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GENERAL

The Army Missile Command has issued a comprehensive report on corrosion prevention and deterioration in electronic components and assemblies.<sup>(1)</sup> The objective of the report is to aid the designer in meeting environmental requirements. It points out dangerous combinations of materials and processes, emphasizes the importance of proper selection of materials, and provides the designer with techniques for the prevention of deterioration.

The first quarterly progress report on the ARPA coupling program on corrosion has been issued.<sup>(2)</sup> Objectives and areas of research are outlined for the various participating agencies. The program will concentrate on the stress-corrosion cracking of high-strength aluminum, steel, and the titanium alloys in nearly neutral aqueous solutions.

Representatives from approximately eight countries, including the U. S. and Canada, took part in the AGARD Structures and Materials Panel Symposium on Stress-Corrosion Cracking of High-Strength Aircraft Metals and Alloys held in Turin, Italy, April 17-20, 1967. The discussions involved the general theory of stress-corrosion cracking as well as the effect of stress level, heat treatment, alloy content, and environment on the stress-corrosion-cracking behavior of high-strength low-alloy steels, high-strength stainless steels, aluminum alloys, and titanium. In addition, each country presented a review of the current research presently being conducted on stress-corrosion cracking.

In general, the French, Italian, German, and English research is concerned primarily with the effect of heat treatment and alloy composition on the stress-corrosion-cracking behavior of high-strength aluminum alloys of the 7075 and 7079 types. A large portion of the research has been concerned with the effect of silver and zirconium additions along with modifications in the chromium and copper contents of the alloys. The substitution of zirconium for chromium plus the use of silver has resulted in alloys having improved resistance to stress-corrosion cracking. However, much of this research has been concerned with sheet materials rather than heavy-section forgings.

The English are also conducting research on titanium-alloy stress-corrosion cracking. Results presented indicate that hydrogen plays a role in the mechanism of stress-corrosion cracking in a number of environments, including methanol and salt water.

CORROSION OF ALUMINUM ALLOYS

The effect of long-term storage of hydrazine in 2014 aluminum tanks on corrosion and subsequent ignition tests has been studied at Jet Propulsion Laboratory.<sup>(3)</sup> Slight pitting to a maximum depth of less than 1.7 mils was observed after 46 months of storage in the open. Although the hydrazine was degraded slightly, it ignited and burned as smoothly with nitrogen tetroxide as did stock hydrazine. Screening tests with N<sub>2</sub>O<sub>4</sub> in 2014 aluminum canisters revealed a slight pitting of less than 0.2 mils after 2 months of exposure.

STRESS-CORROSION CRACKING

The effect of minor alloying additions to 7075 aluminum alloys on their susceptibility to stress-corrosion cracking is being studied by Boeing.<sup>(4)</sup> Of the elements studied (silver, boron, cerium, yttrium, zirconium) only silver reduced susceptibility to cracking. This beneficial effect was attributed to the increased tendency of the silver-bearing alloys to pit.

Fatigue-crack propagation and delayed failure (precracked specimens) of aluminum and titanium alloys in salt solutions and air has been studied by Langley.<sup>(5)</sup> Fatigue-crack-growth rate was faster in seawater than in air by the following ratios: 7075-T6 Al (all stresses), 2:1; 2024-T3 Al (low stress), 1.5:1; (high stress), not much difference; (highest stress), 1:2 (higher in air); Ti-8Al-1Mo-1V (all stresses), 2 or 3:1. The delayed failure strengths of the titanium alloys were lower than their residual static strengths in air, while they were similar with the aluminum alloys.

The stress-corrosion-cracking behavior of 7001-T75 aluminum has been studied at Boeing.<sup>(6)</sup> Alternate immersion tests in 3.5 percent NaCl solution were performed at gross-area stress levels of 20,000, 30,000, and 50,000 psi with steel Taper-Lok and titanium lockbolt fasteners in plain and cold-worked holes in the gage section of flat tensile specimens. Fasteners were installed with clearance and interference fits. At the 50,000 psi level, the 7001-T75 exhibited stress-corrosion-cracking resistance superior to that of 7079-T6, 7079-T62, or 7079-T611. Alloy 7075-T73, also included in the study, cracked because its ultimate tensile strength was exceeded at the 50,000 psi gross loading.

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## CORROSION OF FERROUS ALLOYS

**High-Strength Steels.** The effect of moisture and of repeated loading on the slow crack growth of 4340 steel has been reported by the University of Illinois.<sup>(7)</sup> Center-cracked 0.07-inch-thick sheet specimens were loaded in tension. Crack growth in moist argon was 20 times that found in dry argon at the same cyclic loading.

The effect of explosive forming on the stress-corrosion-cracking susceptibility of several high-strength steels and aluminum alloys has been reported by Martin-Denver.<sup>(8)</sup> Four-point beam-loaded specimens taken from each alloy before and after forming were stressed to 80 percent of the 0.2 percent offset-yield strength and were exposed 200 hours to 3.5 wt% NaCl solution in an alternate immersion test. The stress-corrosion-cracking resistance of D6ac steel and 7039-I62 aluminum was affected adversely by the explosive-forming operation, while that of 12Ni-5Cr-3Mo, HP 9-4-25, and 18 percent nickel maraging steel was unaffected by forming.

The stress-corrosion-cracking behavior of 9Ni-4Co steel has been studied by Douglas.<sup>(9)</sup> Alternate immersion tests in synthetic seawater of tensile-type specimens indicated that HP 9-4-30 (0.30 carbon) martensite was resistant to stress-corrosion-cracking under most surface preparation conditions except those severe treatments that produced untempered martensite. HP 9-4-45 martensite was susceptible to cracking under all conditions studied except shot peening. The more resistant HP 9-4-45 bainite was cracked only when cadmium plated. Pre-cracked specimens of HP 9-4-30 martensite and HP 9-4-45 bainite were susceptible to stress-corrosion cracking in alternate immersion. Although pre-cracked HP 9-4-45 bainite failed in constant immersion, HP 9-4-30 martensite did not. Oxide films formed in air at 400 F increased the stress-corrosion-cracking resistance of all alloys in all conditions tested.

**Stainless Steels.** The effect of cold work on the stress-corrosion-cracking behavior of Types 301, 304, 310, and 321 stainless steels has been studied at the Bureau of Standards.<sup>(10)</sup> Cold reductions ranged to 50 percent. Cracking was not detected in any specimens that were stressed to 90 percent of yield strength and exposed for 452 days in a marine atmosphere. Laboratory studies, using boiling 0.5N NaCl-0.1N NaNO<sub>2</sub> solution, revealed a maximum in the threshold-stress-level curves at 24 percent cold reduction (93,000 psi) for Type 304 stainless steel and at 33 percent cold reduction (113,000 psi) for Type 321 stainless steel. The threshold level for Type 301 stainless continued to increase with increasing cold work to 33 percent (166,000 psi). The Type 310 stainless did not generally crack in this solution. Tests in boiling 42 percent MgCl<sub>2</sub> indicated that the annealed Type 310 stainless is more resistant to cracking than the cold-worked material.

## CORROSION OF NICKEL-BASE ALLOYS

Studies of the sulfidation of superalloys during combustion with salt-contaminated air are continuing at AVCO.<sup>(11)</sup> Reduction of the sulfur content of the fuel (JP-4) from 0.16 to 0.02 percent significantly reduced the amount of sulfidation at salt-to-air ratios of 4 and 8 ppm. The depth of

attack and the threshold temperature (incidence of attack) varied with chromium content. At the 8 ppm salt level, alloys containing less than 14 percent chromium had threshold temperatures equal to or less than 1500 F, and alloys containing more than 15 percent chromium had threshold temperatures equal to or greater than 1500 F.

## CORROSION OF TITANIUM ALLOYS

**Pyrophoric Reactions.** The reaction between five halogenated-hydrocarbon fire-extinguishing agents and titanium in hydrocarbon fires has been studied by the Bureau of Mines.<sup>(12)</sup> Little or no reaction was obtained when the titanium specimens were large and their surfaces were neither porous nor highly irregular. Visible burning was observed with titanium sponge, wire, or turnings equal to, or less than, 0.020 inch in thickness. The 1,2,2-trifluoropentachloropropane (CCl<sub>3</sub>CF<sub>2</sub>CFCl<sub>2</sub>) and dibromodifluoromethane (CBr<sub>2</sub>F<sub>2</sub>) compounds were the most reactive with titanium and bromochloromethane (CH<sub>2</sub>BrCl) was the least reactive.

**Stress-Corrosion Cracking.** The Defense Metals Information Center was host to a seminar on accelerated crack propagation of titanium in various environments that was held at Battelle's Columbus Laboratories on March 6, 1967. Environments discussed included methanol, halogenated hydrocarbons, and chlorine. Publication of a transcript of the meeting is planned.

The Naval Research Laboratory has conducted stress-corrosion tests on remnants of the Ti-6Al-4V Apollo fuel tank that failed during pressure testing with methanol.<sup>(13)</sup> Side-notched, fatigue-pre-cracked specimens were loaded in a cantilever-bend configuration. Cracks propagated in contact with methanol at plane-strain intensities as low as 15,000 psi  $\sqrt{\text{in}}$ . The material was also found to be somewhat susceptible to cracking in distilled water with a crack propagating at a plane-strain-stress intensity of about 30,000 psi  $\sqrt{\text{in}}$ .

MASA has also conducted stress-corrosion studies with Ti-6Al-4V in methanol using virgin metal and remnants from the Apollo fuel-tank failure.<sup>(14)</sup> Results obtained using notched specimens indicate that cathodic protection and additions of greater than 1 percent water will inhibit stress-corrosion cracking in methanol.

Stress-corrosion studies with pre-cracked titanium alloys in distilled water and 3 percent NaCl solution have been continued at Douglas Astro-power.<sup>(15)</sup> It was found that alpha type Ti-5Al-2.5Sn and duplex annealed, alpha-beta type Ti-8Al-1Mo-1V and Ti-6Al-4V alloys exhibited susceptibility to stress-corrosion cracking in the salt solution, whereas, beta type Ti-13V-11Cr-3Al did not. The beta alloys exhibited ductile dimple fracture surfaces in air and salt solutions. Alpha-beta and alpha type alloys exhibited mixtures of ductile dimple and brittle cleavage areas in fracture with the cleavage areas being much larger in stress-corrosion cracking than in air fracturing. In general, the stress-corrosion cracks propagated transgranularly through alpha grains, but followed by cleavage to the alpha-beta phase boundaries. It is believed that the segregation of hydrogen in the beta phase affects this brittle behavior of the beta regions.

The effect of environment, applied potential, and metallurgical structure on the stress-corrosion-cracking behavior of Ti-6Al-4V-Mo alloy has been reported by Boeing.<sup>(16,17)</sup> Tensile tests were conducted with notched specimens in air and in various solvents and salt solutions. Cracking occurred in chlorinated solvents, such as carbon tetrachloride, methylene chloride, and trichloroethylene. Of the many ions investigated, only chloride, bromide, and iodide produced stress-corrosion cracking. It was found that inhibiting ions, such as sulfate or nitrate, overcame the effects of small concentrations of these halides in water or methanol. Crack-propagation velocity was found to increase linearly with applied potential from -900 to +500 mv (SCE) regardless of the halide ion studied.

A final report has been issued by Southwest Research Institute on the effects of commercially available protective coatings on the stress-corrosion properties of Ti-6Al-4V-Mo supersonic-transport skin material.<sup>(18)</sup> The hot-salt tests were conducted at 550 F for durations to 7000 hours. Several coatings prevented stress-corrosion cracking. White-pigmented, catalytically cured silicone was the optimum coating based on the SSI requirement of high IR emissivity on large areas of the outer skin. On areas not subject to IR control, aluminum-modified silicone was probably superior, particularly on engine components exposed to temperatures to 950 F.

A seawater stress-corrosion-resistant titanium alloy has been developed and evaluated as a candidate pressure-hull material by the Marine Engineering Laboratory.<sup>(19)</sup> The alloy, Ti-6Al-2Cu-1Ta-0.8Mo, was resistant to stress-corrosion cracking (precracked cantilever specimen) and to low-cycle and high-cycle corrosion fatigue (notched specimen). Corrosion properties of the weldments were as good as those of the base metal. It was concluded that it is feasible to use this alloy as pressure-hull material of 100,000 psi yield strength in 1-inch and of 96,000 psi yield strength in 2.5-inch thickness.

#### REACTIVE METALS

Aqueous Corrosion. The effects of water vapor/hydrogen environments on the mechanical properties of columbium and B-66 columbium alloy have been reported by Rocketdyne.<sup>(20)</sup> Test environments were argon and H<sub>2</sub>O/H<sub>2</sub> in the ratios of 3 to 1 and 1 to 1. A minimum ductility was observed at 1050 F for the unalloyed columbium upon exposure to H<sub>2</sub>O/H<sub>2</sub>, while the B-66 alloy exhibited considerable embrittlement at about 1500 F. A hydride phase was found in the unalloyed columbium exposed at 1050 F, and it was concluded that the source of the hydrogen is the molecular hydrogen in the environment. On the other hand, the hydrogen absorbed by the B-66 alloy was believed to result from the reaction of the alloy with water vapor.

The corrosion behavior of beryllium-aluminum alloys in flowing water at 163 C (325F) has been reported by Phillips Petroleum.<sup>(21)</sup> Weight loss results for the two alloys were approximately 450 mg/dm<sup>2</sup> after 1300-hr exposure. Metallographic examination revealed selective removal of aluminum to a depth of ~ 1.5 mils in the 38 wt % aluminum alloy and to a depth of about 2 mils in the 48 wt % alloy.

Oxidation. The gettering rate for oxygen, of columbium, zirconium, and tantalum at low pressures and high temperatures has been determined at G.E.'s Missile and Space Division.<sup>(22)</sup> Exposure conditions ranged from 10<sup>-5</sup> to 5 x 10<sup>-8</sup> torr oxygen and 885 to 1100 C (1625 to 2012 F). The pressure and gettering rate for each condition were used to calculate "sticking factors" (the fraction of total molecules striking the specimen that does not rebound).

The air oxidation of iridium and rhodium-iridium alloy has been reported by TRW Systems.<sup>(23)</sup> The key parameters in the oxidation of pure iridium in the temperature range of 1050 to 1500 C (1922 to 2732 F) were velocity and air temperature. As air velocity increased and air temperature decreased (iridium at constant temperature) it appeared that gaseous diffusion of reaction products became less important and surface reactions became more important in determining the overall oxidation rate. Alloying with rhodium reduced the oxidation rate of iridium. The high-temperature oxidation of iridium-rhodium alloys was characterized by the formation of internal porosity at the grain boundaries. It was concluded that the porosity was the result of solid-state diffusion and subsequent oxidation of rhodium in the grain boundaries. The penetration of porosity decreased with time, thus indicating that as oxidation proceeded the tendency for individual voids to grow larger was more predominant than the tendency for the pores to penetrate deeper into the metal.

Coatings. Various compositions of fused-silicide coatings for D43 columbium alloys have been studied by Sylvania.<sup>(24)</sup> Twenty-five compositions in the Si-Cr-Ti-Fe-V system were investigated in 1-hour cyclic-oxidation tests in air at 800 to 2500 F. Optimum compositions were found to be Si-20Cr-20Fe-10VSi<sub>2</sub> and Si-20Cr-20Fe. These compositions displayed the longest lives, about 30 and 50 cycles, respectively.

An evaluation of the oxidation resistance of silicide coatings on columbium and tantalum has been made at Lockheed Palo Alto Research Laboratory.<sup>(25)</sup> TaSi<sub>2</sub> on tantalum and MoSi<sub>2</sub> on columbium oxidized uniformly to form a two-phase oxide layer that was not as protective as that of MoSi<sub>2</sub> on molybdenum which oxidized selectively to form only SiO<sub>2</sub>. The addition of aluminum to the silicide coatings moderately improved their oxidation by promoting selective oxidation.

Oxidation-resistant coatings for Cb-12Zr alloy have been investigated by the Jet Propulsion Laboratory.<sup>(26)</sup> Exposure conditions were 500 hours in 2000 F argon containing 1 to 3 ppm oxygen and 1 to 10 ppm water vapor. Of the coatings tested, molybdenum disilicide applied over a molybdenum subcoating appeared to be the most effective. A tin aluminum coating also appeared promising. Chromium-molybdenum silicides were unprotective, as chromium diffused into the substrate. Several proprietary coatings allowed some oxidation of the substrate.

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