**NEW LIMITATION CHANGE**

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**AUTHORITY**

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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. (4)

The systems included titanium-modified chromium silicides, 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-0.4Y containing 6 and 12 volume percent MgO. The barrier layer was formed by slurry-sinter or electrophoretic deposition, and the Cr-Ti-Si layer 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 CrO3, sometimes containing TiO2 and unidentified phases. Metallography indicated porosity around MgO particles and some instability during the coating process. The uncoated annealed specimens were ductile in bending at 1090 F, while the coated and exposed specimens were brittle at 1420 to 1490 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 were promising, but 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-YO3 mixtures show promise for protecting chromium alloys for at least 100 hours at 2100 F in air. (5)

COATING EVALUATION

Nondestructive test methods for characterizing coatings 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 testing can provide a measure of coating thickness. The test involved Cr-7523 in an air, 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 repaired 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. (6) 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 [55S-Si] or TNV-13 and Sylvania [71815] 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
unacceptable in others, especially in simulated re-entry conditions at 3500 F. As a result, other fused coating systems including W/MSi1.2-2W2, Sylvanite Hf-Ta and HfB2-Hf-Ta, Vac Hyd silicides, and Bodi Industries Hf-Ta were evaluated, but these did not show sufficiently reproducible results to warrant consideration. Therefore, the temperature limit was lowered. The Sylvanian Si-2071-10 or RSi2C fused 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 RSi2C. 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 emphasis on thermal environment, post-test metallurgical conditions, and useful service life. (3) The coating/substrate systems studied included Hf-20Ta cladding or Hf-20Ta-0.25Si. Slurries on Ta-10W, W-HfO2 plasma-sprayed composite, iridium or iridium-rhenium slurry on tungsten, and pack-cementation MES12 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 coating 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.
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.

REFERENCES