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DMIC review OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

B. C. Allen November 5, 1969

COATING DEVELOPMENT

In its continuing coating development and evaluation program, Solar investigated a series of silicided molybdenum-tungsten-titanium-vanadium modifier alloys for their ability to protect T-222 tantalum and FS-85 columbium, Table 1.(1) One of the better modifier alloys, 20Mo-50W-15Ti-15V, yielded a silicide coating that provided protection (1) in cyclic (room temperature to 2400 F) furnace oxidation for over 800 hours at 2400 F in air, (2) up to 10 hours at 1600 and 2400 F after ballistic impacting at 170 ft/sec at room temperature or at 1600 F, (3) during 22 slow thermal cycles from 850 to 2300 F, and (4) in oxidation-erosion rig tests at mach 0.85 at 2400 F for over 200 1-hour cycles (room temperature to 2400 F) in JP-5 fuel and air. Bend and tensile tests on samples before and after exposures of 800 hours at 2400 F revealed that the 0.030-inch-thick substrates had considerable room-temperature ductility (1-T 90-degree bend or 10 to 20 percent elongation).

Coatings were applied by slurry spraying the metallic elements and hydrides, vacuum sintering, and then siliciding by pack cementation. Maintaining the oxygen content of the modifier under 0.2 percent by using vanadium and titanium hydrides was advantageous; maintaining the combined titanium plus vanadium near 30 percent in the slip produced a well-bonded and sintered coating. The coating was sintered at above 2400 F to remove a significant portion of those elements through vaporization ; however, retention of some vanadium was needed to prevent 1600 F failure. The addition of small amounts of iron, nickel, or palladium to promote activated sintering did not give satisfactory coatings for a sintering temperature of 2200 F. Coating uniformity was adequate for elemental powder sizes under 3 microns while prealloyed powder size could be as large as 12 microns. Dip coatings provided less protection than spray coatings, but offered potential for further development.

OXIDATION OF COATED COLUMBIUM ALLOYS

The oxidation behavior of silicided columbium-titanium alloys has been studied by United Aircraft.(2) Titanium-modified columbium disilicide coatings, prepared by pack siliciding columbium, Cb-5Ti, Cb-10Ti, and Cb-15Ti, were evaluated in air or argon atmospheres between 1470 and 2190 F. The oxidation resistance of the coatings increased as the titanium content of the substrate increased (as indicated in Figure 1). Oxidation resistance was related both to the composition of the oxide formed on the coating and to thermal crack formation. The titanium-modified disilicides were less diffusionally stable than $CbSi_2$. Above 1830 F, a titanium-rich ternary MSi phase formed in substantial amounts both as a dispersion within the MSi_2 phase and as a discrete layer between MSi_2 and M_5Si_3 layers in the coating. The MSi phase was less oxidation-resistant than MSi_2, and presented a potential failure mechanism above 2190 F.

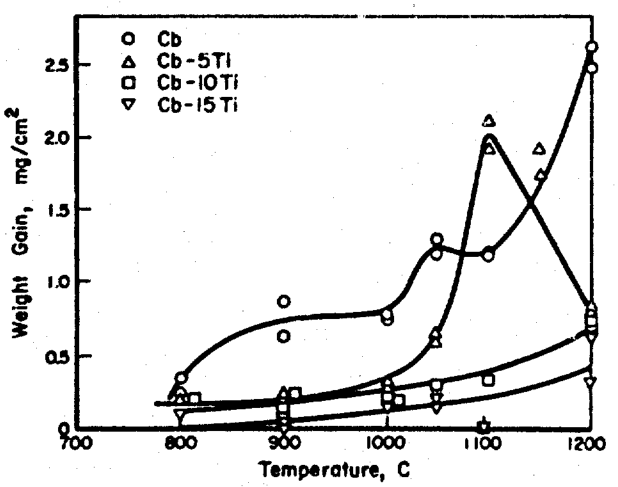

FIGURE 1. WEIGHT GAIN IN 10 HOURS FOR SILICIDED COLUMBIUM-TITANIUM ALLOYS IN AIR(2)

In part of its program on evaluating materials for aerospace systems, the University of Dayton Research Institute has investigated oxidation of coated refractory metals at pressures above 1 atmosphere.(3) A fused silicide coating, Si-20Cr-20Fe (Sylvania R512E), was applied to the inside of Cb-752 columbium-alloy tubing. Testing was accomplished by using 1-hour exposures at 3 and 5 atmospheres of nitrogen containing 10 or 20 percent oxygen at 2650 and 2800 F. No failures were noted at 2650 F, and nine of the sixteen specimens failed at the higher temperature. Although oxidation occurred more rapidly at higher pressures than at 1 atmosphere, failure mechanisms appeared similar. Relatively slow coating deterioration through $CbSi_2$ oxidation was followed by oxidation of the chromium and iron-rich sublayers. Eventually, a pin hole formed which led to rapid failure.

TABLE 1. FURNACE CYCLIC OXIDATION LIVES OF SILICIDE-COATED T-222 TANTALUM AND FS-85 COLUMBIUM(1)

Modifier Alloy Designation	Modifier Composition, wt.%					Sintering Time and Temperature, hr/F	Silicon Modifier Atomic Ratio	Maximum Oxidation Lives After Siliciding	
	Mo	W	Ti	V	Other			Hours at 1600 F	Hours at 2400 F
T-222 Alloy									
TNV-7	35	35	15	15	--	15/2760	--	> 630	> 1064
TNV-12	95.3	--	4.7	--	--	15/2760	--	> 659	947
TNV-13	--	95	5	--	--	15/2760	--	47	> 615
NS-1	35	35	15	15	--	15/2760	2.3	> 237	> 237
NS-2	35	35	10	20	--	15/2760	2.3	> 214	> 214
NS-3	35	35	20	10	--	15/2760	2.2	> 218	> 808
NS-4	20	50	15	15	--	15/2760	2.0	> 218	> 808
NS-5	50	20	15	15	--	15/2760	2.2	> 218	> 218
NS-6	40	40	10	10	--	15/2760	2.7	> 209	> 209
NS-7	45	45	5	5	--	15/2760	2.3	> 214	> 214
NS-8	40	40	5	5	--	15/2760	2.4	> 218	> 218
NS-9	42.5	42.5	--	15	--	15/2760	2.5	> 218	> 218
NS-10	70	20	5	5	--	15/2760	1.9	> 214	> 214
NS-11	33	33	14.2	14.2	5.6 Ni	1.5/2200	3.2	> 218	> 218
NS-12	35	35	14.5	14.5	1 Ni	1.5/2200	3.1	> 218	> 218
NS-13	35	35	14.5	14.5	1 Pd	1.5/2200	3.3	40	> 238
NS-14	15	65	10	10	--	15/2760	2.6	> 209	> 209
NS-15	15	65	15	5	--	15/2760	2.2	> 209	> 808
NS-16	15	65	15	--	5 Fe	15/2760	2.6	60	> 209
NS-17	28	42	15	15	--	15/2760	2.4	> 209	> 209
NS-18	20	50	20	10	--	15/2760	2.1	> 209	> 209
NS-19	41.5	41.5	15	--	2 Fe	15/2760	2.8	> 209	> 209
NS-20	42	42.5	15	--	0.5 B	15/2760	2.3	> 209	> 209
NS-21	68	20	5	5	2 Fe	15/2760	2.2	> 209	> 209
NS-22	69.5	20	5	5	0.5 B	15/2760	2.2	20	> 209
NS-23	15	63	15	5	2 Fe	15/2760	2.2	> 209	> 808
NS-24	15	64.5	15	5	0.5 B	15/2760	2.3	2	> 209
NS-3Fe	35	35	20	--	10 Fe	15/2760	2.5	80	> 209
NS-10Fe	70	20	5	--	5 Fe	15/2760	2.1	> 209	> 209
FS-85 Alloy									
NS-1	35	35	15	15	--	15/2760	2.3	> 209	> 800
NS-3	35	35	20	10	--	15/2760	2.2	> 209	> 209
NS-4	20	50	15	15	--	15/2760	2.3	> 209	> 800
NS-15	15	65	15	5	--	15/2760	2.2	> 209	> 209
NS-23	15	63	15	5	--	15/2760	2.2	121	> 209

HARDWARE EVALUATION

Boeing has described the results of research aimed at utilization of coated-columbium alloy components to aid in noise suppression on the SST turbojet gas-turbine engines.(4) Under take-off conditions with full afterburning, the exhaust gas temperatures from these engines can be in excess of 3000 F. This condition imposes service requirements on the sound-suppressor components that are exposed directly to the jet exhaust.

The most promising sound-suppressor consists essentially of a cluster of uncooled tubes mounted on a water- or air-cooled base plate. The number of tubes for the various design configurations ranges from 37 to 152 tubes per engine. In operation, the engine burns a kerosene-type fuel and air mixture which results in a slightly oxidizing gas exhausting from the tubes with a velocity near mach 1 and a maximum temperature in excess of 3000 F. The suppressor tubes will be exposed to rapid heating in the exhaust gas for a 3 to 5-minute cycle during each take-off. The initial goal for the suppressor-tube material is a 100-hour part life in 5-minute cycles.

Coated columbium was selected as the most promising material to meet these requirements. As substrate materials, both the C-103 (Cb-10Hf-1Ti) and the WC-3015 (Cb-28Hf-15W-4Ta-1Zr-0.1C) alloys are being used. As coatings, the TRW Cr-Ti-Si pack-diffusion coating was initially tried, but this has been dropped in favor of two proprietary Vac Hyd slurry-diffusion coatings, VH-101 and VH-109. Both are believed to be of the silicide type.

Several test models are being used to evaluate these materials. An early model incorporated a 37-tube cluster of Cr-Ti-Si coated, C-103 alloy tubes. This model was subjected to a "large number" of acoustic and performance tests at gas temperatures to 2800 F. After an undisclosed number of cycles, pinhole-type coating failures were observed in the form of small white columbium oxide spots on the outside of each tube. Since these failures were regarded as noncatastrophic, additional tests on this model with a 3000 F gas temperature have been scheduled.

Some 3000 F gas-temperature testing was completed on simple 3-tube-cluster models. One series used tubular alloy specimens of 3.2 inch length with an ID of 1.66 inches and a wall thickness of 0.050 inch. These were coated with a 4-mil layer of either VH-101 or VH-109 using a duplex coating process. Thirty-minute firing cycles were used during which a maximum outside tube-surface temperature of 2640 F was achieved, as determined by radiation pyrometry. Results from these tests are summarized in Table 2. Each of the coated tubes withstood from 15 to 34 cycles to initial coating failure and 8 or 9 additional cycles to structural failure (i.e., *tube perforation*). For all tubes, the mode of failure was similar: oxidation initiated on the outside in the hottest areas. Initially, one or more white oxide spots appeared; then with continued cycling, they progressed to a larger, dark, oxidized area and eventual perforation through the tube wall.

A longer, 3-tube model was also tested to determine the capability of coated columbium at the higher surface temperatures expected with full-scale sound-suppression components. Here, tubes of 9 inch length and 1.66-inch ID were tested in the 3000 F burner, and a bank of quartz lamps was added to simulate the minimum radiation-type-cooling conditions on the innermost rows of tubes in a full-scale suppressor. Two 15-minute test cycles at 3000 F were conducted during which the measured part surface temperatures were maintained at "greater than 2740 F and 2800 F", respectively. After the second cycle, coating failures (due to "exceeding the melting temperature of the coating") were observed on the inside of all three tubes. Again, coating failure was not catastrophic, and the researchers believed that additional cycles could have been accommodated prior to the structural failure of these tubes.

The study led to the conclusion that the columbium systems evaluated do not appear to have the performance capability of withstanding for long times the maximum gas temperatures at the primary nozzle which exceed 3000 F. "However, coated columbium remains a promising sound-suppressor material *for design concepts with lower gas temperatures* and for concepts involving some degree of active cooling." Also, investigations are continuing to identify coated columbium alloy systems with higher temperature capability, improved reliability, and longer lifetimes.

TABLE 2. RESULTS OF 3000 F BURNER TESTS OF COATED-COLUMBIUM-TUBE MODELS(4)

Coating	Alloy	No. of 30-Minute Cycles to Initial Coating Failure	No. of 30-Minute Cycles After Coating Failure to Tube Failure
VH 109	C-103	34	Not tested
VH 109	C-103	24	9
VH 109	C-103	15	8
VH 109	C-103	28	Not tested
VH 109	C-103	25	Not tested
Duplex VH 101	WC 3015	22	9

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