February 29, 1968," USAEC Report ORNL-4254, Oak Ridge National Laboratory, Oak Ridge, Tenn., Contract W-7405-eng-26 (August 1968).

(15) Preliminary information from Savannah River Laboratory, E. I. duPont de Nemours & Company, Inc., Aiken, S. C., on USAEC Contract AT(07-2)-1.

(16) Wolf, J. S., and Sandrock, G.D., "Some Observations Concerning the Oxidation of the Cobalt-Base Superalloy L-605 (HS-25)", Report TN D-4715, NASA Lewis Research Center, Cleveland, O., Nasa Grant NGR-36-002-070 (June 4, 1968).

(17) Kofstad, P., and Hed, A. Z., "Oxidation Behavior of Co-25Cr and Co-35Cr Alloys", Report NASA CR-72420, Columbus Laboratories, Battelle Memorial Institute, Columbus, O., NASA Grant NGR-36-002-070 (June 4, 1968).

(18) Van der Linde, A., "Sulfide Intergranular Stress-Corrosion Cracking of K-Monel Studs That Failed During Service in High Temperature", Report RCN-91, Reactor Centrum Nederland, Petten, Netherlands (November 1967).

(19) Ferguson, J. M., "The Oxidation and Contamination of Titanium and Its Alloys", DMIC Memorandum 238, Defense Metals Information Center, Battelle Memorial Institute, Columbus, O., Contract F33615-68-C-1325 (July 1, 1968).

(20) Reinhart, F. M., "Corrosion of Materials in Hydrospace. Part III-Titanium and Titanium Alloys", Technical Note N-921 (AD 821257), Naval Civil Engineering Laboratory, Port Hueneme, Calif., (August 1967).

(21) Mackay, T. L., and Tiner, N. A., "Stress-Corrosion Cracking of Titanium Alloys at Ambient Temperature in Aqueous Solutions", Report SM-49105-F2, Astropower Laboratory, McDonnell-Douglas Corporation, Newport Beach, Calif., Contract NAS 7-488(July 1968).

(22) Sanderson, G., and Scully, J. C., "The Stress Corrosion of Ti Alloys in Methanolic Solutions", Corrosion Science, Vol. 8, 541-548 (July 1968).

(23) Cocks, F. H., Russo, J. F., and Brummer, S. B., "The Separation of Corrosion and Stress Effects in Stress Corrosion: Ti-6Al-4V in Bromine-Methanol Solutions", Corrosion, 24 (7), 206-208 (July 1968).

(24) Royster, D. M., "Hot-Salt-Stress-Corrosion Cracking and Its Effect on Tensile Properties of Ti-8Al-1Mo-1V Titanium-Alloy Sheet", Report TN D-4674, Langley Research Center, Langley Station, Hampton, Va. (August 1968).

(25) Ackerman, W. L, Carter, J. P., and Schlain, D., "Corrosion Properties of TZM and Molybdenum-30 Tungsten Alloys", Report of Investigation 7169, Bureau of Mines, U. S. Department of the Interior, Washington, D. C., (1968).

DMIC Reviews of Recent Developments present brief summaries of information which have become available to DMIC in the preceding period (usually 3 months), in each of several categories. DMIC does not intend that these reviews be made a part of the permanent technical literature. Copies of referenced reports are not available from DMIC; most can be obtained from the Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314.

R. W. Endebrock, Editor