Status of Coated Refractory Metals

ROGER A. PERKINS*
Lockheed Missiles & Space Company, Palo Alto, Calif.

An objective analysis of the capabilities and limitations of coated refractory metals is presented. In particular, experimental results for silicide-coated Mo alloys (and some Cb alloys) are discussed. It is shown that useful coating life can be predicted on the basis of the time required to complete the diffusion of silicon into the substrate to form intermediate and lower silicides (e.g., to form Mo_5Si_3). For $MoSi_2$ on Mo, the Arrhenius-type relation $t = [S_0/1140 \exp(-33{,}400/RT)]^2$ was found for coating failure, where t = time (minutes), S_0 = coating thickness (mils), and T = temperature (degrees Kelvin). Thus doubling S_0 gives a fourfold increase in coating life, and a ±100°F temperature variation from a nominal 2600°F also makes a fourfold change in life. Performance limitations due to temperature, pressure (maximun degradation occurs between 0.1 and 10 mm Hg), defect tolerance limit (cracks are self-healing up to a point), and structural stability are discussed. Problems are particularly severe on thin sheet.

Introduction

WITHIN the past three years, coatings based on compounds of Si, Al, Cr, and Ti have been improved to the point where adequate reliability and performance for high-temperature structural applications can be realized. Processes for applying coatings to complex parts and to assemblies have been devised and scaled up to semicommercial production levels. Good-quality parts have been produced and tested successfully in experimental aerospace powerplants and vehicles. Successful use requires careful matching of design features, manufacturing sequences, and service requirements to the characteristics of available coating systems. No one system has universal applicability, since many factors other than temperature govern the basic performance and useful life of coated parts. Even the best of coating systems has an imposing number of limitations with respect to design, manufacture, and use. Most of the problems in using coated refractory metals result from a failure to recognize and to live within their inherent limitations. This note presents an objective analysis of the capabilities and limitations of silicide-base coatings for refractory metals.

Performance Capabilities

The available performance data for specific coating systems are difficult to evaluate because of a lack of standardized testing procedures. Although coating compositions are standardized, uncontrolled variations in specimen geometry, specimen preparation, coating thickness, and testing conditions have produced a somewhat confusing picture of performance capabilities. The situation has improved in the past year, but much work remains to be done to characterize these materials accurately and adequately. Utility is judged first by the effect of the coating and its deposition process on the mechanical properties of the substrate alloy. Silicide-base coatings, in general, do not degrade significantly the tensile strength and creep or stress-rupture properties of refractory metal alloys. Some reduction can be found where the thermal cycle for coating deposition transcends the recovery or recrystallization range of sheet alloys that are strengthened by cold work. However, this problem largely has been overcome by the development of alloys having softening or recrystallization temperatures considerably above the coating deposition temperature.

Often, reductions in strength after coating may reflect changes in cross-sectional area rather than metallurgical changes of the substrate alloy. Apparent strength often is calculated on the original cross section of sheet material before coating. Since sheet thickness is decreased by 1 mil/side or more in forming the coating, strength values of a thin sheet will be considerably lower if calculated on original rather than on residual cross-sectional area. The effect of residual cross section assumes even greater importance when solid-state diffusion that occurs in use is taken into account. However, the most significant effect of coatings is on ductility at ambient temperatures. Heat effects of the coating thermal cycle and the coating per se (brittle surface layers) tend to raise the ductile/brittle transition temperature of many alloys. Mo-base alloys and certain Cb-base alloys may show brittle behavior in tension or bending at or near room temperature after coating. Virtually all alloys have reduced ductility in the coated condition.

The second utility criterion is useful service life in an oxidizing environment. Coating life usually is reported as the total length of time a coating can be held at a given temperature before failure occurs. This may involve either steady-state, high-temperature exposure or cyclic heating and cooling with short holding periods at the test temperature. Coating failure may be based on either localized or complete breakdown of the coating with resultant oxidation of the substrate. As a general rule, most coatings fail by localized attack at random defects such as cracks or fissures in the coating. Although the formation of one or more small holes may be classified as a coating failure, localized attack does not necessarily result immediately in structural failure. Continued use, however, eventually will lead to complete destruction of the part. Coating failures tend to be gradual rather than catastrophic, with the rate of substrate degradation after initial coating failure increasing with increased temperature.

In air at 1 atm, the useful life of silicide-coated refractory metals is governed primarily by temperature and coating thickness. Generalized curves for coated Mo, Cb, and Ta are given in Fig. 1a, which represents a variety of coating and substrate compositions, coating thickness, test parameters, and failure criteria.[1] The effect of coating thickness (1 to 3 mils/side) is shown indirectly by the range of life expectancy at any given temperature. Recent tests have shown that the average useful life for silicide-coated refractory metals tested in steady state at a given temperature is about the same for many different coating systems at comparable coating thickness.[2] (Coating modifications are more important in minimizing the formation of local defects that lead to premature coating failure.)

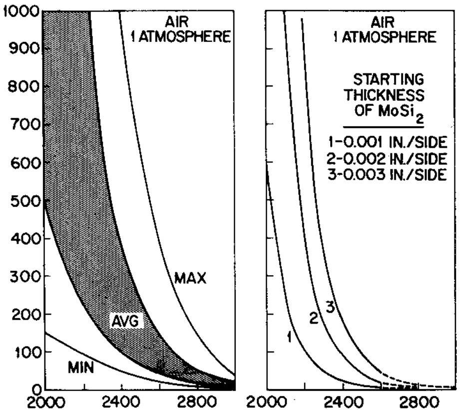
Presented as Preprint 64-357 at the 1st AIAA Annual Meeting, Washington, D. C., June 29–July 2, 1964; revision received January 15, 1965.

* Senior Staff Scientist.

These observations suggest that a common factor controls over-all performance. If this factor were known, it might be possible to obtain reasonable predictions of coating life for all silicide-base coatings as a function of temperature and thickness. Studies of $MoSi_2$ coatings on Mo have resulted in a new interpretation and more complete understanding of coating behavior that may provide the key to this problem.[3] The exponential nature of the curves in Fig. 1 indicates that a simple Arrhenius relation may govern the rate of oxidation of the silicides. These are known to be diffusion-controlled reactions and would yield relations similar to Fig. 1. Measured oxidation rates of compounds such as $MoSi_2$ are orders of magnitude too low[4] to produce these curves, but oxidation rates of intermediate and lower silicides (Mo_5Si_3, Mo_3Si) are very large and would predict a rather short life for coated metals. This suggests that useful life may be governed by the time required to convert the coating from the higher silicide ($MoSi_2$) to the next lower silicide (Mo_5Si_3) by diffusion. In other words, coating life would be determined by solid-state diffusion or interface reaction kinetics instead of an oxidation process.

As shown in Fig. 2, the structure and thickness of an $MoSi_2$ coating on molybdenum changes with use by diffusion of silicon into the substrate to form intermediate and lower silicides. Figure 2a shows a 1.65-mil coating, which is $MoSi_2$ from surface to substrate. After 15 min at 3000°F, coating thickness has increased to 2.4 mils with only a thin layer of $MoSi_2$ remaining near the surface. The bulk of the coating is now Mo_5Si_3 with a thin zone of Mo_3Si at the coating/metal interface. After 120 min, the coating has approximately doubled in thickness (3.5 mils) and has been converted completely to Mo_5Si_3 with a thin zone of Mo_3Si at the interface. This sequence of phase changes occurs in all silicide-base coatings on all refractory metals and alloys. The effect of this change on oxidation behavior is shown in Fig. 3. Here, a 1.7-mil coating of $MoSi_2$ on Mo has been converted completely to Mo_5Si_3 by diffusion in 2 hr at 3000°F. On subsequent heating in air at 2600°F, instantaneous failure occurs because of rapid oxidation of Mo_5Si_3 (Fig. 3a). At 2700°F and higher, this phase becomes more oxidation-resistant, and the substrate is protected (Fig. 3b). However, the coating fails instantaneously when the temperature subsequently falls below 2700°F (Fig. 3c). Thus, useful coating life can be predicted on the basis of time required to complete the change to Mo_5Si_3, which in turn will be a function of temperature. The following relation, which predicts time for complete conversion (t, minutes) as a function of initial coating thickness (S_0, mils) and temperature (T, degrees Kelvin), was determined experimentally for an $MoSi_2$ coating on Mo_2:

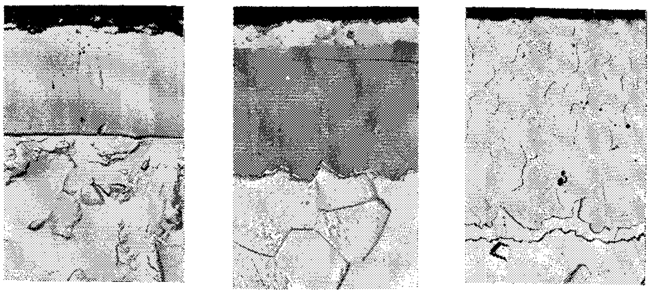
$$t = [S_0/1140 \exp(-33{,}400/RT)]^2 \qquad (1)$$



a) GENERALIZED CURVES FOR SILICIDE COATINGS ON Mo, Cb, AND Ta

b) PREDICTED MAXIMUM LIFE OF $MoSi_2$ COATINGS ON Mo

Fig. 1 Life expectancy of coated refractory metals.



a) As received **b) 30 min** **c) 120 min**

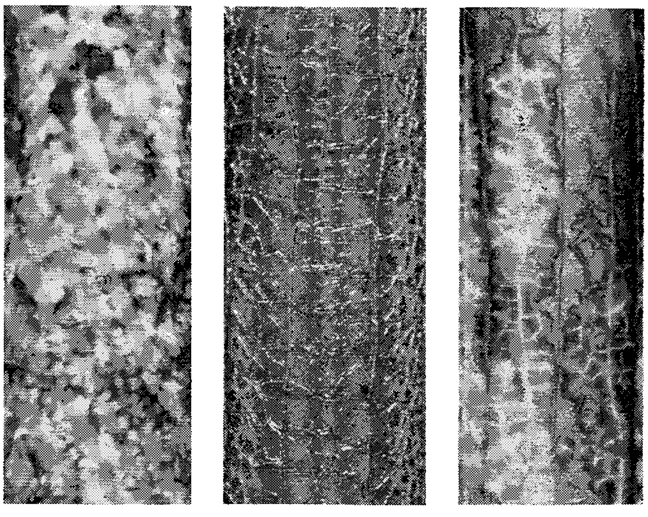
3000°F, air 760mm

Fig. 2 Effect of temperature on coating structure and thickness, $MoSi_2$ on Mo (×330).

This mechanism of coating failure clearly explains for the first time the important role that thickness has in determining coating life. Doubling coating thickness gives a fourfold increase in coating life. It also explains premature failure of coatings at defects, which reduce effective coating thickness in local regions. Figure 1b shows the predicted life of $MoSi_2$ coatings on Mo calculated from the preceding equation for thicknesses of 1, 2, and 3 mils. The good agreement with the "average" band in Fig. 1a tends to support the validity of Eq. (1). Similar relations can be derived easily for any given silicide-base coating system by means of solid-state-diffusion studies.

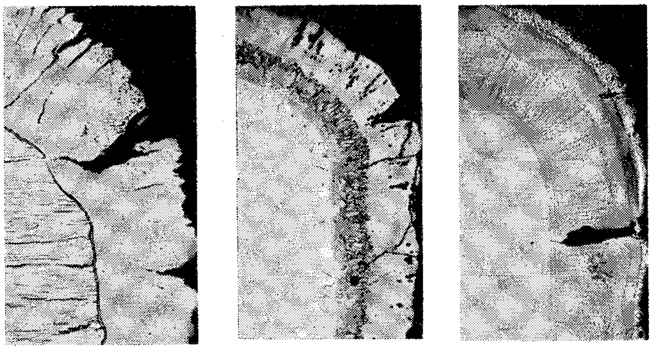
Coating limitations with respect to temperature are controlled by true operating temperature and not by an apparent measured or calculated temperature. Under radiant heating conditions, true temperature is determined by total hemispherical emittance of the surfaces (ϵ_H) which depends on temperature, environment, and surface condition. Temperature errors occur in using silicide coatings, because ϵ_H fluctuates in an unpredictable manner, and it is doubtful that true temperature during service can be estimated to better than ±100°F at temperatures above 2600° and ±50°F at lower temperatures. From Fig. 1b, a 2-mil $MoSi_2$ coating on Mo at a nominal temperature of 2600°F could have a useful life of between 10 and 40 hr if true service temperature were between 2700° and 2500°F. Obviously, minimum service requirements for parts must be considerably below minimum performance capabilities of coatings for good reliability.

A similar limitation arises from the inability to determine accurately the minimum coating thickness of finished parts.



a) 2600°F **b) 2700°F** **c) 3000°F 2 min at 2400°F**

Fig. 3 Failure of $MoSi_2$ coating on Mo after complete conversion to Mo_5Si_3 by diffusion (×10).

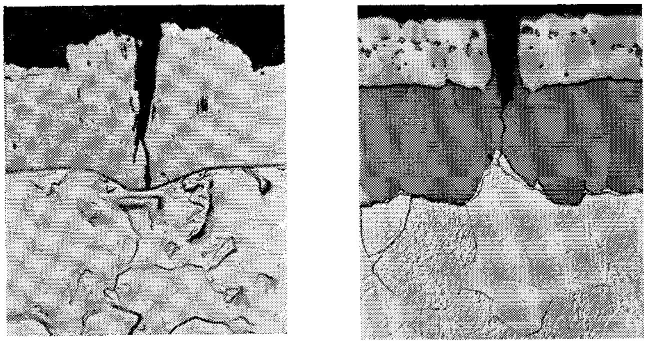


a) Deep edge **b) Shallow edge and subsurface** **c) Subsurface**

Fig. 4 Typical defects, silicide-coated Mo- and Cb-base alloys (×200).

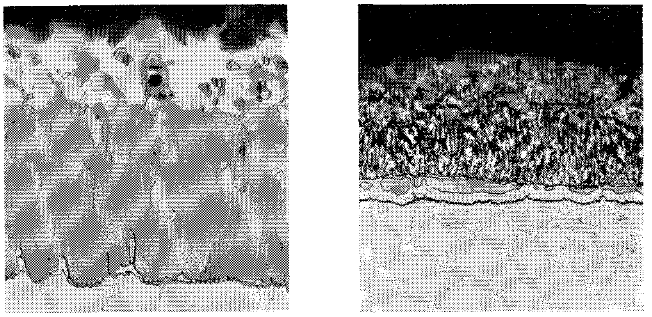
Two factors are involved: 1) nonuniformity and 2) local defects. For example, the thickness of a silicide-base coating on a sample of TZM (Mo-base) alloy was found to vary between 1.7 and 2.3 mils over a short distance along the surface.[5] Since coating life varies approximately as the square of coating thickness, the thinnest regions would have about $\frac{1}{2}$ the useful lifetime of the thickest regions at any temperature. This problem is difficult to solve; nondestructive methods for measuring coating thickness and thickness variations on complex parts have not been developed. It is necessary, therefore, to use a statistical approach based on destructive testing of samples. The problem of local defects is more serious; all silicide-base coatings contain cracks, voids, or fissures. Defects such as those illustrated in Fig. 4 are formed in deposition, not only at edges or corners, but also on flat or curved surfaces. Defects can also be formed during assembly or use by stressing the coating beyond its brittle fracture strength. The critical factor with respect to coating life is the relative width and depth of such defects. Narrow fissures can be healed effectively and generally do not degrade performance, but wide fissures cannot be healed at the surface and will degrade performance to an extent dependent upon the depth (Fig. 4).

The maximum size cracks that cannot be healed during use might be called the defect tolerance limit of the coating. Cracks larger than this shorten coating life, as shown in Fig. 5. A crack in the original MoSi$_2$ coating (Fig. 5a) penetrates about $\frac{2}{3}$ of the average coating thickness. In service, the Mo$_5$Si$_3$ formed by diffusion reaches the root of the crack before it reaches the surface (Fig. 5b). At 2600°F and below, rapid oxidation will occur at the crack root whereas the bulk of the coating, which has MoSi$_2$ at the surface, remains protective. Thus, the coating at this point behaves as if the effective thickness were the distance from the crack root to the substrate.



a) As received **b) 15 min, 3000°F**

Fig. 5 Reduction of effective coating thickness by local defects (×300).



a) 760 mm Hg
4 hr, 2708°F

b) 0.10 mm Hg
4 hr, 2600°F

Fig. 6 Low-pressure degradation of silicide-coated Mo-alloy (×400).

Defect tolerance limits have not been determined for any of the silicide-base coating systems. The effect of crack size on the relative degradation of coating life currently is under investigation for several promising systems.[5] However, even if such data were available today, it would be difficult to utilize. Nondestructive inspection techniques for measuring critical crack dimensions have not been developed. Visible surface cracks can be measured optically with calibrated microscopes. This technique, however, will not detect subsurface cracks like those shown in Figs. 4b and 4c. The problem, like the variation in coating thickness, must be approached today on a statistical sampling and testing basis. The severity of random defects can be minimized by selecting the best type of coating for a given substrate alloy, designing parts with generous radii at all edges and corners, applying a minimum thickness of coating, and controlling all stages of processing and assembly.

An important limitation on thin sheet is related to the *loss of substrate* by interdiffusion with the coating during use. For example, a 2-mil coating of MoSi$_2$ combines with 2 mils of substrate to form a 4-mil coating of Mo$_5$Si$_3$. If such a coating were applied to both sides of a 10-mil sheet, only 6 mils of substrate would remain after conversion to Mo$_5$Si$_3$. This would occur in less than 2 hr at 3000°F. In many cases if diffusion effects are not taken into account, coated parts can fail by tensile or creep during service at stress levels well below design allowables based on as-coated properties. Where stress is involved, maximum load-carrying capacity should be calculated on the basis of residual cross section that will exist near the end of the useful oxidation life of the part. This requires a knowledge of diffusion kinetics from which the rate of substrate loss as a function of temperature can be calculated. Equation (1) can be used to solve for S_0, the rate of substrate loss per side. Relations of this type are needed for other coating systems in order to design reliable light gage structures.

In many aerospace applications, a further limitation on the use of coated structures results from accelerated attack of silicide-base coatings in air at reduced pressure. This effect was first discovered for MoSi$_2$ coatings on unalloyed molybdenum.[6] Subsequent studies show that all silicide-base coatings on both Mo- and Cb-base alloys exhibit this behavior.[5] The nature of this effect is illustrated in Fig. 6, which compares the coating structure after testing at 2700°F in air at 1 atm and at 2600°F in air at 0.10 mm Hg. In the low-pressure test, almost all of the coating has been oxidized to a mixture of Mo sponge and glass, and the sample is on the verge of failure in 4 hr. At 1 atm, the coating would survive for at least 40 hr at 2600°F.

Preliminary results of tests on other systems reveal that the maximum degradation occurs in the pressure range of 0.1 to 10 mm Hg, with a minimum in performance at about 1 mm Hg. Even the best silicide-base coatings on Mo and Cb alloys (2–3 mils thick) have a maximum life of about 4 hr at

2550° to 2700°F in air at 0.10 to 1.0 mm Hg.[5] A similar effect of pressure has been found for Sn-Al base coatings on tantalum-base alloys.[7] In this case, volatilization of tin at low pressure destroys the coating and results in premature failure.

The only approach to this problem at present is to allow for degradation effects in the design and use of parts that will operate in low-pressure environments. The performance of eight different coating systems is being characterized as a function of air pressure at this time, and results should be available for use by early 1965.[5]

References

[1] Srp, O. O. and Geyer, N. M., "Protective coating requirements and recent developments," *Proceedings of International Symposium on High Temperature Technology* (Stanford Research Institute, Menlo Park, Calif., September 1963).

[2] Moore, V. S. and Stetson, A. R., "Evaluation of coated refractory metals foils," Aeronautical Systems Div. ASD-TDR 63-4006, Part I (September 1963).

[3] Perkins, R. A., Price, W. L., and Coons, W., "Factors affecting the performance of silicide base coatings on refractory metals," Gordon Research Conferences (July 1963).

[4] Berkowitz, J. B., "Kinetics of oxidation in the Mo-Si system," Aeronautical Systems Div. ASD-TDR-62-203, Part I (May 1962).

[5] "Coatings for refractory metals in aerospace environments," Air Force Contract AF 33(657)-11150, Lockheed Missiles and Space Co., 3rd Quart. Progr. Rept. LMSC 2-04-64-1 (April 1963).

[6] Perkins, R. A., Riedinger, L. A., and Sokolsky, S., "Oxidation protection of refractories during re-entry," Space/Aeronautics **39**, 107–115 (June 1963).

[7] "Evaluation of coatings for refractory metals in aerospace environments," Air Force Contract AF 33(657)-11150, Lockheed Missiles and Space Company, 1st Quart. Progr. Rept. LMSC 2-04-63-1 (September 1963).

JULY-AUG. 1965 J. SPACECRAFT VOL. 2, NO. 4

Low-Density, Autorotating Wings for Manned Re-Entry

H. Schuerch*
Astro Research Corporation, Santa Barbara, Calif.

A number of structural and aerodynamic concepts for centrifugally deployed, variable-geometry atmospheric entry aids are discussed. These include means for controlling apex angle of centrifugally stabilized conical flight bodies, the concept of isothermal flight, i.e., atmospheric entry at constant surface temperature, and analytical design of optimum rotor-blade structures. Materials for flexible rotor construction are reviewed and classified according to a temperature-strength parameter that is characteristic for the intended application. Several aerodynamic rotor models subject to qualitative tests are described. An application of the entry rotor concept to a Mars and Earth landing capsule is presented in the form of a conceptual design configuration.

Nomenclature

A = area, ft^2
c = chord width, ft
D = drag, lbf
f = Gazley's total energy fraction
$\mathfrak{F}$ = optical view factor
g = gravitational acceleration, ft/sec^2
g_c = gravitational acceleration on earth surface, 32.2 ft/sec^2
I_p = probability function
$J_{(R,\,\Omega)}$ = auxiliary integral function
l = blade length, ft
L = lift, lbf
m = mass, lbm
m' = mass per unit length, lbm/ft
n = load factor
q = dynamic pressure, lbf/ft^2
Q = materials strength: radiation temperature parameter, lbf/sec
R = nondimensional radial coordinate
s = stress, lbf/in^2
T = axial blade force, lbf
v = velocity, fps
v^* = specific vehicle velocity, fps
β = coning angle
γ = flight-path angle
ϵ = surface emissivity
θ = absolute temperature, °K
λ = specific strength, in.
ρ = material density, lbm/in.^{3}
ρ_a = atmospheric density, slug/ft^3
σ = Boltzmann constant, in.-lbf/sec-in.^{2}-°K^4
ω = rotational speed, rad/sec
Ω = nondimensional tip speed-to-stress ratio

Introduction

Atmospheric entry and planetary landing of spacecraft are usually considered in view of fixed-geometry flight configurations with relatively high ($\gg$1 lb/ft^2) ballistic parameters.[1] Such configurations emerged from development of ballistic missiles, which, in many respects, were the forerunners of the current generation of space vehicles.

In recent years, various deployable and variable-geometry configurations have been studied[2–5] including inflatable wings, paragliders, variable drag brakes and "rotochutes." In these techniques, large, lightweight surfaces are deployed for aerodynamic control of atmospheric entry. Operational advantages of deployable, variable-geometry configurations include the following: 1) their low ballistic parameters ($\leq$1 lb/ft^2) materially reduce heating rates and prolong flight time, thus simplifying both heat protection and flight-path control aspects of manned atmospheric entry, and 2) variable geometry adds a means of control that permits selection of survivable entry trajectories from those initial entry conditions (hyperbolic velocities and steep entry angles) that

---

Presented at the Engineering Problems of Manned Interplanetary Exploration Meeting, Palo Alto, Calif., September 30–October 1, 1963 (no preprint number; published in bound volume of preprints of the meeting); revision received September 21, 1964. This work has been performed with the financial assistance of NASA.

* President, Astro Research Corporation. Associate Fellow Member AIAA.