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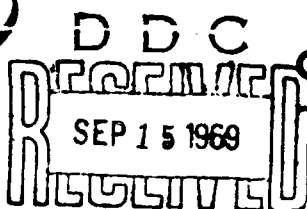
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review

OF RECENT
DEVELOPMENTS



Corrosion and Compatibility

W. E. Berry • August 29, 1969

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GENERAL

The current status of theories for stress-corrosion cracking has been reviewed by the Research Institute for Advanced Studies.(1) Emphasis was placed on research conducted since 1965 as it applies to four proposed models of crack propagation: (1) the rupture of a passive film at the crack tip by continual plastic deformation; (2) the dissolution of anodic deformed film-free metal at the crack tip; (3) the adsorption of a specific species that interacts with strained bonds at the crack tip causing a reduction in bond strength among atoms and producing a brittle fracture; and (4) the brittle fracture of an embrittled surface layer which proceeds discontinuously in repeated cycles of formation and rupture of the film.

The anodic polarization behavior of titanium, nickel, stainless steel, and carbon steel in molten salts has been investigated in South Africa.(2) Regions of corrosion and passivation were found in the anodic polarization curves. Carbon steels and stainless steels could be anodically protected in molten sodium nitrate at 350 C (662 F) and molten ammonium acetate at 130 C (266 F). However, anodic protection could not be achieved with steel or stainless steel in molten sodium hydroxide at 350 C despite indications of a passive region in the polarization curves for these materials in this environment.

The Naval Civil Engineering Laboratory has exposed specimens of 215 different alloys for 6 months in the sea at a depth of 5 feet, and has compared the results with exposures in the deep ocean at 2500 and 6000 feet.(3) Highly alloyed nickel alloys, titanium alloys, silicon cast irons, specialty stainless steels, columbium, tantalum, and tantalum-tungsten alloy were uncorroded after exposure at both shallow and great depths. The corrosion rates of the copper-base alloys, nickel-base alloys, steels, and cast irons decreased as the oxygen concentration in the seawater decreased (dissolved oxygen content at 5 feet > 6000 feet > 2500 feet). The copper-base alloys, steels, cast irons, molybdenum, tungsten, leads, and lead-tin solder corroded uniformly. All the aluminum alloys exhibited pitting and crevice corrosion which was more severe at depth than near the surface. The stainless steels exhibited crevice attack, pitting, and edge and tunnel corrosion except for Types 310, 317, and 329 as well as 20 Cb, 30 Cb-3, and AM-350 which had only incipient crevice corrosion. The crevice corrosion on the stainless steels was more severe near the surface than at depth.

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The Naval Civil Engineering Laboratory has also studied the effect on fouling and corrosion of Saran and polytetrafluorethylene (TFE) films applied with pressure sensitive adhesive to painted and unpainted carbon steel and unpainted stainless steel and K-Monel panels.(4) The Saran- and TFE-coated panels were exposed in the sea for 5 and 8.5 months, respectively. All panels were covered with heavy marine growth when removed from the sea. The marine growth was removed rapidly by stripping off the plastic film. In general, the plastic films protected the metal from fouling and corrosion, although crevice corrosion occurred on Type 302 stainless steel where seawater entered through ruptures in the film.

The efficacy of sealing compounds, paint coatings, and galvanic anodes for preventing corrosion, crevice corrosion, and galvanic corrosion in seawater also has been studied by the Naval Civil Engineering Laboratory.(5) Specimens were immersed 91 days in tide water at Point Mugu, California. A polyurethane paint system provided good protection to metal panels, effectively prevented galvanic corrosion between panels and dissimilar metal strips, and prevented crevice corrosion. The relative effectiveness among sealing compounds in excluding seawater from crevices at fasteners was (from best to worst) PRI532, DC780, DC93046, PRI422, PRI527, DC11, sprayed PVC. A zinc anode prevented corrosion and galvanic corrosion of anodized 6061-T6 aluminum samples fastened together with Type 304 stainless steel and Monel 400 rivets.

ALUMINUM ALLOYS

The behavior of intermetallic compounds in aluminum alloys during anodizing has been reported by Alcan Research and Development.(6) $MnAl_6$ was found to be relatively inert and was carried into the anodized coating. $FeAl_3$ oxidized at about the same rate as the aluminum matrix and the oxidation products were retained in the film. Mg_2Si and $CrAl_3$ oxidized more rapidly than the matrix. The intermetallic compounds which were inert or dissolved rapidly were detrimental to the brightness, appearance, and corrosion resistance of the anodic films. Manganese, silicon, and chromium in solid solution in aluminum were retained in the anodic film, but magnesium was dissolved.

The stress-corrosion-cracking behavior of 7075-T651 aluminum alloy in organic environments has been reported by Carnegie-Mellon University.(7) U-bend specimens did not crack after a 210-day exposure to carbon tetrachloride and ethanol, although duplicate specimens exhibited stress-corrosion

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cracking in 3.5 percent NaCl solution. On the other hand, stress-corrosion cracks propagated from fatigue-precracked cantilever-beam specimens exposed to methanol, ethanol, carbon tetrachloride, isopropanol, and ethylene glycol, with the latter two being least aggressive. Analyses of the ethanol and carbon tetrachloride solutions revealed the presence of aluminum for the stress-corrosion tests, while no aluminum was found for the tests conducted without stress. The crack propagation in these organic environments was concluded to be analogous to that observed in aqueous environments, and hydrogen was probably not a factor because of the observed cracking in carbon tetrachloride.

FERROUS ALLOYS

High-Strength Steels

The fatigue crack growth rate of three new high-strength structural steels has been studied at the Naval Research Laboratory.⁽⁸⁾ The steels were 9Ni-4Co-0.20C quenched and tempered, 10Ni-2Cr-1Mo-8Co dual strengthened, and 13Cr-8Ni-2Mo PH precipitation-hardened stainless, and they ranged in yield strength from 176 to 193 ksi. Notched cantilever-bend specimens of each steel were cycled zero-to-tension in room air and in 3.5 percent NaCl solution. The results revealed that the three steels possessed significantly greater resistance to fatigue-crack propagation and less sensitivity to the environment than previously studied steels of comparable strength, although the 13Cr-8Ni-2Mo alloy exhibited greater sensitivity to the salt-water environment than the other two steels.

The effect of 0.09 to 2.15 percent silicon additions on the stress-corrosion-cracking resistance of 4340 steel in 3.5 percent NaCl solution has been studied by Boeing.⁽⁹⁾ In the 280- to 300-ksi range of tensile strength, silicon did not increase the threshold stress intensity parameter K_{ISCC} , but crack velocity was significantly retarded at silicon levels above 1.5 percent. In the 230- to 240-ksi tensile-strength range, silicon additions of less than 1.5 percent improved K_{ISCC} , but silicon had no effect on crack velocity at any of the silicon levels.

The factors affecting stress-corrosion-crack branching in 4330V, H11, 9Ni-4Co-0.45C, 4340, and maraging steels have also been studied by Boeing.⁽¹⁰⁾ Tests were conducted in 3.5 percent aqueous NaCl solution with deadweight-loaded fatigue-precracked notched specimens in either four-point or cantilever bending. Two conditions were associated with stress-corrosion-crack branching: (1) a constant crack velocity and (2) a critical stress-intensity K_{IB} . For several of the steels, K_{IB} equalled two to four times K_{ISCC} (K_{ISCC} is the plane-strain threshold stress-intensity factor below which stress corrosion does not contribute to crack propagation). When the K_{ISCC}/K_{IC} ratio exceeds 0.5, rapid brittle failure is surmised to occur before K_{IB} can be reached (K_{IC} is the plane-strain fracture toughness of the material).

The effect of prior austenite grain size on the susceptibility of AISI 4340 steels to stress corrosion cracking has been studied by Carnegie-Mellon University.⁽¹¹⁾ The grain size of the alloys covered the range ASTM 7 to 12 and the yield strength covered the range 240 to 270 ksi. Stress-corrosion tests were conducted in 3.5 percent NaCl

solution using fatigue-precracked plane-strain cantilever-beam specimens. Under these conditions, the value of K_{ISCC} was independent of prior austenite grain size and ranged from 14 to 16 ksi. However, the crack growth rates decreased (time to failure increased) with decreasing prior austenite grain size. The results were interpreted to indicate the feasibility of increasing the yield strength of steels by grain refinement without increasing the susceptibility to stress-corrosion cracking, or, alternatively, the stress-corrosion resistance at a particular strength level can be improved by using an ultrafine-grained steel tempered at higher temperatures.

Estimates of the pH at the tip of an advancing stress-corrosion crack in high-strength steels have been made at the Naval Research Laboratory.⁽¹²⁾ The specimens were frozen while the crack was propagating, the crack was opened up, and the pH was then measured when the frozen corrodent melted. In neutral 3.5 percent NaCl solutions, the pH near the crack tip in martensitic, precipitation-hardening, and maraging steels was between 3.6 to 3.8. The alloying elements in solution near the crack tip were present in the same proportion as in the steel.

Stainless Steel

Commercial and experimental iron-chromium-nickel alloys have been evaluated in H_2S in laboratory and pilot-plant corrosion tests conducted by the Sinclair Refining Company.⁽¹³⁾ Iron-20Cr-33Ni alloys with additions of 4 percent aluminum were resistant to one atmosphere H_2S at 1100 F, and were superior to the best commercial stainless steels. At 1200 and 1425 F, the corrosion rate decreased markedly with increasing aluminum additions through 14.8 percent. However, at 1800 F, even the 14.8 percent aluminum alloy was severely attacked.

Atomics International has continued the study of the helium embrittlement of stainless steels.⁽¹⁴⁾ Helium was injected into tensile specimens of Type 405 stainless steel by alpha-particle irradiation from a cyclotron. Subsequent tensile testing at 550, 650, and 750 C (1020, 1200, and 1380 F) of material containing 4×10^{-5} atom fraction of helium revealed an increasing loss in ductility with temperature which reached 55 percent at 750 C. The helium caused the failure mode to change from transgranular to intergranular. Large helium bubbles formed voids at grain-boundary carbide particles and were the origin of the intergranular cracking failure. The behavior of the ferritic Type 405 stainless steel containing helium was similar to that of the austenitic stainless steels studied previously.

TITANIUM ALLOYS

The Navy Materials Laboratory has determined the cause of cracking and ultimate failure of the cast Ti-6Al-4V forward port propeller from the hydrofoil craft HIGHPOINT.⁽¹⁵⁾ The results of fractographic and radiographic examinations indicated that the initial cracking resulted from residual stresses associated with a weld repair. The ultimate failure was attributed to the rapid propagation of these cracks by stress-corrosion cracking, although the growth of the dominant crack was also aided by fatigue.

Estimates of the pH of the solution at the tip of an advancing stress-corrosion crack in titanium alloys have also been made at NRL (see section

on iron-base alloys).⁽¹²⁾ A pH of 1.5 was observed at the crack tip in 7Al-2Cu-1Ta and 8Al-1Mo-1V alloys exposed to neutral 3.5 percent NaCl solution. Aluminum ions were found in the corrodent at the crack tip, but not further back where the pH was higher. Titanium ions were also found in solution at the crack tip.

Additional research on the mechanism of hot-salt cracking of titanium alloys was performed by Du Pont.⁽¹⁶⁾ Ultraviolet spectroscopic studies of the products of reaction of Ti-8Al-1Mo-1V chips with NaCl revealed significant quantities of HCl but little or no chlorine at temperatures of 340 to 650 C (645 to 1200 F), indicating that HCl, rather than chlorine, causes hot-salt cracking. Salt coatings of NaCl, NaBr, and NaI caused cracking of titanium alloy specimens. No cracking occurred with NaF. This was attributed to the fact that NaF does not occlude water and that any HF which might be generated reacts to form TiF₄ which immediately sublimates, sweeping hydrogen gas with it. Thus, hydrogen (which is believed to be the ultimate cause of cracking) does not enter the metal, and cracking does not occur.

NRL has developed procedures for incorporating stress-corrosion-cracking characteristics into the Ratio Analysis Diagram (RAD) system for providing generalized engineering solutions for fracture-toughness assessments of structural titanium alloys.⁽¹⁷⁾ The features of the combination RAD system are limit lines that indicate (1) the highest level of K_{Isc}/σ_{ys} ratios for which accurate plane-strain interpretation to flaw size-stress conditions for stress-corrosion cracking can be made for 1-inch thick plate and (2) the highest level of stress-corrosion-cracking resistance measured in extensive surveys of plate materials 1-inch thick.

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