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review

OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

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COATING DEVELOPMENT FOR COLUMBIUM ALLOYS

Results of an investigation on improving self-regenerative coatings for columbium involving zinc have been reported.⁽¹⁾ One approach was to add a third element (aluminum or nickel) to lower the vapor pressure of zinc. The temperature limit for oxidation resistance was raised about 150 F. Replacement of zinc by magnesium and addition of a third element (copper, nickel, iron, silicon, or antimony) were unsuccessful. Formation of $CbSi_2$ in a molten zinc-aluminum bath in the presence of 5% resulted in oxidation protection for 50 hours at 2400 F. Binary alloying of the substrate with up to 15 percent vanadium, 5 percent chromium, or 5 percent zirconium offered no improvement. However, addition of 10 to 15 percent titanium not only gave about a 10 percent increase in oxidation life, but also eliminated the "silicide pest" behavior at 1100 to 1650 F.

COATING DEVELOPMENT FOR CHROMIUM ALLOYS

Under NASA sponsorship, Chromalloy⁽²⁾ has investigated a variety of pack cementation aluminum-base coatings for the protection of Cr-5W-0.1Y sheet.⁽³⁾ Of the systems studied, a simple aluminum (Cr_5Al_8 - type) and iron-aluminum [$(Fe-Cr)_xAl_y$ - type] gave the best results. Under cyclic air oxidation, these systems survived over 600 hours at 2100 F, compared with 100 hours for the uncoated alloy. Oxidation life was about 200 hours at 2400 F. Under dynamic conditions of a mach 0.5 flame and 450 rpm rotation, the systems tended to fail in about 100 hours at 2100 F. Protectiveness of the systems was closely related to $AlCr_2O_4$ and $FeO-Al_2Cr_2O_4$ -type spinel formation which also limited nitrogen penetration. By causing substrate recrystallization, the coating process increased the bend ductile-brittle transition temperature (no cracks produced in a 90 to 105-degree bend) from about 500 to 800 F. However, the oxidation exposures raised the transition to above 1600 F, primarily because of aluminum diffusion into the substrate, and secondarily because of atmosphere contamination of the coating.

Also under NASA sponsorship, Battelle-Columbus has investigated protection of Cr-W-0.1Y⁽³⁾ using gas-pressure-bonded alloy foil.⁽⁴⁾ The outer 5 to 10 mil-thick layer consisted of Ni-30Cr or Ni-20Cr-20W which were modified with 3 to 5 percent aluminum in some cases. The study also included barrier layers of molybdenum, W-1ThO₂, W-25Re, and tungsten, with the latter being the most useful in preventing interdiffusion of nickel and chromium. Compatibility layers of platinum or vanadium

between the outer and barrier layers were not beneficial. The outer cladding layers gave cyclic oxidation resistance of over 600 hours at 2100 F and about 100 hours at 2300 F, with the aluminized Ni-20Cr-20W alloy giving the best performance. Rapid oxidation occurred at 2400 F. After exposure for 100 hours at 2100 F, the bend ductile-brittle transition temperature was a minimum of about 1000 F. After exposure at 2300 F, edge cracking was observed and the transition was over 1600 F. The mechanisms of embrittlement included metallic interdiffusion at 2100 F and by both interdiffusion and nitrogen contamination at 2300 F.

COATING PROTECTION FOR THERMIONIC DIODES

In its development of thermionic diodes for operation in hot oxidizing gases, Consolidated Controls is developing coatings for protecting refractory metals.⁽⁵⁾ Elimination of free silicon made possible an impermeable grade of pyrolytic SiC, which appears to be of adequate quality for use at 2550 to 2900 F in air as a barrier envelope. This material demonstrated the required thermal shock qualities, corrosion resistance, and adequate permeation levels. Also developed was a multi-element system consisting of iridium overlaid with CaO-stabilized ZrO₂ for protecting tungsten in air at 3600 F for 2 to 5 hours. The protection concept involved maintenance of a finite partial pressure of iridium oxide within the coating by impeding vaporization.

SPACECRAFT APPLICATIONS

Martin-Marietta has used coated columbium alloys in brazed honeycomb sandwich panels on the lower wing surface of a 1/3-scale model of a high L/D winged reentry vehicle, ASCEP.⁽⁶⁾ Vacuum brazing and coating D-43 alloy with pack cementation TiW Cr-Ti-Si seriously degraded the alloy. Substitution of Sylvania Si-20Cr-5Ti slurry coating gave better coating uniformity and reasonable oxidation protection. However, considerably more effort is required to develop a reliable material-coating system for flight applications.

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