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review

OF RECENT
DEVELOPMENTS

Corrosion and Compatability

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W. E. Berry • June 5, 1968

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GENERAL

A review of the hydrogen embrittlement of metals has been prepared by the General Electric Research Laboratory.⁽¹⁾ Topics covered include the effect of electroplating, corrosive environments, and gaseous hydrogen on hydrogen entry into metals; the various types of failures, such as hydrogen attack, blistering, reversible embrittlement, and delayed failure; crack propagation; and mechanism of embrittlement.

A new friction-impact test device has been described by McDonnell-Douglas.⁽²⁾ It is based on a pendulum impact and rotating-plate friction. It can produce impact velocities to 16 in./sec, contact pressures to 160,000 psi above yield strength of the materials, and impact-energy rates to about 2000 ft-lb/in.²-sec. Under these conditions, excessive friction as well as plastic deformation occur simultaneously to initiate the reaction with propellants.

Stress-corrosion-cracking problems associated with the Saturn Space Vehicle have been discussed in a recent paper from Marshall Space Flight Center.⁽³⁾ The failures occurred in 7075-T6, 7079-T6, and 2024-T6 aluminum alloys and in 17-7PH and AM 355 precipitation-hardened stainless steels. The problems with the aluminum alloys were eliminated by using a less susceptible temper (-T73), redesigning to eliminate stresses, or substitution of another material such as austenitic stainless steel. Alloy 718 was substituted for 17-7PH (RH 950). Rigid controls were imposed on the material processing of the AM 355 alloy to prevent the erratic formation of carbides in the grain boundaries.

The effectiveness of finishing systems for aluminum and magnesium to protect against tropical exposure is being evaluated by the Army Coating and Chemical Laboratory.⁽⁴⁾ Scored panels have been exposed 26 months in a rain forest in Panama and 4 miles away at a breakwater on the Caribbean Sea. On aluminum, an anodic pretreatment, MIL-A-8625, and a chemical film pretreatment, MIL-C-5541, are showing the best protection. On magnesium, anodic pretreatment, MIL-M-45202 Types I and II, was most effective. The breakwater exposure (salt spray) was more corrosive than the rain-forest exposure, particularly on the coated aluminum panels.

CORROSION OF ALUMINUM ALLOYS

The mechanism of the inhibiting effect of chromate primers on aluminum has been studied by IIT Research Institute.⁽⁵⁾ The mode of failure was

found to be the destruction of the protective oxide layer on aluminum at cathodic sites where hydrogen is evolved. Apparently protection by the chromate occurs from precipitation of insoluble trivalent chromium compounds at the cathode surface which prevent hydrogen evolution. Because chromates block the cathode reaction, they are not effective in stopping corrosion at adjacent anodic sites, such as in crevices or under blisters. A cadmium phosphate-chromate pigment ($6\text{CdO} \cdot 4\text{CrO}_3 \cdot 2\text{P}_2\text{O}_5 \cdot \text{K}_2\text{O}$) gave improved protection at crevice areas compared with standard chromate pigments.

The corrosion and stress-corrosion-cracking behavior of 7000 series aluminum alloys in flowing seawater has been reported by the Naval Marine Engineering Laboratory.⁽⁶⁾ Alloys studied were 7002-T6 (0.5-1.0Cu, 2.0-3.0Mg, 3.0-4.0Zn), 7106-T63 (1.7-2.8Mg, 3.7-4.8Zn), and 7039-T64 (2.3-3.3Mg, 3.5-4.5Zn). Bent beams stressed to 60, 75, and 90 percent of the 0.2% yield strength and U-bends were exposed for periods ranging up to 481 days. Welded specimens were included in the study. Alloy 7002-T6 exhibited severe pitting while 7106-T63 and 7039-T64 alloys were only mildly attacked. The weld metal in 7002-T6 alloy was corroded severely, while the heat-affected zones were attacked in welded 7106-T63 and 7039-T64 alloy specimens. Specimens stressed in the short-transverse grain direction were most susceptible to stress-corrosion cracking as is characteristic of the 7000 series of alloys.

The mechanism of the beneficial effects of the -T73 temper on improving the stress-corrosion cracking resistance of 7075 aluminum alloy has been studied at Tyco Laboratories.⁽⁷⁾ Specimens were exposed to NaCl buffered to pH 4.7 after having been overaged from the -T6 temper for varying lengths of time. During the first 6 hours of overaging, the tensile strength increased slightly, and cracking time remained essentially constant at 15 minutes. Subsequently, the tensile strength declined, and the time to failure increased rapidly, becoming about 3000 minutes after 18 hours of overaging. The true period of stress corrosion was found to be about 5 minutes for the -T6 temper and during the first 6 hours of overaging from the -T6 temper. It then decreased. This sequence suggested that the beneficial effects noted in going from the -T6 to the -T73 temper are not the result of improvement in resistance to true stress corrosion, but the result of an improvement in the mechanical properties of the alloy, so that it is less sensitive to notch effects produced by pure corrosion.

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CORROSION OF STAINLESS STEELS

Oxidation

A review of the high-temperature corrosion behavior of stainless steels has been prepared by Falconbridge Nickel.⁽⁸⁾ Data from the published literature, company laboratory and field tests, and commercial plant experience are summarized. Included is information on the resistance of stainless steels to high-temperature gases found in industrial operations, e.g., air, carbonaceous gases, steam, sulfur dioxide, hydrogen sulfide, hydrogen, and ammonia. Also included are reactions by molten metals and molten salts and a section on fuel-ash corrosion.

Aqueous Corrosion

The effect of uranium and molybdenum alloying additions on the corrosion behavior of ferritic Type 430 stainless steel has been investigated at the Canadian Department of Energy, Mines, and Resources.⁽⁹⁾ Alloying levels were 0.24 and 0.55 wt% uranium and 1.02 and 2.03 wt% molybdenum. Tests were conducted in 1N solutions of H_2SO_4 and HCl at 75 to 158 F and as crevices in 3 percent NaCl at 122 F. Both the uranium and molybdenum alloy additions improved the corrosion resistance with the molybdenum being slightly better. No appreciable benefit of these alloying additions was observed in tests conducted in 1N $FeCl_3$ at 75 and 158 F and in boiling 65 percent HNO_3 (Huey Test).

The effects of alloying additions on the intergranular corrosion of nonsensitized austenitic stainless steel in boiling nitric acid-dichromate solution has been reported by the General Electric Nucleonics Laboratory.⁽¹⁰⁾ Controlled additions of carbon, nitrogen, oxygen, manganese, sulfur, silicon, and phosphorus were made to a high-purity Fe-14Cr-14Ni alloy. Of the elements studied, only phosphorus (>100 ppm) and silicon (>1000 ppm to <20,000) promoted intergranular attack in nonsensitized specimens exposed to boiling 5N HNO_3 - 0.46N Cr^{+6} solution. The adverse effect of these elements was explained in terms of a solute segregation mechanism in which phosphorus and silicon are adsorbed at grain boundaries.

Passivation in crevices during anodic protection of stainless steels has been reported by Rensselaer Polytechnic Institute.⁽¹¹⁾ In long narrow crevices, internal portions of the crevice often were found to remain active resulting in rapid localized corrosion. The crevice potential was not an absolute value, but depended on crevice dimensions as well as anodic polarization characteristics. The Fokin Timonin equation for analyzing potential distribution along thin wires polarized in relatively large-diameter tubes also was found to accurately predict the length of the passive zone in partially protected narrow crevices.

Electrochemical polarization techniques have been used to study the corrosion behavior of Type 304 stainless steel and carbon steel in deoxygenated 554 F water by General Electric Nucleonics Laboratory.⁽¹²⁾ Excellent agreement was obtained between corrosion rates obtained gravimetrically and those obtained by linear polarization techniques. Corrosion rates determined by these techniques were linear after the first 100 to 250 hours' exposure.

These linear rates were 0.15 and 0.11 mg/dm²-hour for carbon steel and stainless steel, respectively.

Stress-Corrosion Cracking and Embrittlement

The stress-corrosion-cracking behavior of high-purity 18/10 stainless steels in boiling $MgCl_2$ is being studied by the French.⁽¹³⁾ The beneficial effect of martensite in the steel's microstructure on prolonging time to failure was attributed to cathodic protection of the austenite by the martensite. Solution potential measurements revealed that the martensite was electronegative (anodic) to the austenite. Metallographic studies indicated that the martensite was corroded but that the austenite was unattacked.

Helium embrittlement of Type 304 stainless steel has been studied by Atomics International in connection with nuclear reactor operation where neutrons transmute residual boron in the stainless steel to helium and lithium.⁽¹⁴⁾ Helium was uniformly injected into small tensile specimens by irradiation with a beam of alpha particles produced by a cyclotron. Concentrations of 1×10^{-7} and 3×10^{-5} atom fraction of helium produced a progressive ductility loss with increasing temperature in tensile tests above 1000 F. Loss of ductility was associated with premature intergranular cavitation originating at grain-boundary carbide particles presumably through the action of grain-boundary sliding. The role of helium apparently was to form bubbles on the carbide particles thus reducing the amount of grain-boundary sliding needed to create a void.

CORROSION OF MAGNESIUM ALLOYS

The oxidation of magnesium and magnesium-beryllium alloys in steam and moist air at 520 to 580 C (968 to 1076 F) has been reported by Russian scientists.⁽¹⁵⁾ Protective oxide films formed on the magnesium-beryllium alloy at a parabolic rate at the start of oxidation. However, the alloy was rapidly saturated with hydrogen. Molecular hydrogen liberated at internal defects exerted high pressure causing pore formation and eventual disintegration of specimens. This mechanism of failure is similar to that which has been proposed for aluminum alloys in high-temperature water.

CORROSION OF NICKEL- AND COBALT-BASE ALLOYS

The degradation of oxides on superalloys as a source of oxygen contamination in gas-loop environments has been demonstrated at Battelle-Northwest.⁽¹⁶⁾ Oxides formed on superalloys at 1000 C (1832 F) were easily degraded in inert (10^{-4} torr vacuum) or reducing (0.02 torr hydrogen) atmospheres at 1100 C (2012 F). Experiments with preoxidized Hastelloy X (13.8 mg oxygen total) and columbium in a container with 80 torr hydrogen at 1100 C produced a weight gain of 26.9 mg on the columbium and a weight loss of 26.1 mg on the Hastelloy X. The weight gain of the columbium was attributed to pickup of contaminants in the system plus the oxygen from evaporation of the oxide on the Hastelloy.

The cyclic oxidation of nickel-iron- and cobalt-base alloys has also been studied by Bendix.⁽¹⁷⁾ Specimens representing 12 different alloys were exposed for 600 hours in cycling tests from room temperature to 1400, 1600, 1800, 2000, 2100, and 2200 F.

Six alloys showed optimum behavior based on oxidation and spalling resistance and mechanical and fabrication properties. They were:

ID Nickel-Chromium (Ni-20Cr-2ThO₂)
 DH 242 (Ni-20Cr-1Cb)
 Chromel A (Ni-20Cr)
 Bendel 65-35 (Ni-35Cr-3Al₂O₃·MgO spinel)
 Hastelloy X (Ni-22Cr-18.5Fe-9Mo-1.5Co)
 Udimet 500 (Ni-19Cr-19.5Co-4Mo-3Ti-3Al).

Iron-chromium-aluminum alloys also exhibited excellent oxidation and spalling resistance, but had lower ductility retention.

The effects of additions of 0.1 to 0.2 at.% yttrium, gadolinium, lanthanum, cerium, thorium, and 0 to 0.8 wt% manganese to René 100 on its oxidation resistance is being studied by General Electric Materials Development Laboratory.⁽¹⁸⁾ Cyclic tests at 1800 F revealed that yttrium, gadolinium, manganese, yttrium plus thorium plus manganese and lanthanum plus manganese additions improved oxidation resistance. Cyclic tests at 2000 F also indicated that yttrium and gadolinium were favorable additions, but that manganese additions promoted catastrophic oxidation. Hot salt corrosion tests of 50 hours in 1700 F air containing 100 ppm Na₂SO₄ + NaCl and flowing at 75 ft/sec revealed that lanthanum, cerium, and gadolinium additions of 0.1 at.% or greater reduced the extent of attack of René 100 by a factor of 10 to 30.

Metal cladding to protect a Cr-5W-0.1Y alloy from oxidation has been studied at Battelle-Columbus.⁽¹⁹⁾ The cladding alloys were Ni-30Cr, aluminized Ni-30Cr, and aluminized Ni-20Cr-20W. All three cladding layers were resistant to oxidation at 2100 F, and all but the Ni-30Cr were resistant at 2300 F under the conditions studied. However, these claddings permitted nitrogen contamination of the substrate and also resulted in contamination of the chromium alloy by nickel. Barrier layers were investigated, but during cyclic oxidation, these showed varying degrees of cracking, which permitted contamination of the substrate. The most promising system examined contained an aluminized (5Al) Ni-20Cr-20W cladding layer 5 mils thick and a 1.5-mil-thick tungsten barrier layer.

CORROSION OF TITANIUM ALLOYS

Stress-corrosion-cracking and fracture-toughness studies have been conducted on 1-in.-thick plate of Ti-6Al-4V alloy at Aerojet-General.⁽²⁰⁾ As compared with mill-annealed material, a duplex heat treatment which produced an elongated platelet alpha in a beta matrix increased the threshold stress intensity for stress-corrosion cracking (K_{ISCC}) by about 70 percent and increased the apparent plane-strain fracture toughness (K_{IC}) by about 45 percent. A number of large stress-wave emissions were detected during stress-corrosion cracking in 3 percent NaCl. From this, it was concluded that crack growth was at least partially a jump process, and thus was not entirely a dissolution mechanism.

Fundamental studies on the stress-corrosion cracking of titanium and titanium alloys in methanol-iodine solutions are being conducted at RIAS.⁽²¹⁾ The stress-corrosion cracking of titanium and Ti-2.09Al alloy was concluded to involve preferential anodic dissolution at grain boundaries based on ob-

servations that: (1) anodic currents reduced the time to failure while cathodic currents inhibited failure, (2) the introduction of large quantities of water to the environment inhibited both corrosion and stress-corrosion cracking, and (3) corrosive attack in both stressed and unstressed specimens was intergranular. In titanium alloys containing greater than 5 wt% aluminum, intergranular dissolution appeared to be responsible only for the crack-initiation stage. This was followed by a transgranular failure which had the characteristics of a mechanical failure. Cathodic currents prevented the intergranular attack and the initiation of cracking.

Research is continuing at Du Pont Savannah River on the role of HCl gas in the hot-salt cracking of titanium alloys.⁽²²⁾ Reactions between titanium alloys and hot salt were found to produce significant amounts of HCl. The HCl gas also was found to cause cracking. Titanium reacted with HCl to produce TiCl₂, TiCl₃, TiCl₄, and hydrogen at 662 F. Also produced was Al₂Cl₆ when aluminum was present in the alloy. In the presence of moist air, hydrated aluminum chloride was formed, TiCl₄ was hydrolyzed, and TiCl₂ and TiCl₃ were hydrolyzed and oxidized to form TiO₂, HCl, and hydrogen. Fractographs of specimens cracked with NaCl, HCl, and SnCl₂ showed that the fracture mechanism was the same in all environments and was consistent with a stress-sorption process. The sorbing species is believed to be hydrogen.

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