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REVIEW OF RECENT DEVELOPMENTS ON OXIDATION-
RESISTANT COATINGS FOR REFRACTORY METALS

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DEFENSE METALS INFORMATION CENTER
BATTELLE MEMORIAL INSTITUTE
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REVIEW OF RECENT DEVELOPMENTS ON OXIDATION- RESISTANT COATINGS FOR REFRACTORY METALS

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This memorandum reviews developments on oxidation-resistant coatings for molybdenum, tungsten, and their alloys, as reported in information received by DMIC during the period from August through October, 1961.

COLUMBIUM

Both silicide-base and aluminide-base coatings continue to receive attention for protecting columbium alloys.

Indications of room-temperature ductility in a silicide-coating on FS-82 columbium alloy have been observed at the Boeing Company.(1)** Panels coated by the fluidized-bed technique were deformed by impact at room temperature. The coating showed no fracture and was subsequently protective at 2700 F. The coating ductility may be associated with the thinness of the coating (1 to 2 mils) and/or self-healing of microcracks at elevated temperatures.

Modified silicide coatings under development at the Pfaudler Company(2) have shown promise up to 3000 F. The protectiveness varies with substrate composition, as also shown recently by the Tapco Group.(3) Typical life ranges for the Pfaudler PFR-1 coating at 3000 F (apparent temperature) on FS-82 (Cb-34Ta-0.75Zr) and D-31 (Cb-10Mo-10Ti) columbium alloys are 0.5 to 0.75 hour and 2 to 4 hours, respectively.

Proprietary coatings from the American Machine and Foundry Company(4) also are protective at very high temperatures. Their AMFKOTE-3 coating, which may be applied by a variety of techniques including pack cementation and hot dipping, is protective to columbium in air for 10 hours at 2800 F and for 8 hours at 3000 F.

Coating of the prototype McDonnell Aircraft Corporation fin-rudder section has been successfully completed at the General Electric Company.(5) This complex section is constructed of F-48 alloy and was coated to a thickness of 3 to 4 mils with the LB-2 slurry aluminide coating. Evaluation of the section is incomplete at this time.

Modification of the straight LB-2 coating with silver appears to reduce the notch sensitivity of the coated F-48 alloy (Cb-15W-5Mo-1Zr-0.05C).(6) The silver may be plated before slurry coating or may be incorporated as powder in the slurry.

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**References are listed at the end of this memorandum.

The Tapco coating, which is silicide modified with chromium and titanium, has been tentatively selected by Republic Aviation Corporation⁽⁷⁾ to protect F-48 and Cb-74 (Cb-10W-5Zr) alloys in the Republic program on refractory metal fasteners.

TANTALUM

Recent data on protective coatings for tantalum are available from Air Force-sponsored studies at the Sylvania-Corning Nuclear Corporation and at Battelle Memorial Institute.

The Sylcor coating of Al-50Sn has previously been shown to possess excellent self-healing properties through the presence of a liquid tin-rich phase. In recent studies⁽⁸⁾, the coating was protective for several hours at 3100 to 3150 F with a plasma torch. Thus, the liquid phase appears not to affect the coating protectiveness under high-mass-flow conditions.

Recent Battelle studies⁽⁹⁾ indicate that manganese may be an attractive addition to silicide coatings. The manganese-modified coatings were significantly more protective to unalloyed tantalum than were straight silicide coatings. The glassy oxide produced on exposure was self-healing on Ta-10W and on one experimental alloy (Ta-30Cb-5V) at 2700 F, although no self-healing was observed on unalloyed tantalum.

MOLYBDENUM

The protective life and self-healing properties of silicide coatings on molybdenum may be significantly improved by alloying, according to recent information from American Machine and Foundry.⁽⁴⁾ Their AMFKOTE-2 coating, a heavily modified silicide applied by pack cementation, is protective in air for up to 9 hours at 3200 F and 40 minutes at 4000 F. This coating, which also exhibits good self-healing properties, is included in a comparative evaluation program currently being conducted by the NASA.

The Chromizing Corporation also is studying improved coatings for molybdenum.⁽¹⁰⁾ Its Durak B coating, a modified silicide, has a life expectancy in excess of 150 hours at 2700 F.⁽¹¹⁾

Application of pack-cementation silicide coatings in two cycles improves the protectiveness, according to studies at Chromalloy⁽¹¹⁾ and at Pfaudler⁽¹²⁾. The Chromalloy study, aimed at optimization of process variables for their chromium-modified silicide coating (W-2), showed that two-cycle processing for a total of 24 hours at 1900 F produces the most protective coating. The minimum life (95 per cent confidence) was established statistically as 18.1 hours at 2700 F.

The Pfaudler PFR-6 coating, a columbium-modified silicide, is applied by pack cementation for a total of 7 hours at 2050 F. Deposition in two cycles rather than one cycle increases the average life from 1.4 hours to 2.5 hours at 3125 F. The PFR-6 coating is resistant to accelerated "pest" oxidation at 1700 F and higher. This coating has been tentatively selected by Republic Aviation⁽⁷⁾ for protecting TZM and TZC molybdenum alloys in Republic's refractory-alloy fastener program.

TUNGSTEN

Studies on protective coatings for tungsten are currently in progress at General Telephone and Electronics Laboratories, Inc., and at Tapco.

Early results at GTE⁽¹³⁾ have shown lives in excess of 10 hours at 3300 F for tungsten wires in air protected with modified silicide coatings. The type and sequence of phases appearing during oxidation and factors affecting oxide adherence are also being considered in this study.

Titanium and zirconium-modified silicide coatings on tungsten are being evaluated at Tapco⁽¹⁴⁾, but performance data are not yet available.

REFERENCES

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- (2) Chao, P. J., Zupan, J., and Priest, D. K., "Recent Development of Oxidation Resistant Coatings at Pfaudler", presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (3) Jeffreys, R. A., and Gadd, J. D., "Development and Evaluation of High Temperature Protective Coatings for Columbium Alloys. Part I. Coating Development", ASD TR 61-66, Part I (May 31, 1961).
- (4) Withers, J. C., "Protective Coatings for Refractory Metals", presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (5) Dotson, L. E., "LB-2 Processing of the McDonnell F-48 Fin-Rudder Components", presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (6) Foldes, S., "An Oxidation Resistant Aluminide Coating on Columbium Alloy F-48", presented at Fall Meeting, Met. Society of AIME, Detroit, Michigan (October, 1961).
- (7) Republic Aviation, preliminary information under an Air Force contract.
- (8) Geyer, N. M., information presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (9) Klopp, W. D., and Ogden, H. R., "Protective Coatings for Tantalum and Tantalum Alloys", presented at Fall Meeting, Met. Society of AIME, Detroit, Michigan (October, 1961).
- (10) Commanday, M. R., information presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (11) Wachtell, R. L., "Activities of Chromalloy Corporation in the Development of Coatings for Refractory Metals", presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (12) Private communication from P. J. Chao, Pfaudler Company, Rochester, New York (October, 1961).
- (13) Pranates, A. L., Whitman, C. I., and Dickinson, C. D., "Protection of Tungsten Against Oxidation at Elevated Temperatures", presented at Refractory Composites Meeting, Dallas, Texas (August, 1961).
- (14) Nolting, H. J., et al., Tapco, preliminary information under an Air Force contract.

LIST OF DMIC MEMORANDA ISSUED
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Copies of the technical memoranda listed below may be obtained from DMIC at no cost by Government agencies and by Government contractors, subcontractors, and their suppliers. Others may obtain copies from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

A list of DMIC Memoranda 1-90 may be obtained from DMIC, or see previously issued memoranda.

DMIC Memorandum Number	Title
91	The Emittance of Titanium and Titanium Alloys, March 17, 1961, (PB 161241 \$0.50)
92	Stress-Rupture Strengths of Selected Alloys, March 23, 1961, (AD 255075 \$0.50)
93	A Review of Recent Developments in Titanium and Titanium Alloy Technology, March 27, 1961, (PB 161243 \$0.50)
94	Review of Recent Developments in the Evaluation of Special Metal Properties, March 28, 1961, (PB 161244 \$0.50)
95	Strengthening Mechanisms in Nickel-Base High-Temperature Alloys, April 4, 1961, (PB 161245 \$0.50)
96	Review of Recent Developments in the Technology of Molybdenum and Molybdenum-Base Alloys, April 7, 1961, (PB 161246 \$0.50)
97	Review of Recent Developments in the Technology of Columbium and Tantalum, April 10, 1961, (PB 161247 \$0.50)
98	Electropolishing and Chemical Polishing of High-Strength, High-Temperature Metals and Alloys, April 12, 1961, (PB 161248 \$0.50)
99	Review of Recent Developments in the Technology of High-Strength Stainless Steels, April 14, 1961, (PB 161249 \$0.50)
100	Review of Current Developments in the Metallurgy of High-Strength Steels, April 20, 1961, (PB 161250 \$0.50)
101	Statistical Analysis of Tensile Properties of Heat-Treated Mo-0.5Ti Sheet, April 24, 1961, (AD 255456 \$0.50)
102	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, April 26, 1961, (AD 255278 \$0.50)
103	The Emittance of Coated Materials Suitable for Elevated-Temperature Use, May 4, 1961, (AD 256479 \$2.75)
104	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, May 5, 1961, (AD 255659 \$0.50)
105	Review of Recent Developments in the Metallurgy of Beryllium, May 10, 1961, (AD 256206 \$0.50)
106	Survey of Materials for High-Temperature Bearing and Sliding Applications, May 12, 1961, (AD 257408 \$2.00)
107	A Comparison of the Brittle Behavior of Metallic and Nonmetallic Materials, May 16, 1961, (AD 258042 \$0.50)
108	Review of Recent Developments in the Technology of Tungsten, May 18, 1961, (AD 256633 \$0.50)
109	Review of Recent Developments in Metals Joining, May 25, 1961, (AD 256852 \$0.50)
110	Glass Fiber for Solid-Propellant Rocket-Motor Cases, June 6, 1961
111	The Emittance of Stainless Steels, June 12, 1961
112	Review of Recent Developments in the Evaluation of Special Metal Properties, June 27, 1961
113	A Review of Recent Developments in Titanium and Titanium Alloy Technology, July 3, 1961

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LIST OF DMIC MEMORANDA ISSUED
(Continued)

DMIC Memorandum Number	Title
114	Review of Recent Developments in the Technology of Molybdenum and Molybdenum-Base Alloys, July 5, 1961
115	Review of Recent Developments in the Technology of Columbium and Tantalum, July 7, 1961
116	General Recommendations on Design Features for Titanium and Zirconium Production-Melting Furnaces, July 19, 1961
117	Review of Recent Developments in the Technology of High-Strength Stainless Steels, July 14, 1961
118	Review of Recent Developments in the Metallurgy of High-Strength Steels, July 21, 1961
119	The Emittance of Iron, Nickel, Cobalt and Their Alloys, July 25, 1961
120	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, July 31, 1961
121	Fabricating and Machining Practices for the All-Beta Titanium Alloy, August 3, 1961
122	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, August 4, 1961
123	Review of Recent Developments in the Technology of Beryllium, August 18, 1961
124	Investigation of Delayed-Cracking Phenomenon in Hydrogenated Unalloyed Titanium, August 30, 1961
125	Review of Recent Developments in Metals Joining, September 1, 1961
126	A Review of Recent Developments in Titanium and Titanium Alloy Technology, September 15, 1961
127	Review of Recent Developments in the Technology of Tungsten, September 22, 1961
128	Review of Recent Developments in the Evaluation of Special Metal Properties, September 27, 1961
129	Review of Recent Developments in the Technology of Molybdenum and Molybdenum-Base Alloys, October 6, 1961
130	Review of Recent Developments in the Technology of Columbium and Tantalum, October 10, 1961
131	Review of Recent Developments in the Technology of High-Strength Stainless Steels, October 13, 1961
132	Review of Recent Developments in the Metallurgy of High-Strength Steels, October 20, 1961
133	Titanium in Aerospace Applications, October 24, 1961
134	Machining of Superalloys and Refractory Metals, October 27, 1961
135	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, October 31, 1961
136	Fabrication of Tungsten for Solid-Propellant Rocket Nozzles, November 2, 1961