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AD869538

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AUTHORITY

Air Force Materials Lab ltr dtd 12 Jan 1972

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A literature survey of recent European papers of the stress-corrosion cracking of aluminum alloys has been prepared by Battelle's Frankfurt Laboratories. The survey covers mechanism studies, new stress-corrosion tests, effects of cold work, and a general review of the problem. Also included in the survey are tables and graphs selected from the papers reviewed.

The exfoliation corrosion and stress-corrosion cracking behavior of several high-strength aluminum alloys has been studied at Alcoa as part of an overall program to determine fracture toughness, fatigue, and corrosion characteristics. Resistance in salt spray, marine atmosphere, and industrial atmosphere was 7075-T73 > X7080-T7, and X7080-T7 > 7075-T6 and 7178-T6. Stress-corrosion tests with precracked specimens (continuous immersion in 3.5 percent NaCl solution) and smooth tensile specimens (alternate immersion in 3.5 percent NaCl) rated the alloys and tempers in the same order. No failures were detected in any alloys stressed 75 percent of the yield strength in the longitudinal direction. Several 7075-T6 and 7178-T6 type samples showed some susceptibility to cracking at 75 percent of yield stress in the long transverse direction.

**TABLE 1. MAXIMUM DEPTH OF PENETRATION OF VARIOUS CORRODED SPECIMENS**

<table>
<thead>
<tr>
<th>Alloy and Temper</th>
<th>Number of Corroded Specimens</th>
<th>Number of Corroded Specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>7075-T6S1</td>
<td>7079-T6S1</td>
<td>7178-T6S1</td>
</tr>
<tr>
<td>1100</td>
<td>7.4</td>
<td>75</td>
</tr>
<tr>
<td>2024</td>
<td>75.5</td>
<td>23</td>
</tr>
<tr>
<td>7075</td>
<td>75.5</td>
<td>34</td>
</tr>
<tr>
<td>7079</td>
<td>51.0</td>
<td>51.0</td>
</tr>
</tbody>
</table>

**TABLE 2. STRESS-CORROSION BEHAVIOR OF SAMPLES STRESSED IN THE SHORT-TRANSVERSE DIRECTION**

<table>
<thead>
<tr>
<th>Alloy and Temper</th>
<th>Percentage of Yield Strength at Which Failures Were Observed</th>
<th>Approximate $\Delta$$_{\text{sec}}$ ksi</th>
</tr>
</thead>
<tbody>
<tr>
<td>7075-T7S510</td>
<td>Very high</td>
<td>75</td>
</tr>
<tr>
<td>X7080-T7S42</td>
<td>High</td>
<td>50</td>
</tr>
<tr>
<td>X7080-T7S41</td>
<td>Medium</td>
<td>50</td>
</tr>
<tr>
<td>7075-T6S10</td>
<td>Low</td>
<td>50</td>
</tr>
<tr>
<td>7178-T6S51</td>
<td>Low</td>
<td>15</td>
</tr>
</tbody>
</table>

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The stress-corrosion behavior of samples stressed in the short-transverse direction is shown in Table 2.

A thermal-mechanical treatment for 7075 aluminum was developed by Rocketdyne that develops the yield strength of the -76 treatment and the stress-corrosion-cracking resistance of the -T3 treatment. The short-transverse yield strengths of 70 to 75 ksi and stress-corrosion lifetimes as long as those of 7075-T73 were achieved by an average treatment of 7075-T6 for 5 to 10 hours at 550°F followed by a press-forming operation to give a 20 percent reduction in the longitudinal direction of grain orientation. These properties were obtained to the center of 3.125-inch-thick rolled stock and 4-inch-thick forged stock.

Australian scientists have studied the factors controlling stress-corrosion cracking in precipitation-hardened Al-5.7Zn-2.7Mg-1.35Cu alloy. Prenotched specimens were stressed by cantilever loading in the short-transverse grain direction, and a 0.5 NaCl/0.005N NaHCO₃ solution was allowed to drip continuously over the notch. Ninety-five percent of the life of the specimen was taken up by the formation of grain-boundary attack to a certain degree of acuity from which the stress-corrosion cracks emanated. The length of the incubation period was markedly influenced by stress level and aging treatment (metallurgical structure).

STEELS

Aqueous Corrosion

Means of protecting the nongrouted tendons of the prestressed concrete reactor vessel of the Fort St. Vrain Nuclear Generating Station have been investigated at Gulf General Atomic. The steel was conform to ASTM Specification A421-65, Type BA. It was cold worked and thermalized (simultaneously stress and heat) to an ultimate tensile stress of 225 to 260 ksi. Marine-atmosphere exposure tests at LaJolla, California, indicated that a suitable combination of protective coatings and wraps would protect the tendons from rusting during fabrication, shipment, installation, and operation in the reactor. Studies with bare and coated notched specimens revealed that the tendons were not susceptible to stress-corrosion cracking or hydrogen-stress cracking. Irradiation tests with five organic systems revealed that the hydrogen generated as the result of radiolytic break down of the organic did not cause hydrogen-stress cracking of notched tendons stressed to 75 percent of the ultimate strength. Irradiation fluences were 1.3 × 10¹⁷ n/cm² (E > 1 MeV) and gamma doses of 4.2 × 10⁹ rads.

The effect of applied potential on the crack-growth rate of 180-ksi-yield-strength 1ONI-2Cr-1Mo-Ko steel in 3.5 percent NaCl has been studied by U.S. Steel. Fatigue precracked cantilever specimens were used. Crack-growth was observed with both applied cathodic current and applied anodic current indicating that the alloy was susceptible to hydrogen cracking and stress-corrosion cracking. The mode of failure with no applied potential (at stress intensities above K₁c) could not be identified specifically as either hydrogen embrittlement or active-path stress corrosion.

U.S. Steel also has used applied potential to study the mechanism of corrosion fatigue of 12Ni-5Cr-3Mo maraging steel in low-pressure, gaseous hydrogen at pressures less than 1 atm. The embrittlement was caused by hydrogen-induced slow crack growth. The comparison of the characteristics of gaseous-hydrogen embrittlement with those of embrittlement of hydrogen-charged steels suggested that both types of embrittlement were basically the same phenomenon. The proposed mechanism of embrittlement involved a surface reaction between the hydrogen and the steel which facilitated crack propagation by either lowering the surface energy or changing the energy of plastic deformation.

Hydrogen Embrittlement

Studies on the embrittlement of 4130 steel in low-pressure, gaseous hydrogen have been reported by NASA - Ames Research Center. High-strength 4130 steel was embrittled by straining in gaseous hydrogen at pressures less than 1 atm. The embrittlement was caused by hydrogen-induced slow crack growth. The comparison of the characteristics of gaseous-hydrogen embrittlement with those of embrittlement of hydrogen-charged steels suggested that both types of embrittlement were basically the same phenomenon. The proposed mechanism of embrittlement involved a surface reaction between the hydrogen and the steel which facilitated crack propagation by either lowering the surface energy or changing the energy of plastic deformation.

A generalized model for hydrogen embrittlement of steel has been proposed by Argonne National Laboratory scientists. The model proposes that hydrogen embrittlement does not occur until a hydrogen-rich phase has been precipitated from solution, and the precipitation of this phase can be induced by triaxial tensile stresses. Considered were the effects of substructure (including prismatic dislocation loops), test temperature, cooling rates, solubility, diffusivity, and notch-sensitivity on ductility. Two of the more popular models for hydrogen embrittlement were shown to have salient features that were compatible with the proposed generalized model.

Lead Embrittlement

The load-embrittlement of steel has been studied by Illinois Institute of Technology. Embrittlement occurred when the load was present either internally in the steel (loaded steel) or soldered to the surface. Embrittlement occurred...
over a temperature range of 500 °F (more than 300 °F below the melting point of lead) to a brittle-to-
ductile transition temperature of 700 to 900 °F. Eembrittlement was more severe in steels with l w-
ductile transition temperature of over a temperature
nucleates, it grows rapidly. is controlled
below the melting point of lead, the
steel,steel
rates lowered the brittl4 to-ductile transition transgranular
while, at higher temperatures, lowering the loading pile ups, occuring on slip planes, account for the
ai temperatures below the melting point of lead. Increasing formation of parallel tunnels across a grain.
but prevented cracking and crevice corrosion of the in seawater. It is cathodic to most matei'tals and
AM-350 alloy
stress-corrosioh cracking in all conditions, studied NaOIl-1120 over a broad temperature range. Informa-
and air Iried (50, minutes
The stress-corrosion cracking behavior of (nitrogen, phorphorus, arsenic, antimony, bismuth),
Cracking, occurred in both the 900 and, 1050
Beams, laded tensile specimens, beryllium, carbon, silicon, and possibly boron.
A-286, Almar
The stress-corrosion cracking of U-bends of
17-4P11
17-7P11
and Unitemp-212 stainless fast-breeder
900. The 17-4P11
30.1 stainless

CRANIGRAMS THEACCECTECH THE SCD PILE 
and the environment. The
intergranular cracking, while
of dislocation pile ups and the environment. The
pile ups, occurring on slip planes, accounts for the
transgranular mode of crack propagation.

The effect of alloy additions on the stress-
corrosion cracking of iron-chromium-nickel alloys
in boiling NaCl solutions has been studied at The
Ohio State University.(18) The review was
prepared in support of the liquid-metal cooled,
fast-breeder reactor program in considering an
accident or leak that would permit sodium to oxidize
or hydrolyze to produce NaOH-NaO-H2O solutions.
Accordingly, the environment considered was primarily
NaOH-H2O over a broad temperature range. Informa-
tion is presented in areas of thermodynamics,
electrochemical kinetics, corrosion rates, stress-
corrosion-cracking phenomena, structures of passive
films, and inhibitors.

NICKEL- AND COBALT-BASE ALLOYS

The corrosion behavior of Multiphase Alloy
MP35N (35Ni-35Co-20Cr-10Ag) has been studied by
Standard Pressed Steel.(19) The alloy exhibited
good-to-excellent corrosion resistance at 50 C
(122 F) in 10 and 78 percent H2SO4, 10 and 65 per-
cent H2SO4, 10 percent NaCl (pH 2 with HCl), 10 per-
cent FeCl3, and 10 percent HCl (plus 1 percent FeCl3
but not compound HCl alone). U-bends of the
alloy did not crack after 192 hours in boiling 42
percent NaCl2. The alloy is an extremely noble
metal with a potential of +0.056 (versus Ag-AgCl)
in seawater. It is cathodic to most materials and
corelated galvanic corrosion of K-Nomel, Type 316
stainless steel, and carbon steel in couple tests
conducted in seawater. No galvanic corrosion was
noted in similar tests conducted with titanium-
MP35N couples. Wire-rope samples made of MP35N

Precipitation-Hardening Stainless Steels

The stress-corrosion cracking behavior of precipitation-hardening stainless steels has been
studied at the George C. Marshall Space Flight
Center.(14) Bent beams, loaded tensile specimens, and C-rings were used to test the materials in the longitudinal and transverse directions of grain orientation. The stressed specimens were alternately immersed (10 minutes) in 3.5 percent NaCl solution and air dried (30 minutes) at room temperature. The results indicated that PH13-8Mo, PH14-8Mo, 15-5PH, A-286, Almar 362 and Unitemp 212 stainless steels were resistant to stress-corrosion cracking under those conditions in all heat treatments studied. The PH15-7Mo and 17-7PH alloys were susceptible to stress-corrosion cracking in all conditions studied except 17-7PH - CH 900. The 17-4PH - II 900 treated specimen cracked in the transverse grain direction. Alt-50 alloy was susceptible to cracking in the SCT 450 condition, but not in the SCT 1000 condition.

The cathodic protection of stressed 17Cr-4Ni-
4Cu precipitation-hardened steel in seawater has
been studied by the Naval Ship and Development Laboratory. The specimens were aged at 900 and 1050 F (175 and 154-ksi yield strength) prior to testing as-bent beams at 900 percent of yield strength. Cracking occurred in both the 900 and 1050 F aged specimens that were not cathodically protected. Applied potentials of -160mV to SCE prevented stress-corrosion cracking in both aged conditions, but did not prevent crevice corrosion. An applied potential of -1375mV to SCE caused cracking of the 900 F aged specimen (presumably from hydrogen embrittlement), but prevented cracking and crevice corrosion of the 1050 F aged specimen.

Austenitic Stainless Steels

The stress-corrosion cracking of U-bends of
Type 304 stainless steel in 5X H2SO4 + 0.5X NaCl at
room temperature has been studied by scanning electron microscopy in England. Specimens were
solution annealed at 1050 and 1300 C (1920 and
2370 F) or were cold worked 11 and 35 percent.
Cracking times ranged from 4 to 21 days, and
calculated corrosion rates ranged from 10 to 117
mils/year. In general, cracks initiated intergranu-
larly, but propagated in a transgranular fashion.
Crack propagation occurred as the result of the formation of parallel tunnels across a grain.
alloy have shown no evidence of attack after 2.5 years' exposure in the mud, seawater, tidal zone, splash zone, or marine atmosphere.

**TITANIUM ALLOYS**

The second annual report on the mechanism of stress-corrosion cracking of titanium alloys in \( \text{Na}_2\text{O}_3 \) and aqueous and hot-salt environments has been issued by Battelle's-Columbus Laboratories. (20) The mechanism of aqueous stress-corrosion cracking most consistent with the experimental observations was related to the formation of strain-induced hydrides in the active [1010] slip bands, which inhibited plastic flow around the crack tip and, thereby, promoted cleavage. The mechanism of stress-corrosion cracking in pure \( \text{Na}_2\text{O}_3 \) was related to oxygen which acted as a cathodic depolarizer. That is, titanium reacts with \( \text{Na}_2\text{O}_3 \) to form \( \text{Na}_2\text{O} \), \( \text{Na}_2\text{O}_2 \), and unstable nonprotective \( \text{TiO}(\text{NO})_2 \) (anodic reaction). Oxygen reacts with \( \text{Na}_2\text{O}_3 \) (cathodic reaction outside the crack) and \( \text{Na}_2\text{O} \) and \( \text{Na}_2\text{O}_2 \) (cathodic reaction inside the crack). The unstable \( \text{TiO}(\text{NO})_2 \) decomposes to \( \text{TiO}_2 \), \( \text{Na}_2\text{O}_2 \), and \( \text{O}_2 \), and the latter helps to depolarize cathodic reactions within the crack. Results with hot salt were inconclusive and these studies are being repeated.

The stress-corrosion cracking of titanium and Ti-5Al-2.5Sn alloy in methanol-chloride has been examined by scanning electron microscopy in England. (21) Unbonds and dynamic tensile straining were used. The alloy exhibited transgranular cleavage, and the mode of cracking in unalloyed titanium changed from intergranular separation to transgranular cleavage as the impurity levels were increased in the titanium. Small amounts of hydrogen introduced into the most impure titanium resulted in a larger amount of cleavage in subsequent stress-corrosion tests and, in air, fractures that were similar to stress-corrosion fractures. The results were interpreted in terms of intergranular dissolution or as arising mainly from impurity segregation and transgranular cleavage due to a form of hydrogen embrittlement.

The influence of salt and elevated-temperature exposure on the maximum compressive strength of titanium-alloy skin-stringer panels has been investigated by the National Aeronautics and Space Administration. (42) Ti-5Al-2.5Sn specimens were tested to failure at room temperature after being coated with a 3.4 percent NaCl solution and exposed 1000 hours at 600 F to develop stress corrosion cracks. The hot-salt stress-corrosion cracks had little effect on the compressive strength of the panels, although considerable tearing and deformation appeared to initiate from the cracks at maximum load.

**BRAZE ALLOYS**

The compatibility of brazed joints with \( \text{Na}_2\text{O}_3 \) has been studied by the Air Force Rocket Propulsion laboratory. (23) Lap-joint panels of Type 347 stainless steel were prepared with each of the following braze alloys: 82Al-18Ni-0.1Si, 70Au-22Ni-8Pd, and 72Ag-28Cu-0.2Li (weight percents). Stressed and unstressed specimens were exposed 360 days to the liquid, vapor, and liquid-vapor interface of \( \text{Na}_2\text{O}_3 \) with 0.2 percent water (in conformance with MIL-P-26539A). Some surface corrosion was detected on all alloys after exposure, but there was no evidence of stress-corrosion cracking or galvanic attack. It was concluded that these braze alloys were acceptable for use with \( \text{Na}_2\text{O}_3 \) systems.

**COATINGS**

The reasons for accelerated attack caused by one particular antifouling paint have been studied by the Naval Applied Science Laboratory. (24) The paint in question was different from other antifouling paints studied in that it had copper-metal pigment in its formulation and had a lower electrical resistance, and it was the only coating to exhibit a potential in seawater (-0.15 volt versus SCE). Circular holidays 1/8 in. in diameter produced pit depths in the underlying steel of up to 47 mils in 2 months' exposure in aerated "sea salt" in the copper-metal-pigmented paint and less than one-half that value in the other antifouling formulations.

Treatments for aluminum aircraft surfaces which confer corrosion resistance and enhance the adhesion characteristics of the surface and, if appropriately substituted with epoxide reactive groups, would also tie into the paint coating. Most of the evaluation was based on salt-spray exposure of painted panels followed by an adhesive peel test. The agents were found to be promising: dimethylphosphonoacetamide (DMPA) and 1-amino-2-phenylethyl phosphonic acid (APEPA); the DMPA was favored because of its greater water solubility. The optimum formulation consisted of a 3-minute (or longer treatment) with a pH 3 aqueous solution containing 1 to 2 weight percent DMPA. The shelf life of DMPA-treated panels was acceptable on the basis of extended atmospheric exposure of treated samples which produced only a slight loss in effectiveness. The performance of the DMPA treatment was equal to or slightly better than that of conventional chromate pretreatments and, in addition, the DMPA required no surface cleaning, was cheaper, was not restricted by a critical application time, and had better shelf life. Preliminary tests indicated that the DMPA and APEPA were suitable treatments for promoting adhesion of paint to titanium.

The results of a study to develop aerodynamically smooth corrosion-protective systems for fastener-head countersinks in highly loaded aircraft skins have been presented in a final report issued by Vought Aeronautics. (25) Corrosion tests in acetic acid salt spray and at Kure Beach showed that a polyurethane elastomer was protective after simulating limit loads of A-7 wing fold areas. Polysulfide and epoxy films cracked during loading and a silicone material was easily abraded and not protective. Permeability measurements showed the polyurethane was protective in films as thin as one mil in the peripheral groove around the fastener. The polyurethane elastomers yellowed in the sunshine, but a linear-polyurethane nonyellowing coating could be used as a topcoat material to form a durable flexible system.

**GENERAL**

A manual on Corrosion Control for Manned Space Flight Network Facilities has been prepared by
various forms of corrosion, the corrosion resistance of aluminum, iron, magnesium, and nickel-base alloys, the behavior of metal and organic coatings, and the methods of corrosion control.

A chemical engineer's guide to seawater has been prepared by the Dow Chemical Company. Information in the papers on seawater covers average monthly temperature and salinity at various locations off the U.S. coast, chemical composition, physical properties at concentrations varying from that of fresh water to four times normal seawater, foaming and turbidity characteristics, deposition of solids, and marine life.

The ARPA Coupling Program on Stress-Corrosion Cracking has compiled abstracts from journal articles, recent reports, and talks generated under this program. The abstracts cover aluminum alloys, high-strength steels, high-strength stainless steels, and titanium alloys, as well as fundamental studies on the mechanisms of stress-corrosion cracking. Also included are selected abstracts from outside the ARPA program in the field of stress-corrosion cracking.

The role of oxide plasticity on the oxidation behavior of metals is reviewed in a paper by Denny of the University of California at Los Angeles. Included in the discussion are the structural aspects of the scale; the effects of stoichiometry, temperature, and film thickness on plasticity of oxides; causes of micro- and macro-stresses in the oxide film; measurement of stresses in the oxide; and film spalling.

In-line corrosion probes to detect and measure galvanic and crevice corrosion in seawater have been developed by Battelle Northwest. The probes were evaluated in ambient seawater, artificial seawater in a pilot plant at 150 °C (302 °F) and 20 ft/sec. The steel probes developed an adherent FeO film and corroded at low rates (about 1 mil/year) at 150 °C. This film afforded short-term protection when the probe was transferred to saline water at a lower temperature; but, eventually the film broke down and the specimen corroded at a higher rate more characteristic of those for bare specimens at the lower temperature. Crevice probes made with 6061 aluminum and exposed at 150 °C revealed an initial low rate (incubation period) before the onset of crevice corrosion. The indicated corrosion rate during crevice attack determined by measuring the diameter of the wire in the area of greatest attack was about 500 mils/year compared with a calculated corrosion rate of about 900 mils/year. The measured attack appeared to be less severe because the resistance probe tends to measure an average value over the entire probe.

REFERENCES

(2) Private Communication to DMIC from Battelle-Frankfurt, January 1970.


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R. W. Engebretson, Editor