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COATINGS FOR CHROMIUM ALLOYS

Three coating systems for protecting Cr-7Mo-2Ta-0.09C-0.1Y alloy were investigated by TRW. (1) The systems included titanium-modified chromium silicide, Cr-Ti-Si, formed directly on the substrate; Cr-Ti-Si formed on a barrier layer of chromium containing 6 and 12 volume percent MgO; and Cr-Ti-Si formed on a barrier layer of Cr-0.3Y containing 6 and 12 volume percent MgO. The barrier layer was formed by slurry-sinter or electrophoretic deposition, and the Cr-Ti-Si by pack cementation involving temperatures up to 2400 F. Coated and uncoated substrate specimens were oxidized in air for 200 hours at 2100 F under cyclic conditions. Specimens without barrier layers showed the least spalling. The nitrogen content of all specimens increased from nominally 0.0022 to 0.01 weight percent after exposure. The surface oxide on coated specimens after exposure was Cr₂O₃, sometimes containing TiO₂ and unidentified phases. Metallography indicated porosity around MgO particles and some instability during the coating process. The uncoated unannealed specimens were ductile in bending at 1090 F, while the coated and exposed specimens were brittle at 1420 to 490 F. An uncoated specimen given the coating thermal treatment in inert atmosphere was also brittle at 1490 F, and indicated that the relatively high temperature associated with the coating process could have produced the embrittlement. The results indicate that the coating concepts evaluated did not produce useful coatings for chromium alloys.

NASA also has funded three additional efforts involving coating protection of high-strength chromium alloys from oxidation and nitridation. (2-5) Preliminary results indicate that Cr-Y₂O₃ mixtures show promise for protecting chromium alloys for at least 100 hours at 2100 F in air. (3)

COATING EVALUATION

Nondestructive test methods for characterizing coated refractory metals are under investigation by General Dynamics. (6) Preliminary results of a radionuclide tag study to incorporate inherent radiation-emitting properties indicate (1) autoradiography can provide a detailed and high resolution picture of the coating and probably show distribution of heavy elements, and (2) direct counting can provide a measure of coating thickness. The test involved Cb-752 columbium alloy coupons coated with Vac Hyd fused silicide, Si-Hf-Cr-Fe (VH-101), containing promethium-147 in a La₂O₃ carrier. Radio-

active loading was 0.02 $\mu\text{c}/\text{cm}^2$ which could be safely increased several orders of magnitude. The feasibility of using Mössbauer spectroscopy for measuring coating life also was discussed.

HARDWARE EVALUATION

In an in-house program, General Dynamics has designed, fabricated, and tested two columbium-alloy structures typical of those used in Space Shuttle Vehicles. (7) The first was a control surface representing a hot load-carrying structure, and the second a heat shield and support structure representing a radiative thermal-protection system. The first consisted primarily of Cb-752 columbium alloy coated with TRW Cr-Ti-Si, and the second, C-129Y columbium alloy coated with Vac Hyd fused silicides Si-Hf-Cr-Fe (VH-101) and/or Si-Hf-Ta-Cr-Fe (VH-109). The control surface or elevon was cyclicly tested in a hot-gas-flow facility for 15 cycles to a peak temperature of 2475 F with accumulated time above 2000 F of about 5.3 hours. The gases were air/hydrogen and oxygen/hydrogen at low pressure and subsonic velocity. The heat shield was cyclicly tested in a radiant heat lamp reduced-pressure chamber to 2470 F. The accumulated time above 2000 F for 42 cycles was about 15.3 hours. The coatings were evaluated for thickness, uniformity, and integrity using electron-emission-radiography, eddy-current, and thermoelectric techniques. Although there were minor imperfections, the structures were essentially sound. The main difficulty experienced was that rivets had to be repeatedly repair coated. Also, a coating breakdown occurred on the sharp-radius trailing-edge section of the elevon.

Efforts have been made by McDonnell Douglas to extend the useful temperature limits of refractory metals by designing, developing, and evaluating representative, self-sustaining, radiative structures of coated tantalum alloys. (8) In particular, the objective was to test full-scale flat-panel and leading-edge components in simulated reentry flight conditions that would induce peak temperatures of 3500 F. Three substrates (T-222 tantalum, Ta-7W-3Re, Ta-10W-2.5Mo) and two coatings [Solar (95W-5Ti)-Si or TNV-13 and Sylvania W/WSi₂ or R516] were evaluated in various tensile, fatigue, and creep tests as well as in subscale panels. The substrate alloys behaved similarly, except that T-222 tantalum gave ductile welds and the others required ductilizing heat treatments. Lack of uniformity in the tungsten barrier layer eliminated the Sylvania R516 coating. The Solar TNV-13 coating was marginal in some tests and

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unacceptable in others, especially in simulated re-entry conditions at 3500 F. As a result, other fused slurry coatings including W/WSi₂ZrB₂, Sylvania Hf-Ta and HfB₂-Hf-Ta, Vac Hyd silicides, and Bodi Industries TaB₂ were evaluated, but these did not show sufficiently reproducible results to warrant consideration. Therefore, the temperature limit was lowered. The Sylvania Si-20Ti-10Mo or RS12C fused slurry coating was selected for further tests, since it qualified for 1-hour protection under simulated flight conditions up to 3000 F. The final effort consisted of analysis, design, and fabrication of a full-scale flat panel and a leading-edge component using T-222 tantalum coated with RS12C. In the near future, these will be tested in the Air Force Flight Dynamics Laboratory 50 Megawatt Electrogasdynamics Facility.

The protectiveness of refractory-metal coatings under chemical rocket environments has been studied by TRW with emphases on thermal environment, posttest metallurgical conditions, and useful service life.⁽⁹⁾ The coating/substrate systems evaluated included Hf-20Ta cladding or Hf-20Ta-0.25Si slurry on Ta-10W, W-HfO₂ plasma-sprayed composite, iridium or iridium-rhenium slurry on tungsten, and pack-cementation MoSi₂ on molybdenum. All tests were conducted at ambient sea-level conditions utilizing the propellant combinations N₂O₄/N₂H₄ and/or a N₂H₄/H₂O blend to give combustion temperatures of 3300 to 4700 F, generally for 10 and 1000 seconds. The silicide-coated molybdenum nozzles had the best overall performance, but had a melting point limitation of 3200 F. The other coatings showed considerable promise for protection above 4000 F, pending resolution of fabrication difficulties. Preoxidation or nitriding of the Hf-Ta coatings produced no improvement in performance.

GENERAL

A summary report on high-temperature oxidation-resistant coatings has been prepared by the National Materials Advisory Board.⁽¹⁰⁾ Coatings for superalloys, refractory metals, and graphite were described from the points of view of fundamental principles, specific substrates, and applications. General and specific conclusions were reached and were followed by recommendations for upgrading coatings capabilities. Areas of interest included gas turbines, hypersonic vehicles, chemical propulsion, energy conversion, and industrial applications. At present, the major use of coated refractory metals appears to lie in the area of hypersonic vehicles for which the panel reached the following conclusions:

- (1) The current generation of coatings is adequate for existing and near-term future applications.
- (2) The reuse capability of coated parts will extend to one or two flights. Current test and performance data are inadequate for making a better assessment of reuse capability.
- (3) Coated columbium alloys are limited to a 2500 F maximum temperature (coating life-time of 150 to 200 hours) by inadequate creep resistance and not coating technology.

DMIC Reviews of Recent Developments present brief summaries of information which has become available to DMIC in the preceding period (usually 3 months), in each of several categories. DMIC does not intend that these reviews be made a part of the permanent technical literature. Copies of referenced reports are not available from DMIC; most can be obtained from the Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314.

- (4) Satisfactory coatings do not exist for use on molybdenum or tantalum alloys above 3000 F or on tungsten above 3500 F. Further work on silicide-base coatings to extend the service temperature is not warranted, and a new approach to coating must be taken.

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