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review

OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

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COATINGS FOR TANTALUM ALLOYS

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Many coating systems have been explored by TRW for the protection of Ta-10W and T-222 tantalum alloys from air oxidation up to 4000 F. (1) Among those explored were five vendor applied coatings which performed as follows. Sylvania Hf-20Ta-0.25Si (RS15) and RS15 + 2Al coatings showed some edge failures at 2400 F and general failure at 3500 F. Premature failure occurred in an experimental IIT Research Institute W/Ir slurry coating, perhaps because of insufficient optimization. Sylvania-TRW W/Si-W duplex coating was protective for about 10 hours at 2400 F and 5 minutes at 3500 F, but appeared to suffer peeling failure at 2000 F. Solar 95W-Sti/Si (TNV-13) duplex coating was protective for 80 to 90 hours at 2400 F, but failed at edges in less than 5 minutes at 3500 F.

A duplex W-Ti/Si-W slurry-sinter coating also was evaluated by TRW. This coating resulted in irregular thicknesses because it had been applied by manually spraying, and it gave only marginal protection. Electrochemically depositing tungsten and titanium gave a significant improvement in oxidation life but edge and corner failures still occurred in less than 30 hours at 2500 F and in less than 5 hours at 3100 F. Protective oxide layers derived from coatings based on hafnium, hafnium-titanium, and titanium-chromium-hafnium also were investigated. Protection in these cases was generally limited to 3000 F. The best system, Cr-Ti-Hf-Mg-Si, gave 48 hours' protection at 2400 F and 2 minutes protection at 3500 F. Metal-bonded refractory oxide coatings, chromium coated MgO, and tungsten-coated HfO₂, could not be satisfactorily applied because of lack of sintering at temperatures in the 2800 to 3200 F range on precoated substrates.

COATING EVALUATION

The results of a 3.5-year investigation of a continuing program on emittance of coated refractory metals have been reported by North American Rockwell. (2, 3) In the studies, the environments used were 0.01 to 760 torr air at 1400 to 3000 F, chosen to simulate hypersonic flight conditions. Total normal and spectral normal emittance was measured using the sliding-specimen technique, which did not involve the use of attached thermocouples. Details of the furnaces, measuring equipment, and calibrations were reported. Total normal emittance values agreed closely with those found by integrating spectral curves over blackbody distributions. According to representative values to 2500 F given

in Table 1 for four coating systems, total normal emittance tended to increase with increasing temperature. Pressure generally did not affect the results except for the reduction caused in the W-3/TZM system at 0.01 torr. For this case, further preliminary measurements indicated little emittance change in the temperature range 2600 to 3000 F. There was usually no relationship between surface roughness and emittance except in the case of the Sn-Al-Mo-Ta-10W system which showed some correlation in the as-received condition (i.e., emittance increased linearly with increasing surface roughness). Total-hemispherical-emittance measurements were made on Cr-Ti-Si, W-3, and Sn-Al-Mo coatings at 1400 F after aging at 3000 F at 760 torr. The values averaged 6 percent higher than corresponding total-normal-emittance values. After exposure, surface composition was determined by X-ray diffraction and oxide film thickness was measured by microprobe. The results were discussed in terms of total-normal- and spectral-normal-emittance results.

The study of nondestructive test methods for detection of coating variability and failure mechanisms in coated refractory metals and superalloys is continuing at Avco. (4) Eddy-current and thermoelectric tests have been applied to Si-20Cr-5Ti (RS12A)-coated B-66 columbium-alloy vanes used by Pratt and Whitney in their engine-testing program. (5) The integrity of the coating was assured by tests during coating in the green stage and after fusion. Eddy-current, thermoelectric, and X-ray backscatter tests have been applied to a number of nickel- and cobalt-base superalloys with chromium-aluminum coatings. As yet, the variables noted have not been correlated with failure sites or failure modes after high-temperature cycling.

The "silicide pest" has been studied in the Solar (50W-20Mo-15V-15Ti) Si₂/Ta-10W coating system. (6) The coating was protective for over 200 hours in air flowing at 20 cm/sec at 1700 to 1900 F, but failed in several hours at 1400 to 1600 F because of spalling and breakaway oxidation. Preoxidation for 5.5 hours at 1900 F rendered the coating protective for over 200 hours at 1400 to 1600 F.

HARDWARE EVALUATION

Seventy-five throat inserts involving various coated refractory systems, refractory composite materials including graphites, carbides, and oxides, and nine complete nozzle designs have been evaluated by NASA-Lewis for ablative rocket engines. (7)

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TABLE 1. TOTAL NORMAL EMITTANCE OF COATED REFRACTORY METALS AS A FUNCTION OF PRESSURE AND TEMPERATURE²

Air Pressure, torr	Total Normal Emittance					
	1400 F		2000 F		2500 F	
	Held 1 hr	Held 3 hr	Held 1 hr	Held 3 hr	Held 1 hr	Held 3 hr
<u>TRW Cr-Ti-Si/Cb-752</u>						
0.01	--	--	0.54	0.68	0.86	0.89
0.1	0.43	0.45	0.71	0.75	0.89	0.90
5	--	--	0.67	0.79	0.90	0.80
100	0.46	0.47	0.63	0.80	0.86	0.87
760	0.48(a)	0.47	0.74	0.83	0.86	0.86
<u>Chromalloy W-3/Mo-TZM</u>						
0.01	--	--	0.37	0.39	0.51	0.59
0.1	0.44	0.43	0.65	0.67	0.80	0.82
5	0.44	0.45	0.56	0.59	0.71	0.71
100	0.47	--	0.56	0.60	0.65	0.69
760	0.50	0.49	0.61	0.66	--	0.70
<u>Sylvania Sn-26.5Al-5.5Mo (R505F)/Ta-10W</u>						
0.01	0.51(a)	--	--	--	0.77	0.90
0.1	--	--	0.68	0.56	--	--
5	--	--	0.67	0.86	0.76	0.74(a)
100	--	--	0.91	0.89	0.77	0.79
760	0.54(a)	--	0.90	0.90	0.77	0.78
<u>Sylvania Si-20Cr-20Fe (R512E)/Cb-752</u>						
0.01	--	--	0.88	0.87(a)	0.76	0.92
0.1	0.76	0.84	0.93	0.93	0.79	0.91
5	--	--	0.92	0.92	0.85	0.89
100	0.77	0.76	0.85	0.83	0.84	0.89
760	0.71(a)	0.78	0.79	0.78	0.82	0.86

(a) Integrated from spectral curves.

The storable propellant consisted of nitrogen tetroxide and a 50 percent blend of unsymmetrical dimethylhydrazine with hydrazine. The object was to develop materials and design concepts capable of surviving a duty cycle consisting of seven cycles totalling 700 seconds. The normal engine operation included an oxidant-to-fuel mixture ratio of 2.0, a throat-surface temperature of about 4000 F, a chamber pressure of 100 psi, and an initial throat diameter of 1.2 inches. Of the coated refractory systems studied, a semi-impervious coating of iridium and rhenium on tungsten gave better results than did plasma-sprayed and gas-pressure-bonded oxide coated Mo-TZM or pyrolytic graphite, ZrC, SiC, or iridium-coated graphite. Of the refractory composites tested, those containing ZrO₂ or HfO₂ modified by wire reinforcement or stabilized with additions were the most successful. The only material to complete the duty cycle with no cracking and erosion of under 5 percent area change was a stabilized HfO₂-Mo macrolaminate composite.

GENERAL

Ten papers relating to the properties of refractory-metal alloys, with and without protective oxidation-resistant coating, were presented at The Sixth Plansee Seminar in Reutte, Austria.⁽⁸⁾ For reader convenience, the titles and authors of these papers are identified below:

- (1) Bückle, H., "Coating Problems", O.N.E.R.A., Paris, France.
- (2) Fitzer, E., Langseth, L. and Schichting, J., "Low-Temperature Siliconizing of Molybdenum", University of Karlsruhe, Germany.
- (3) Chao, P. J., "Application of Refractory-Metal Materials as Diffusion Barriers", Electronic Components, Harrison, N. J.
- (4) Fitzer, E. and Matthias, K., "Silicon Diffusion in Protective-Layer-Forming Silicide Phases of High-Melting Metals", University of Karlsruhe, Germany.
- (5) Fitzer, E. and Rainmuth, K., "The Reaction of High-Melting Silicides with Nitrogen and Oxygen", University of Karlsruhe, Germany.
- (6) Gadd, J. D., "Corrosion-Resistant Coatings for Refractory Metals and Superalloys", TRW Inc., Cleveland, O.
- (7) Koss, P. and Rotter, K., "The Dendritic Growth of Mo, Nb, and Ta Deposits from the Gas Phase", Österreichische Studiengesellschaft für Atomenergie.
- (8) Shroff, A. M., "Vapor Deposition of Refractory Metal", Compagnie Générale de Telegraphic Sans Fil, Corbeville/Orsai.
- (9) Roberts, L. W., "The Properties of CVD Deposits of W and W-Re Alloys", Livermore Calif.

- (10) Stecher, P., Lux, B., and Funk, R., "The Protection of Niobium Alloys Against Oxidation", Battelle Institute, Geneva, Switzerland.

REFERENCES

- (1) Kmiecik, H. A., and Gadd, J. D., "Development and Characterization of High Temperature Coatings for Tantalum Alloys", Final Report AFML-TR-69-195, TRW Inc., Cleveland, O., Contract AF 33(615)-5011 (December 1969).
- (2) Bartsch, K. O., Kimball, L. G., and Hudgins, W. P., "The Role of Emittance in Refractory Metal Coating Performance, Part II -- Total and Spectral Emittance Measurements to 2500° F", Report AFML-TR-66-55, Part II, North American Rockwell Corporation, Los Angeles, Calif., Contract AF 33(615)-3039 (April 1969).
- (3) Bartsch, L. O., Kimball, L. G., and Hudgins, W. P., "The Role of Emittance in Refractory Metal Coating Performance, Part III -- Total and Spectral Emittance Measurements Above 2500° F and Correlation of Emittance with Composition", Report AFML-TR-66-55, Part III, North American Rockwell Corporation, Los Angeles, Calif., Contract AF 33(615)-3039 (November 1969).
- (4) Stinebring, R. S., "The Development and Application of Nondestructive Testing Techniques for Evaluating High Temperature Protective Coatings", Report AFML-TR-69-218, Avco Government Products Group, Lowell, Mass., Contract F33615-68-C-1528 (December 1969).
- (5) Geyer, N. M., "Successful Engine Test of Coated Columbian Turbine Vanes", Research Technology Briefs, No. 4, 114 (April 1969).
- (6) Falco, J. J. and Levy, M., "Alleviation of the Silicide Pest in a Coating for the Protection of Refractory Metals Against High Temperature Oxidation", Report AMMRC TR 69-30, Army Materials and Mechanics Research Center, Watertown, Mass. (December 1969).
- (7) Winter, J. W. and Peterson, D. A., "Development of Improved Throat Inserts for Ablative Rocket Engines", Report NASA TN D-4964, NASA, Lewis Research Center, Cleveland, O. (July 1969).
- (8) Benesovsky, F., (Editor), High Temperature Materials, 703-921, papers presented at the Sixth Plansec Seminar June 24-28, 1968, Reutte, Austria, Metallwerk Plansee A. G., Reutte (1969).

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