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AUTHORITY

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REVIEW OF RECENT DEVELOPMENTS
CORROSION AND COMPATIBILITY

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FOREWORD

This document is the first of a series to be issued on the latest developments in the field of corrosion of metals included within the scope of the Defense Metals Information Center. It is intended to convey the highlights of the significant results and conclusions of current research in corrosion. The review is aimed primarily at presenting new and unusual results, although pertinent contributions in the field, such as detailed reviews, literature searches, and bibliographies, may also be included.

STRESS-CORROSION CRACKING OF ALUMINUM ALLOYS

Test Methods

It has been shown in work at Alcoa that various accelerated laboratory stress-corrosion cracking test methods do not produce the results of natural exposures. Several test methods have been compared using the 7079-T6 alloy. The best correlation was obtained with an acidified 5 percent NaCl intermittent spray test. It was suggested that the above test be backed up by a boiling 6 percent NaCl test to provide a good correlation with similar, but copper-free, alloys.

Work carried out at the Reynolds Metals Company has pointed up the importance of testing conditions in the evaluation of the stress-corrosion susceptibility of aluminum alloys.

The factors that affect the stress-corrosion cracking behavior were found to be as follows:

1. The presence of even a trace of moisture was sufficient to cause cracking.
2. The rate of stress-corrosion cracking was a straight-line function of 1/\(T\) (the absolute temperature).
3. Wide variations of chloride concentration had no effect on rate of cracking.
4. Changes in the solution pH and contamination with copper altered the failure mechanism.
5. The manner of stressing and specimen configuration both affected the rate of crack formation.

Since all of the above factors may vary in experimental work from laboratory to laboratory, the many anomalies observed in published data were attributed to this combination of factors.

Mechanisms

Five theories for the mechanism of stress-corrosion cracking have been discussed in a paper from Battelle-Columbus. These theories have been applied to aluminum-alloy systems, and it was shown that the hydrogen-induced electrochemical mechanism most nearly fitted experimental observations. In turn, it was shown how the theoretical mechanism must be taken into account when designing experimental procedures.

The mechanism of stress-corrosion cracking of aluminum has been studied at Kaiser with reference to previously derived models. Their results have shown that the rate-determining step in the stress-corrosion cracking of 7039 alloy is the anodic dissolution of Mg,Al at the grain boundaries.

Fundamental studies of the nature of stress-corrosion cracking in aluminum-zinc-magnesium-type aluminum alloys at Battelle-Columbus have indicated that stress-corrosion cracking susceptibility is a function of the stress normal to the grain boundaries, rather than a function of the applied stress.

It was also shown that hydrogen tends to concentrate at grain boundaries when these alloys are cathodically charged under stress.

Miscellaneous

An extensive study has been conducted at Alcoa on the stress-corrosion cracking of high-strength aluminum alloys, with emphasis on methods of testing, methods of delaying failure of susceptible alloys, and surface treatments to prevent stress-corrosion cracking. After 2 years' exposure, three protective systems on highly stressed 2014-T651 and 7079-T651 alloys have performed well: (1) shot peened + paint, (2) metallized with 7072 + paint, and (3) metallized with 7072 without paint. After 8 months' marine and industrial atmospheric exposure, welded 7039-T6, 7002-T6, and 7139-T6 alloys have shown high resistance to stress-corrosion cracking at 75 percent of the yield strength. Alternate immersion tests in 3-1/2 percent salt solution of the same material resulted in severe localized corrosion in the heat-affected zone. A post-welding heat treatment practically eliminated the localized attack but introduced stress-corrosion susceptibility.
The Naval Marine Engineering Laboratory has studied the stress-corrosion behavior of the following aluminum alloys in seawaters: 5083, 5086, 5154, 5096, and 5456.(8) The corrosion attack was characterized by mild pitting. No stress-corrosion cracking was observed in the standard mill tempers. The 5456-H24 alloy, aged at 212°F for 1 week, cracked within 1 year. In marine atmospheric exposure, aluminum alloys with 6 and 7 percent magnesium were more susceptible to cracking than those with lower titanium contents. Also, alloys in the H11 and H32 tempers were more likely to fail than those in the H16 and H36 tempers. Time to failure appeared to be a function of overall aging time rather than exposure time. Small amounts of manganese and chromium reduced the susceptibility of these alloys to stress-corrosion cracking.

Corrosion of Titanium Alloys

Stress-Corrosion Cracking

Because of the hot-salt-corrosion cracking susceptibility of titanium alloys, a program has been started at TMF to determine whether stress-corrosion cracking can also be caused by halogenated sealants at temperatures up to 600°F. Preliminary information indicates that some of the sealants being tested do produce stress-corrosion cracking of some titanium alloys. The research is being continued.

A study has been conducted by the Langley Research Center on the problem of hot-salt (NaCl) cracking of the Ti-6Al-4V alloy (duplex annealed).\(\text{10}\) The effect of residual tensile stress in the range of 20 to 65 ksi was investigated in a temperature range of 400 to 600°F. The specimens were bent over dies of 0.25 to 2.5-in. radii to produce the residual bend stresses. No stress-corrosion cracking was found at 400°F regardless of stress level. Severe stress corrosion was found to occur after 20 hours' exposure at 500°F. Stress relieving in argon effectively prevented failures, but the effects of stress relieving in air were inconclusive. The most active salt in causing hot-salt cracking was NaCl followed by seawater, synthetic seawater (7NaCl+3MgCl\(_2\)), and CaCl\(_2\). MgCl\(_2\) by itself had very little effect.

The mechanism of hot-salt stress-corrosion cracking of titanium alloys has been studied at NRL.\(\text{11}\) It was concluded that cracking was not caused by a gas evolved from the salt, but was the result either of a lowering of surface energy due to a creeping solid corrosion product or of hydrogen ions entering the metal during the course of the reaction. Electrochemical studies indicated that cracking occurred only at the cathode of an oxygen differential cell and that anodic polarization prevented cracking.

Crack-growth rates of titanium alloys during low-cycle fatigue in air and 3.5 percent salt-water solution have been studied at the Naval Research Laboratory.\(\text{12}\) An increase in crack-growth rate at all strain ranges was noted for Ti-7Al-2Sn-7Mo alloys in the salt-water environment. On the other hand, Ti-6Al-4V alloys did not appear sensitive to the aqueous environment. Fractographic studies revealed that the increase in crack-growth rate was accompanied by a change from the ductile mode of fatigue fracture to a brittle quasi-cleavage mode of fracture indicative of stress-corrosion cracking.

Miscellaneous

INCA has completed a study on the amount of water that must be present in chlorine gas to produce passivity of titanium.\(\text{13}\) It was found that the amount of water required was dependent upon temperature, gas-flow rate, gas composition, and gas pressure. At room temperature, 0.93 percent water in static chlorine suppressed the reaction with titanium. Somewhat less water was required for the flowing gas. At 200°F (392°F), about 1.5 percent water was necessary to produce passivity.

It has been shown by work at Kobe Steel that in chloride solutions the stability of the passivity of titanium decreases with an increase in chloride and hydrogen-ion concentrations as well as with an increase in temperature.\(\text{14}\) Also, passivation becomes easier with an increase in the titanium concentration. Crevice corrosion occurred in neutral or slightly acidic solutions of over 20 percent chloride salt.

Corrosion of alloys and Superalloys

Low-Alloy Steels

Three types of precracked high-strength steel specimens have been compared at NRL for evaluating the reduction of fracture toughness caused by stress-corrosion cracking in NaCl solutions.\(\text{15}\) The crack configurations studied were part-through-crack tension specimens, part-through-crack tension specimens, and edge-cracked cantilever beam specimens of 4340 steel. It was found that all three types of specimens can be used to determine the value of the plane-strain stress-intensity factor above which cracking will occur in the presence of an aggressive environment.

A number of organic coatings on steel have been exposed 13 months to deep-ocean environments at depths up to 6,800 feet by the Naval Engineering Laboratory.\(\text{16}\) Generally the organic coatings performed better in shallow water than in deep water, except for those which were highly susceptible to barnacle damage. Zinc silicate coatings also provided good protection in either shallow or deep water, but were generally better in shallow water.

An investigation of the compatibility of mild steel, chrome steel, chrome-nickel steel, and tantalum with the molten cadmium-magnesium-zinc system has been conducted by Argonne National Laboratory for the room-temperature to 750°C (1382°F) range.\(\text{17}\) This study has shown that carbon steels and chrome steels can be considered good candidates for containing this liquid metal system at low concentrations of zinc (0-30 at.%). Tantalum possesses good resistance up to 95 wt.% zinc. The 18-8 materials exhibited heavy attack because of the high solubility of nickel in molten zinc.

Stainless Steels

The effect of residual elements on the stress-corrosion cracking behavior of austenitic stainless steels has been summarized by U. S. Steel.\(\text{18}\) It was pointed out that controlling the level of residual elements in AISI grades of austenitic steels is not a fruitful approach to improving resistance to stress-corrosion cracking. Rather, a better approach
would appear to be the development of new alloys outside the present AISI grades, based on the control of the total alloy composition including residual elements.

The beneficial effect of silicon additions on the oxidation resistance of stainless steels in steam has been shown in experiments conducted in France. High-purity 18Cr-10Ni stainless steels exhibited the weight gains indicated below after 894 hours' exposure to steam at 500°C (932°F) and 45 kg/cm² (640 lb/in²).

<table>
<thead>
<tr>
<th>Silicon, wt.%</th>
<th>Weight Gain, mg/dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>None added</td>
<td>196</td>
</tr>
<tr>
<td>1</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
</tr>
</tbody>
</table>

An industrial-grade 18Cr-10Ni alloy gained 130 mg/dm² under similar conditions. This relatively low weight gain was attributed to 0.51 wt.% silicon in this alloy.

Parabolic reaction rates and marked temperature dependence have been observed for the reaction of stainless steel with steam in research conducted at GEMP. Parabolic rate constants varied from 0.6 to 114 mg/cm²·min over the temperature range of 1000 to 1250°C (1832 to 2280°F). The corrosion product was identified as Fe₂O₃ with a surface coating of alpha Fe₃O₄.

Exhaust-Gas Corrosion

A study at General Electric has been directed toward the development of nickel and cobalt alloys for gas turbines that will power Navy surface craft and be used to exhaust products containing sulfur and sea salt. The temperature range being considered is 650 to 1900°F. The following alloying additions improved the corrosion resistance of the nickel system: uranium greater than 15 percent, cobalt 10 to 25 percent, molybdenum less than 4 percent, small additions of lanthanum, titanium to at least 4 percent, high titanium-to-aluminum ratio, and tungsten up to 8 percent for 1900°F service.

The microalloy system, additives of yttrium and tantalum, reduced the rate of attack. The alloys thus far developed, though having acceptable corrosion resistance, fall short of the desired mechanical properties such as rupture strength.

A study has also been conducted at General Electric to determine the mechanism of corrosion of nickel by hot exhaust gases. The results of the investigation have shown that nickel alloys can react directly with either solid or liquid Ni₃S₂ without a need for any reducing agent. A low-melting-point Ni₃S₂-Ni eutectic is believed to be formed. The grain boundaries are penetrated by diffusion of this eutectic liquid, and thus sulfur is transported into the metal. In turn, these sulfur-rich areas oxidize rapidly. In the case of Ni₁₋₀₂₅Cr and in some jet-engine alloys, this sulfur-rich eutectic is not produced, and only Cr₇S₈ is formed.

The corrosion problem in turbine engines resulting from the combined effects of the sulfur content of JP-5 fuels and the presence of sea salt in the air has been studied by Phillips Petroleum Company. Previous work has indicated that a reduction of the allowable sulfur level in the fuel from 0.4 to 0.04 wt.% would not reduce the corrosion of the superalloys, but would in some cases aggravate the problem. It was shown that an aluminum diffusion coating (Misco-NDC-1) provided considerable protection to Inco 713C in short-time tests. In longer tests, the coating gave better protection with high-sulfur fuel (0.4 wt.%), but with low-sulfur fuel (0.0002 wt.%) a reduction of the allowable sulfur level in JP-5 fuels and the presence of sea salt. The corrosion problem in turbine engines results from the combined effects of the sulfur content of JP-5 fuels and the presence of sea salt in the air.

Parabolic rate constants varied from 0.6 to 114 mg/cm²·min over the temperature range being considered for 1900°F service. The application is for containing the molten-salt heat (heat-sink material) of solar-energy power systems for orbiting satellites. Haynes 25 appeared to be the most suitable material of the following alloys that were evaluated: Type 310 stainless, Haynes 56, Inconel 800, Hastelloys N and W, Inconel 750, René 41, Vibramet 500, Waspaloy, TD Nickel, and Haynes 25.

Corrosion of Refractory Metals

The Bureau of Mines has published the results of an extensive investigation of the corrosion behavior of molybdenum, tungsten, and vanadium in numerous environments. These metals were found to possess generally superior chemical and galvanic corrosion properties in many aqueous corrosive media at temperatures up to the boiling points. With few exceptions, molybdenum, tungsten, and vanadium were not adversely affected when coupled with dissimilar metals in galvanic corrosion experiments.

Argonne has studied the reaction of rhenium and tungsten with flowing steam at 1 atmosphere pressure. When rhenium reacts with steam at 850 to 1700°C (1560 to 3090°F), the rate of evolution of hydrogen is constant with time, and the metal remains bright. Sublimation of Re₂O₇ was suggested as the rate-determining step. The mechanism of the reaction of tungsten with steam at the temperature range of 1000 to 1450°C (1832 to 2642°F) is similar to that of molybdenum. The rate-determining step consists of the oxidation of WO₂⁻ to the volatile WO₃(CH₃)₂ and its polymers. Above 1450°C, the tungsten reaction is complicated by the formation of a liquid phase on the surface of the metal.

Rockwell has conducted a program to ascertain the feasibility of using the B-66 columbium alloy (W-Mo·5V-1Zr) and Ta-10W alloy as regeneratively cooled nozzle materials in a hydrogen-fueled engine. Tensile tests conducted on specimens in a hydrogen atmosphere indicated that the utilities of B-66 and Ta-10W were reduced at temperatures up to 800 and 400°F, respectively. Exposure of B-66 or Ta-10W to hydrogen at room temperature 

resulted in continuous disintegration of the alloys under certain conditions. Completely clean or newly made surfaces were especially susceptible to this gross "fragmentation" phenomenon.

Tungsten alloys containing additions of refractory-oxide particles or metallic elements which form refractory oxides were found to have improved oxidation resistance in the 1600 to 1700°F temperature range (28). Oxidation resistance was evaluated by measuring the surface recession of resistance-heated 1/4-inch-diameter, powder-metallurgy-produced bars in an air flow up to 130 fps. Al2O3 containing alloys (up to 10 vol.% Al2O3) exhibited the best oxidation resistance, with the amount of surface recession being nearly an order of magnitude less than that of pure tungsten up to 2500°F (4530°F). Tungsten alloys containing ThO2 and MgO were not so effective in inhibiting oxidation because of a fluing action between these oxides and tungsten oxides.

In a program conducted at Lewis Research Center, a number of refractory metals, refractory compounds, graphites, and reinforced plastics were evaluated in three solid-propellant exhaust gases. These exhaust products had different oxidizing characteristics and different erosion characteristics. No one material performed best under all three conditions. The refractory metals showed the best resistance to erosion and thermal shock. The graphite performed well in the least oxidizing conditions. The refractory compounds were erosion resistant but failed by thermal cracking. The plastics suffered more from erosion.

Miscellaneous

Shock sensitivity of several materials in OF2 has been investigated by Douglas Aircraft using a shock wave with explosive donor. At -70°F, it was found that Teflon (TEF) and graphite could be ignited at 320,000-psi shock, but not at 90,000 psi. Very slight reactions were observed with Ti, tantalum, columbium, and Kel-F grease at 90,000 or 120,000 psi, but the reactions did not propagate.

A preliminary report has been prepared by Subcommittee VI, ASTM Committee G-1 on Solid Propellant Test Environments and Test Durations. The object of the report was to compile data on the presently accepted atmospheres and test periods used for the purpose of investigating and testing of various metals for susceptibility to stress-corrosion cracking, with the end purpose of standardizing test methods.

The Bureau of Naval Weapons has published a report entitled "Corrosion Control for Aircraft," which includes limited discussions of many topics, such as (1) theory and practice of corrosion control, (2) materials used in corrosion control, (3) preventive maintenance, (4) treatment of corroded areas, (5) restoration of paint finishes, (6) consumable materials, and (7) plating and surface treatments. This superseded NAEPS 01-1A-509 (1 Dec 1961).

REPORT ON THE THIRD INTERNATIONAL CORROSION CONGRESS

The Third International Congress on Metallic Corrosion was held in Moscow, USSR, on May 16-25, 1966. The Congress was attended by approximately 1,000 scientists representing 30 countries. The Soviet delegation, which numbered more than 600, was approximately one-half women. The languages used during the Congress were Russian and English, and simultaneous translation of all lectures and papers was arranged.

In general, the organization of the Congress was satisfactory, although quite different from that found in most Western countries. Practically absent were the half-day discussions and private bull sessions in which Western scientists participate. Only a few of the Soviet delegation wore badges, and most did not identify themselves during the discussion of the papers which practically eliminated any further discussions after meetings.

Technical Sessions

The Congress was organized into a number of concurrent sessions including such topics as (1) basic research, (2) stress-corrosion cracking and intergranular corrosion, (3) passivity and anodic films, (4) inhibitors, (5) metallic coatings, (6) nonmetallic coatings, (7) underground corrosion, (8) marine corrosion, (9) high-temperature oxidation, (10) atmospheric corrosion, and (11) corrosion in the power industry. In addition, each day's sessions were opened with a Plenary Lecture by an internationally recognized corrosion scientist.

In general, the papers were of high caliber, dealing with corrosion mechanisms and passivation studies rather than engineering and practical aspects of corrosion problems. As might be expected, the great majority of the Russian papers were concerned with kinetics and mechanisms of electrode reactions, the nature of passivation, and potentiostatic investigations. Their papers also reflected a lack of any use of X-ray diffraction, thin-section transmission electron microscopy, and related metallurgical tools to complement their electrochemical studies of corrosion mechanisms. Such use of combinations of experimental techniques are common in the United States, Canada, United Kingdom, and most Western countries. For the most part, the papers did not involve any basically new information or investigations. They presented no papers dealing with the stress-corrosion cracking of titanium alloys in aqueous salt solutions or nitrogen tetroxide. In fact, discussion with the Russians revealed they were not aware of the recent problems encountered in the United States with the stress-corrosion cracking susceptibility of some titanium alloys. It also appeared that they were not studying the hot-salt titanium cracking problem to any extent.

Notes prepared by W. K. Boyd, Battelle Memorial Institute, Columbus, Ohio, who attended the Third International Corrosion Congress.
On the other hand, the Russians appear to be studying the influence of alloy additions on the corrosion behavior of titanium in acid solutions. Particular attention was focused on alloys containing up to 20 percent of chromium, 40 percent of molybdenum, or 40 percent of columbium with and without additions of palladium up to about 5 or 10 percent. Some studies also were made on titanium alloys containing tantalum, aluminum, and zirconium additions. In general, chromium and aluminum were reported to reduce significantly the corrosion resistance of titanium in nonoxidizing media such as sulfuric and nitric acids. Molybdenum was detrimental in concentrated nitric acid. Palladium additions to columbium-containing alloys were found to reduce the amount of columbium necessary to obtain passivation in sulfuric acid solutions. While this work is interesting, it would appear that the highly alloyed titanium systems have little practical use at this time.

One of the significant papers presented on titanium-alloy corrosion was concerned with the mechanism by which palladium improved corrosion behavior. These studies, conducted by Joseph Cotton at the ICI Labs, England, indicated that the palladium goes into solution and then plates out on the surface, providing a protective film. Using this concept, additions of palladium to the corrosive media were found to plate out on the surface of unalloyed titanium affording passivation. This observation is in contrast to research conducted on tantalum who reported some time ago that the preferential dissolution of tantalum eventually resulted in leaving a layer of palladium on the titanium surface.

A number of the Russian papers involved intergranular corrosion of austenitic stainless steels. Much of the research reported was similar to that done in the United States as long ago as 20 years.

REFERENCES


(5) Preliminary information reported by Battelle Memorial Institute, Columbus, Ohio, under an Air Force contract.


(7) Preliminary information reported by Alcoa Research Laboratories, New Kensington, Pa., under a NASA contract.


(9) Preliminary information reported by TRW Equipment Laboratories, Cleveland, Ohio, under an Air Force contract.


(23) Preliminary information reported by Phillips Petroleum Company, Bartlesville, Okla., under a Navy contract.


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