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OXIDATION BEHAVIOR OF A COMPLEX DISILICIDE COATING-Ta-10W ALLOY SYSTEM AT TEMPERATURES OF 1700 TO 2700 F

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METALS DIVISION

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Technical Report by

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ABSTRACT

The oxidation behavior of a complex disilicide coating – 90Ta-10W alloy system was studied utilizing thermogravimetric, X-ray diffraction and electron microprobe analyses. The coating afforded the alloy substrate complete protection against static oxidation for at least 200 hours at temperatures between 1700 to 2700 F. The excellent oxidation resistance of the coating system is due to the formation of a protective layer which consists mainly of SiO_2 with some Ti, V, and W in solution and a second dispersed phase of TiO_2. While this protective layer is glassy at and above 2100 F, the reaction products become increasingly crystalline with decreasing temperature between 1700 and 2000 F.

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INTRODUCTION

The Army has propulsion systems materials requirements for second generation gas turbine engines which include turbine blade, disk, and vane materials: combustor liner, and duct materials. For the required work extraction (for every 100 F rise in engine operating temperature there is a corresponding increase of 12% in engine performance), turbines must operate at inlet temperatures between 2300 and 3000 F.

Refractory alloys of tantalum and particularly columbium are candidate materials for such applications, provided coatings can be developed to protect them against high-temperature oxidation. One of our efforts is directed at characterizing existing promising coating systems to provide data for further optimization of these coatings.

Pure and alloyed silicide coatings offer some of the most promising means of protecting refractory metals from high-temperature oxidation. However, in the intermediate temperature range (1400 to 1600 F), they fail due to pesting. It has been proposed that pesting essentially involves a type of intercrystalline oxidation of a silicide in which each grain eventually becomes surrounded by reaction products. Pesting is not only common in silicides, but also in other intermetallic compounds and leads to the rapid disintegration of the bulk material.

We have evolved a simple method for alleviating pesting in a modified silicide coating for a Ta-10W alloy, i.e., a preoxidation treatment at 1900 F. Our study of the mechanisms of failure and protection of a modified silicide coating for a Ta-10W concentrates on the oxidation behavior of the coated alloy above the pesting range, namely 1700 to 2700 F.

MATERIALS

A swaged and annealed Ta-10W alloy rod was machined into disks 0.5-inch in diameter and 0.125-inch thick. The disks were coated with a modified silicide by Solar,* employing the following two-step process:

1. A slurry consisting of 50W, 20Mo, 15V, and 15Ti (in powder form) was sprayed onto the disks. The specimens were then sintered at 2780 F for 15 hours under a partial pressure of 10^{-5} Torr.

2. The coated specimens were packed in pure-200-mesh silicon and were silicided for 15 hours at 2150 F in an argon atmosphere under a pressure of 800 Torr. The coating thickness resulting from the two-step process was 7 to 8 mils per surface.

The coating system is a duplex one, having a porous outermost layer (reservoir layer) and a diffusion layer as shown in Figure 1. Electron microprobe analysis (data which accompanies this photomicrograph) shows that the light

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*Division of International Harvester Company, San Diego, California, U.S.A.

areas of the reservoir layer contain mixed disilicides. At Points 1, 2, and 3, Mo Si_2 predominates, whereas W Si_2 is the main constituent 50 microns from the substrate (Point 4). Although the outer layer is referred to as a porous reservoir layer, there are isolated areas that contain SiO_2 and TiO_2 as shown in Figure 2, Points A and B (SiO_2 is present at Point A, while SiO_2 and TiO_2 are present at Point B). This is probably due to the introduction of oxygen as an impurity in the powders during the coating processing.

Mag. 200X

Point	Identification	Si	Ta	W	Mo	Ti	V	Distance from Substrate
1	Mo Si_2	40.6	<0.1	0.1	44.5	8.8	6.0	235μ
2	Mo Si_2	42.3	<0.1	4.0	35.4	7.4	10.4	155μ
3	Mo Si_2	40.4	<0.1	2.2	37.3	9.5	10.5	85μ
4	W Si_2	30.7	<0.1	55.0	4.3	4.2	5.7	50μ
5	(Ta, W) Si_2	25.3	48.1	19.3	1.8	2.8	1.8	25μ
6	(Ta, W) Si_2	22.3	58.1	16.4	0.3	2.2	0.9	10μ
7		10.1	81.5	8.0	<0.3	0.09	<0.1	Coating/Substrate Interface
								Distance from Coating
8	Alloy	0.08	89.5	10.5	<0.3	<0.01	<0.01	10μ
9	Alloy	<0.05	89.5	10.5	<0.3	<0.01	<0.01	20μ
10	Alloy	<0.05	89.5	10.5	<0.3	<0.01	<0.01	30μ

Figure 1. MICROPROBE ANALYSIS OF AS-COATED REFRACTORY ALLOY
19-066-140/AMC-70

Point	Identification	Si	Ta	W	Mo	Ti	V	Area
A	SiO_2	20-25	<0.1	3.8	<0.1	2.5	1.4	Coating Oxide
B	SiO_2 + TiO_2	20-25	<0.1	1.6	<0.1	14.1	<0.1	Coating Oxide

Figure 2. MICROPROBE ANALYSIS OF TYPICAL OXIDES IN THE AS-COATED REFRACTORY ALLOY
19-066- 11/AMC-70

Mag. 1000X

The dense diffusion layer consists mainly of tantalum and tungsten disilicide (Points 5 and 6). It is interesting to note that only small amounts of silicon (0.08%) have diffused into the substrate. Not shown in this photomicrograph, but characteristic of silicide coatings, are microcracks which extend from the diffusion layer into the reservoir layer. These microcracks are due to the mismatch between the thermal expansion coefficients of the coating and the substrate.

EXPERIMENTAL

The Mettler thermogravimetric apparatus described elsewhere[1] was used for obtaining oxidation rates of the coated alloy as a function of time and temperature. Investigations were carried out at atmospheric pressure at an air flow rate of 50 cm/sec.

X-ray diffraction analyses were made with a Norelco X-ray diffractometer using a copper target operating at 35 kV and 20 mA. A two-theta (2θ) scan was made from 15 to 110° at a scanning speed of 1° per minute. A 1° divergence slit with a nickel filter to eliminate the K_β radiation was used.

The diffracted radiation was recorded on a strip chart at a speed of 30 inches per hour. All variables of the unit were held constant so that a semiquantitative analysis of the compounds present at various temperatures could be made from peak heights and widths. Observed d-spacings were compared with known d-spacings from ASTM X-ray-diffraction index cards.

Electron microprobe analysis was performed with an AMR electron beam microanalyzer. The accuracy of the concentrations obtained from the point analysis is generally of the order of ±5% of the amount reported. The analytical precision varies slightly depending upon the element studied, but is generally within ±2% relative for concentrations ranging from 10 to 100 wt %. The precision is ±5% relative for concentrations ranging from 1 to 10 wt % and ±10% for concentrations ranging from 0.1 to 1.0 wt %.

DISCUSSION OF RESULTS

For discussion purposes, results of oxidation-rate studies, X-ray diffraction, and electron-microprobe analyses have been conveniently grouped according to the following temperature ranges: 1700 to 1800, 1900 to 2000, 2100, 2200 to 2400, and 2500 to 2700 F. Thus, identification of reaction products and their topology were related to changes in oxidation kinetics.

1700 to 1800 F

At 1700 to 1800 F, Figure 3, oxidation proceeds parabolically for the first few hours after which it exhibits no further weight gain. This indicates that the protective film formed over the coating during the initial oxidation is maintained throughout the entire run of 200 hours. Figure 4 is a photograph of the coated alloy oxidized at 1700 F for 20 minutes in air. A cracking pattern is observed in the lighter areas. It has been amply demonstrated that large stresses are present in metal-oxide systems during and after oxidation which can result in cracking. Many factors could be operative in the formation of cracks, e.g., ratio of the volume of equivalent amounts of oxide and metal, variations in growth rates of different layers in multilayered scales, differences in thermal expansion of metal and oxide, etc. Additional experiments were carried out at 1700 F in which air was replaced by nitrogen in order to establish the role of oxygen in the cracking process. Under these conditions, neither cracking nor weight gain were observed, suggesting that the formation of an oxide was necessary for cracking to occur. The mechanism is most likely volume expansion due to oxidation rather than difference in thermal expansion or reaction with nitrogen which is in agreement with the work of Hayman and Restall.[5] Regardless of the factors which are operative, the presence of cracks does not necessarily lead to failure of the coated specimen. The darker areas of the photograph show that self-healing of the cracks is occurring. Electron microprobe and X-ray diffraction analysis show in Figure 5 that this outer protective layer contains SiO_2 and TiO_2 (Points A and B) as well as an unknown compound having d-spacings 3.108, 2.735, and 1.938 Å.

The oxides at Point A appear to be denser than Point B (based on total weight percent of elements), suggesting that self-healing initiates at the outer surface of the coating and progresses inward. Since it is difficult to form a protective oxide which remains absolutely sound under all conditions, the self-healing capacity (ability to regenerate protective oxide in case of surface cracking) is important. This capability depends on the preservation of an active reservoir of disilicides in the coating which is identified as (W, Mo, Ti, V) Si_2 at Points 1, 2, and 3. Points C and D are predominantly SiO_2, indicating that Ti is diffusing to the outer layer of the coating where it is present as TiO_2. Some areas of the diffusion layer of the as-coated material [containing (Ta, W) Si_2] have become oxidized as shown in the analysis at Points G and H. This has occurred only at those sites in the diffusion layer where cracks which have formed are broad enough to act as diffusion paths for oxygen (see Point E). Although oxidation of the diffusion layer is undesirable, failure has not occurred because the self-healing capability of the coating system prevents further oxygen diffusion.

1900 to 2000 F

Figure 6 contains oxidation curves at 1900 and 2000 F where the initial segments of both curves are parabolic followed by linear portions. At 1900 F, the linear portion represents no further weight gain; while at 2000 F, there is an increase in weight. In both cases, complete protection is afforded the substrate alloy for 200 hours.

Between 1700 and 2000 F, the initial parabolic oxidation rate increases with increasing temperature. However, if one compares the secondary linear portion of the curves only, the weight gain at 1900 F is less than at 1800 F. This anomaly may be explained with the aid of Figure 5. The photomicrograph (coated alloy oxidized at 1800 F) is not characteristic of the entire coating but is representative of the few sites which exhibited diffusion-layer oxidation. In this case, the crack is much broader than the microcracks observed in the as-coated condition. A volume increase occurs as a result of the localized oxidation of the diffusion layer at the base of the crack which creates internal stresses and a rapid broadening of the crack. However, further oxidation at these sites is totally arrested

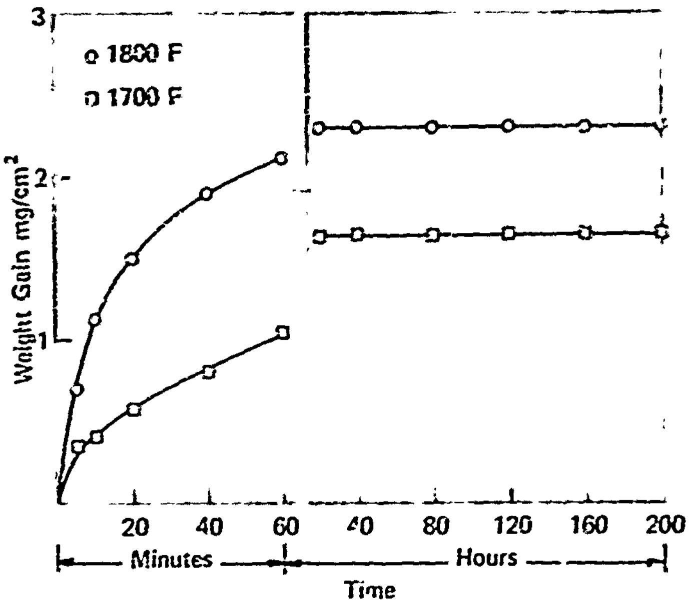


Figure 3. OXIDATION CURVES OF A COATED REFRACTORY ALLOY IN THE TEMPERATURE RANGE OF 1700 F TO 1800 F.
19-066-1024/AMC-71

Figure 4. COATED ALLOY OXIDIZED AT 1700 F FOR 20 MINUTES Mag. 5X.
19-066-929/AMC-69

Point	Identification	Si	Ta	W	Mo	Ti	V	Distance, μ
1	(W, Mo, Ti, V)Si$_2$	40.2	0.4	28.3	9.6	14.1	7.4	225
2	(W, Mo, Ti, V)Si$_2$	37.5	0.4	36.1	12.0	5.4	8.6	170
3	(W, Mo, Ti, V)Si$_2$	27.1	0.6	41.5	15.2	4.8	10.8	100
4	Alloy	<0.05	83.5	9.7	<0.3	3.5	3.3	10*
5	Alloy	<0.05	88.3	10.0	<0.3	0.7	1.0	20*
6	Alloy	0.06	89.5	10.4	<0.3	0.08	0.06	30*
7	Alloy	0.10	0.1	10.5	<0.3	<0.01	<0.02	40*
A	SiO$_2$, TiO$_2$	40.5	<0.1	3.1	0.1	10.3	5.7	240
B	SiO$_2$, TiO$_2$	20-25	<0.1	1.9	0.5	[illegible]	2.1	200
C	SiO$_2$	20-25	<0.1	6.0	1	1.1	1.3	10
D	SiO$_2$	30-40	0.2	1.8	1.0	0.3	0.4	[illegible]
E	Void	1.6	0.1	4.1	[illegible]	0.03	0.3	[illegible]
F	SiO$_2$	20-25	0.2	3.0	0.9	0.3	0.6	[illegible]
G	Mixed Oxides	14.0	22.5	21.3	1.1	1.8	3.8	25
H	Mixed Oxide	8.0	33.7	19.9	1.6	1.8	2.7	[illegible]

*Distances measured from coating, all others from substrate

Figure 5 MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 1800 F Mag. 175X
19-066-1242/AMC-70

within a few hours (as shown by the leveling off of the oxidation curves at 1800 F), because a thin layer of oxides has formed at the coating surface. The oxide layer seals the crack opening and behaves as an oxygen diffusion barrier. The factor which controls coating spallation is largely dependent upon the amount of oxidation that has occurred at various sites throughout the diffusion layer before self-healing is complete. Regardless of the amount of oxidation undergone by this diffusion layer at 1800 F, the coating would likely be susceptible to both mechanical and thermal shock under thermal cycling conditions.

At 1900 F, oxidation of the diffusion layer and hence broadening of cracks did not occur which probably accounts for the lower weight gain observed. At 1900 and 2000 F, the outer protective layer still consisted of SiO_2, TiO_2, and the unknown compound present at 1700 and 1800 F. There was also some diminution of the reservoir of mixed disilicides.

2100 F

Figure 7 shows that oxidation at 2100 F follows the parabolic growth law, and complete protection is afforded the substrate alloy by the coating. Some volatilization of oxidation products may be occurring at this temperature since the initial oxidation rate is less than observed at 2000 F. At this temperature 2100 F the outer protective layer first takes on a glazed appearance. Fitzer[5] reported that disilicide coatings for molybdenum take on this glassy appearance at 2400 F. The lower temperature we report may be due to the complex composition of our coating system. In addition to Mo and Si, the coating contains Ti, V, and W which may lower the melting point of the glassy-like compounds formed and have the beneficial effect of allowing self-healing to take place at lower temperatures. Figure 8 which is a photomicrograph of the coated alloy oxidized at 2100 F along with electron-microprobe analysis shows that the outer glassy layer consists mainly of SiO_2 containing <0.1 wt % Ta, 7.4 wt % W, <0.1 wt % Mo, 1.6 wt % Ti, and 1.9 wt % V in solution (Point A), and small amounts of TiO_2 as a separate phase. This is more readily seen in Figure 9 which magnifies the oxide layer by a factor of 5. Pure SiO_2 (cristobalite) could not be present as a glassy or molten phase at 2100 F since its melting point is 3120 F. X-ray diffraction scans show the presence of an unknown compound which electron microprobe analysis identified as an oxide containing mainly silicon along with the aforementioned elements in much smaller amounts. Note in Figure 8 that the outer protective layer has bridged a crack that has formed in the adjacent porous layer of mixed disilicides (reservoir). There appears to be no significant changes in the reservoir and diffusion layers other than some slight diffusion of tantalum into the reservoir layer (Points 3 and 4). As noted by Points 11, 12, and 13, no diffusion of the coating elements into the substrate Ta-10W alloy was found.

2200 to 2400 F

In this temperature range, oxidation rates increase with increasing temperature as shown in Figure 10. At each temperature, after one hour of oxidation, the oxidation rates decrease with time, particularly at 2300 F probably due to volatilization. Spectrographic analysis of the effluent gases, which were passed through a scrubber containing 10% Na OH, showed that silicon was present in fairly large amounts and Mo, W, and V in lesser amounts and Ti in a trace amount. The electron microprobe analysis for the coated alloy oxidized at 2300 F shown

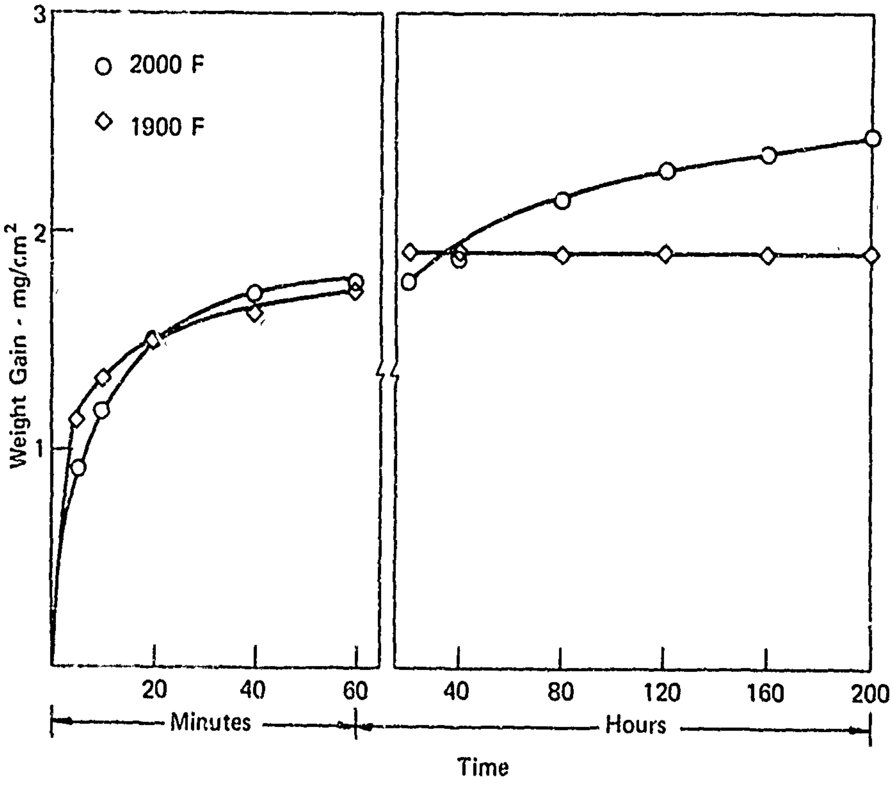


Figure 6. OXIDATION CURVES OF A COATED REFRACTORY ALLOY IN THE TEMPERATURE RANGE OF 1900 F TO 2000 F.
19-066-1023/AMC-71

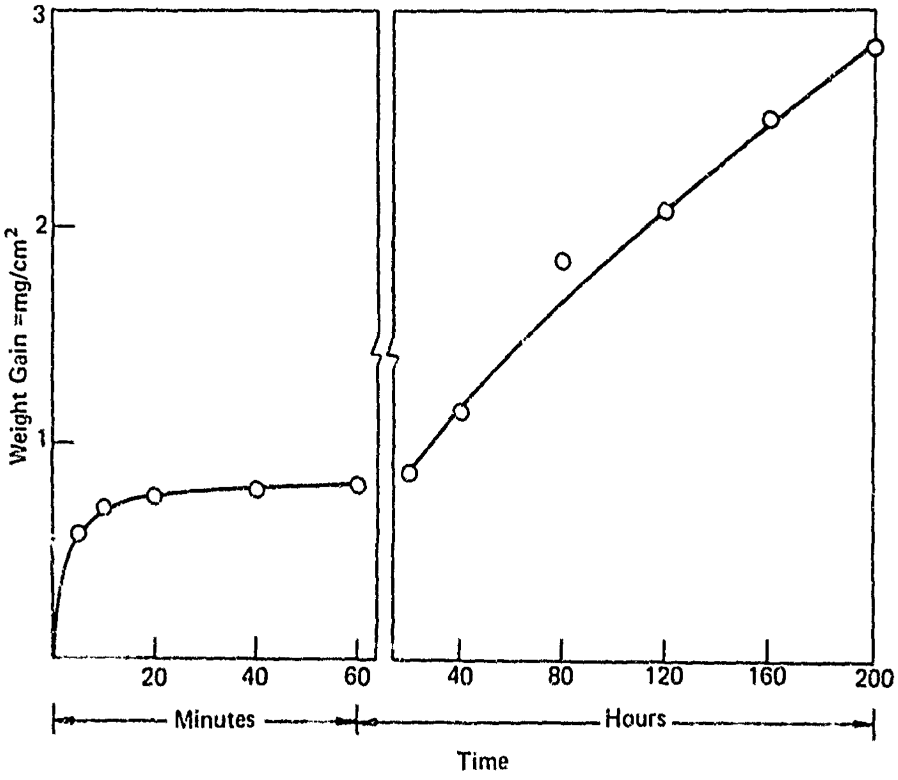
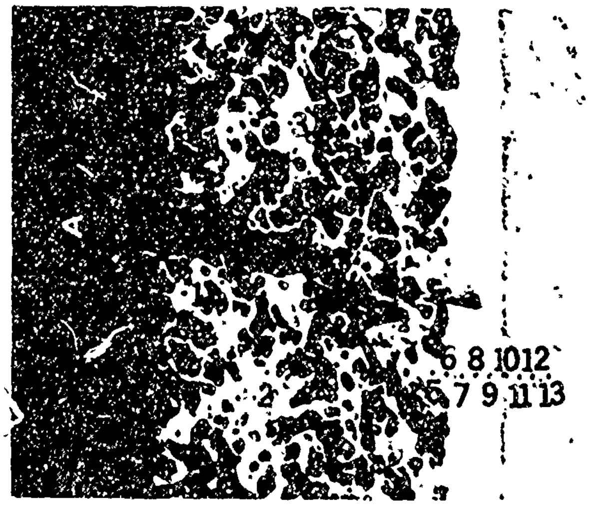


Figure 7. OXIDATION CURVE OF A COATED REFRACTORY ALLOY AT 2100 F.
19-066-1022/AMC071



Point	Identification	Si	Ta	W	Mo	Ti	V	Distance μ
1	(W,Mo,Ti,V)Si_2	43 5	<0.1	26 5	14 5	6.4	9 1	240
2		39 0	<0 1	31 5	18 8	4 4	7.5	185
3		25.0	0 1	56 9	9 4	3 2	5.5	150
4		25.3	0 5	55 5	9 9	3.4	5 2	75
5		27.2	6 9	45 7	12 6	3 8	2.9	50
6	(Ta,W)Si_2	26 6	48.5	15 1	3.9	3 4	2.9	40
7		25.1	61.5	9 3	<0 3	1.8	2 4	30
8		22.9	67.3	9.1	<0 3	0 8	<0 1	20
9		17.5	71 8	10 9	<0 3	0 2	<0 1	10
10		8.3	81 8	[illegible]	<0 3	<0 01	<0 1	Coating/Substrate Interface
11	Alloy	<0 05	87 8	12 2	<0 3	<0 01	<0 1	*0*
12		<0 05	88 0	12 0	<0.3	<0 01	<0.1	20*
13		<0 05	88 1	11 9	<0 3	<0 01	<0 1	30*
A	SiO_2	20 25	<0 1	7[illegible]	<0 1	1 6	1 9	300

*Distances measured from coating, all others from substrate

Figure 8. MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 2100 F. Mag. 200X. 19-066-940/AMC-71

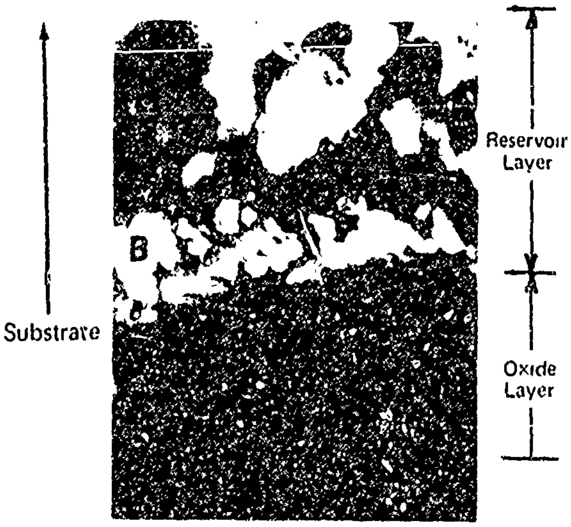


Figure 9. MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 2100 F. Mag. 1000X.
19-066-941/AMC-71

Point	Identification	Si	Ta	W	Mo	Ti	V
B	TiO_2	4.5	0.3	8.7	<0.1	35-40	0.4
C		20-25	<0.1	9.0	<0.1	1.2	<0.1
D	SiO_2	40-50	0.1	0.9	<0.1	1.4	0.8

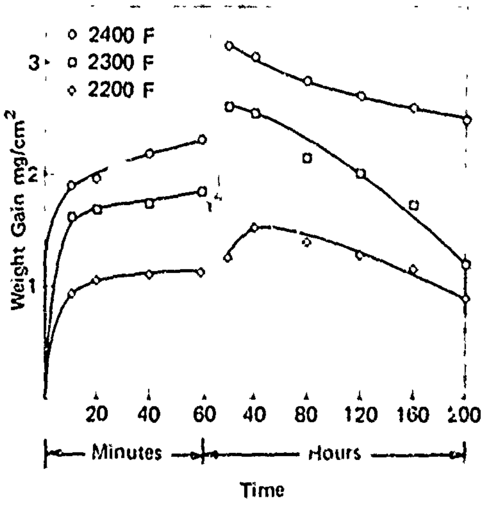


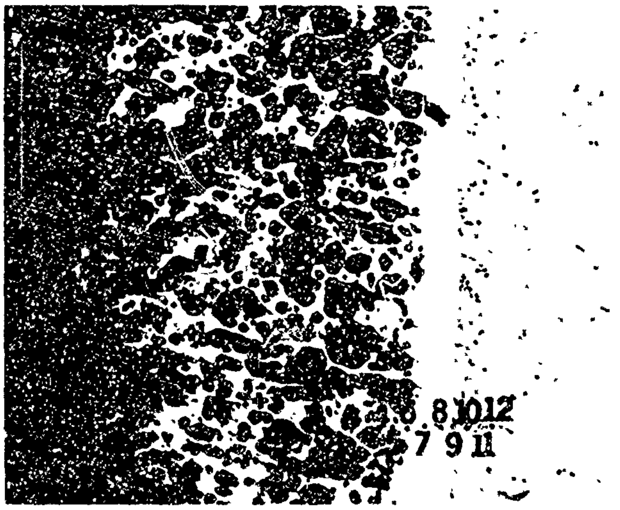
Figure 10. OXIDATION CURVES OF A COATED REFRACTORY ALLOY IN THE TEMPERATURE RANGE OF 2200 F TO 2400 F.
19-066-1021/AMC-71

in Figure 11 when compared to the analysis at 2100 F (Figure 8) does indeed substantiate a volatilization reaction. In general, the elements Si, Mo, Ti, and V decrease in amount as the temperature is raised from 2100 to 2300 degrees. The amount of tungsten on the other hand, increases at 2300 F probably because tungsten diffusion from below the porous or reservoir area occurs more rapidly than does volatilization. The amount of oxide in the reservoir or porous area also appears to be increasing at the higher temperature which, to some extent, diminishes the reservoir layer or amount of disilicide available for self-healing. There is a significant change in the diffusion layer at 2300 F, namely, conversion of (Ta, W) Si_2 to (Ta, $W)_5$ Si_3 and $(Ta, W)_2$ Si. It is likely that the lower silicides will exhibit poorer oxidation resistance but would eventually exhibit protective behavior since larger periods of oxidation would be needed to reach the protective stage, the lower the silicon content.[6] Perkins[7] and Berkowitz-Mattuck and Dils[8] have reported such behavior for molybdenum silicides, namely, oxidation resistances decrease as Mo $Si_2 >$ Mo_5 $Si_3 >$ Mo_3 Si. Figure 12 which magnifies the outer protective oxide layer shown in Figure 11 brings out a point of interest regarding this layer. Points A and C both consist primarily of SiO_2 with small amounts of Ta, W, Mo, Ti, and V in solution. However, Point A, which is in the outermost area of the layer appears to have been in the molten state at 2300 F whereas Point C, further into the layer, does not. The elemental analysis appears to indicate that the higher concentration of elements at Point A has facilitated melting in that area.

2500 to 2700 F

Figure 13 shows that the parabolic rate law still holds in the range 2500 to 2700 F, and oxidation rates increase with increasing temperature. The marked increase in oxidation rate at 2700 F after the first hour indicates that the protective limit of the coating is being approached. However, complete protection was afforded the substrate alloy for the entire run. Some volatilization has probably occurred but is considered to be minor since a net weight gain of 12 mg/cm^2 at 2700 F is noted. This relatively small change in weight again attests to the excellent protective properties of the coating system.

Photomicrographs with accompanying electron microprobe analyses, representing 2700 F oxidation of the coated alloy, are shown in Figures 14 and 15. Figure 14 concentrates on the outermost glassy layer of the coating system which is shown filling and sealing a crack that has formed. This glassy layer is increasing in thickness at this temperature and consists mainly of SiO_2 with small amounts of W and V and a larger amount of Ti in solution (Points B, C, and D) which was also the case at temperatures as low as 2100 F. Again, TiO_2 (Point A) is present as a separate phase dispersed within this layer. The reservoir layer (Points 1 and 2) still contains mixed disilicides (W, Mo) Si_2 with very little if any porosity remaining, because the pores have become filled with oxides. Titanium which is also present in the reservoir layer has diffused to the outer protective layer (based on a comparison of the elements present in both the reservoir and outer glassy layers at temperatures of 2300 and 2700 F). The reservoir layer has further diminished in thickness at 2700 F. The diffusion layer shown in Figure 15 has broadened as a result of the diffusion of silicon toward the substrate where it has formed lower silicides with Ta, W, and V. Also some vanadium has diffused from the reservoir layer toward the substrate alloy. Figure 16 shows how the thickness of the diffusion layer and the combined



Point	Identification	Si	Ta	W	Mo	Ti	V	Distance μ
1	$(W,Mo,V,Ti)Si_2$	25.8	0.6	55.0	7.8	3.9	7.0	195
2		24.1	0.6	53.0	14.3	2.9	5.7	155
3		24.6	0.6	51.0	13.4	3.6	6.5	140
4		22.3	6.5	37.6	25.4	3.0	5.4	55
5		21.6	16.5	42.1	10.6	3.6	5.7	45
6	$(Ta,W)_5Si_3$	8.9	58.3	22.7	3.8	2.6	3.6	30
7	$(Ta,W)_5Si_3$	9.5	75.5	10.8	0.5	2.2	1.4	20
8	$(Ta,W)_2Si$	7.9	79.5	9.9	0.5	1.2	0.6	10
9	$(Ta,W)_2Si$	7.6	83.7	8.4	0.2	0.01	<0.1	Interface
10	Alloy	0.06	89.5	10.5	<0.3	<0.01	<0.1	10*
11	Alloy	<0.05	89.7	10.3	<0.3	<0.01	<0.1	20*
12	Alloy	<0.05	89.0	11.0	<0.3	<0.01	<0.1	30*

*Distances measured from coating, all others from substrate

19-066-939/AMC-71

Figure 11. MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 2300 F. Mag. 200X.

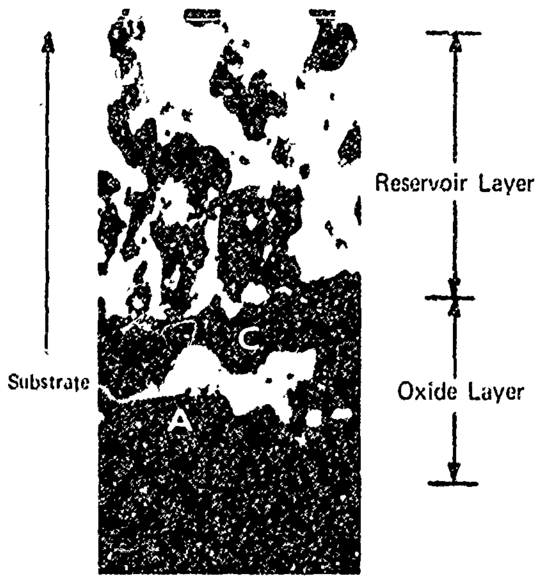


Figure 12. MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 2300 F. Mag. 500X.
19-066-942/AMC-71

Point	Identification	Si	Ta	W	Mo	Ti	V	Distance μ
A	SiO_2	20-25	<0.1	3.1	<0.1	2.6	0.4	270
B	TiO_2	<1.0	0.3	4.3	0.3	55-60	0.3	265
C	SiO_2	35-40	<0.1	<0.1	<0.1	2.9	<0.1	260

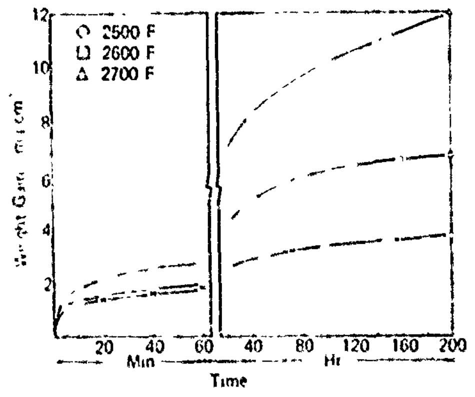


Figure 13. OXIDATION CURVES OF A COATED REFRACTORY ALLOY IN THE TEMPERATURE RANGE OF 2500 F TO 2700 F.
19-066-175/AMC-70

Point	Identification	Si	Ta	W	Mo	Ti	V	Distance from Substrate
A	TiO	0.2	1.7	[illegible]	0.5	58.7	0.9	38[illegible]
B	SiO_2	26.7	0.1	[illegible]	<0.1	4.6	0.4	36[illegible]
C	SiO_2	30.5	<0.1	[illegible]	<0.1	4.1	0.9	30[illegible]
D	SiO_2	26.5	0.1	[illegible]	<0.1	3.8	0.9	2[illegible]
E	$SiO_2 + TiO_2$	14.5	0.8	[illegible]	0.3	19.3	3.7	24[illegible]
1	$(W, Mo)Si_2$	25.3	0.9	57.3	15.0	0.3	1.2	225μ
2	$(W, Mo)Si_2$	24.2	2.1	55.5	15.6	0.3	2.3	145μ

Figure 14. MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 2700 F. Mag. 200X

19-066-139/AMC-70

Point	Identification	Si	Ta	W	Mo	Ti	V	Distance from Substrate
3	$(Ta, W, V)_5Si_3$	10.0	58.3	16.2	2.2	3.8	9.5	90μ
4	$(Ta, W)_5Si_3$	8.4	82.2	8.8	<0.3	0.2	0.3	60μ
5	$(Ta, W)_2Si$	6.2	80.5	13.3	<0.3	<0.01	<0.02	15μ
								Distance from Coating
6	Alloy	1.1	88.6	10.3	<0.3	<0.01	<0.02	5μ
7	Alloy	0.04	89.8	10.2	<0.3	<0.01	<0.02	20μ

Figure 15. MICROPROBE ANALYSIS OF COATED REFRACTORY ALLOY AFTER 200 HOURS OF AIR OXIDATION AT 2700 F. Mag. 200X

19-066-138/AMC-70

reservoir (porous) and outer protective layers vary with temperature after 200 hours of oxidation. Both coating layers generally increase in thickness with increasing temperatures, particularly above 2300 F.

DIFFUSION OF COATING AND SUBSTRATE ELEMENTS

Diffusion of coating and substrate elements was examined by electron microprobe analysis for the as-coated condition and after 200 hours of oxidation at 2100 and 2700 F. This was accomplished by tracing element concentrations across the coating thickness and into the substrate for a short distance. It should be noted that the electron microprobe data is not intended to be taken as a strict point to point analysis because of the inhomogeneity of the coating system. Results showing element concentration as a function of distance from the substrate are plotted in Figures 17 through 22.

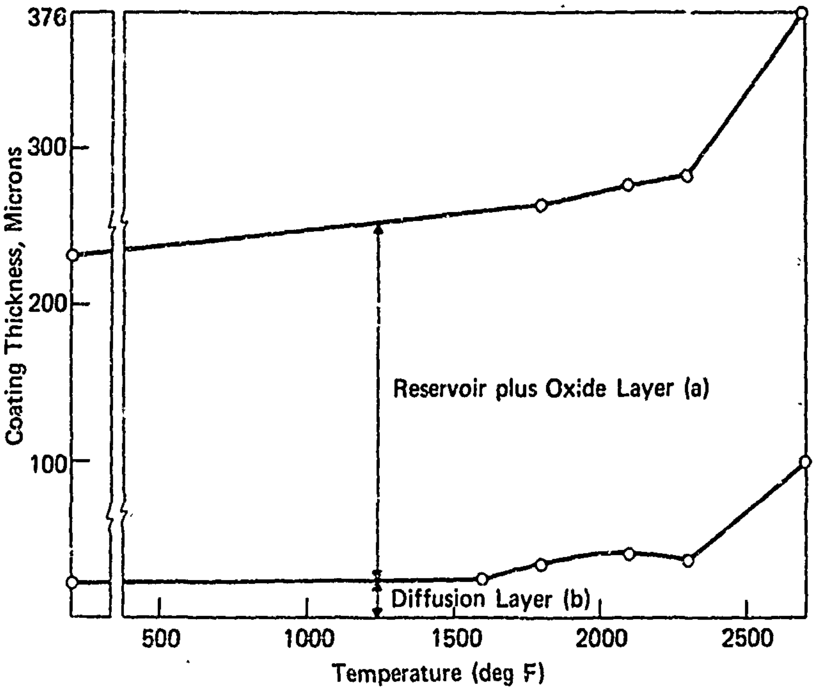


Figure 16. CHANGE OF COATING THICKNESS WITH TEMPERATURE.
19-066-943/AMC-71

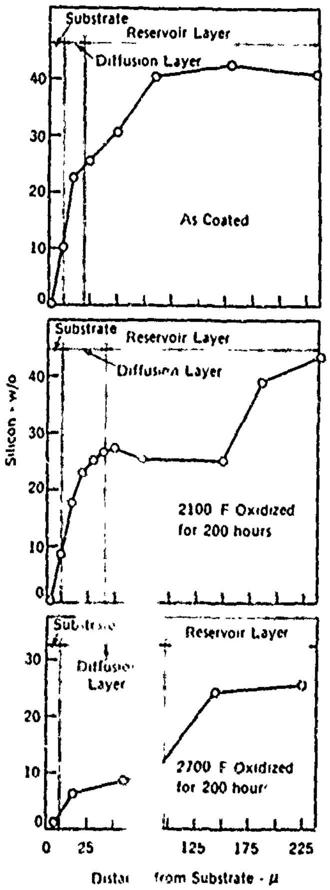


Figure 17. DIFFUSION OF SILICON IN THE COATING SYSTEM
19-066-1020/AMC-71

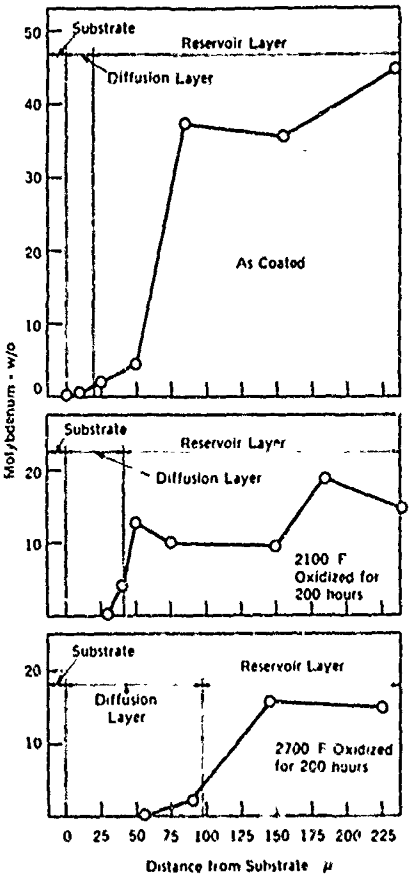


Figure 18. DIFFUSION OF MOLYBDENUM IN THE COATING SYSTEM
19-066-1019/AMC-71

Figure 17, the plot for silicon, shows that the silicon concentration decreases in both reservoir layer and diffusion layer and at the interface between substrate and diffusion layer as the coated alloy is oxidized at 2100 and 2700 F. Some silicon has penetrated into the substrate alloy at 2700 F.

The molybdenum plot, Figure 18, shows that molybdenum concentrations as high as 45 wt % were present in the as-coated condition in the reservoir layer. After oxidation, the molybdenum concentration decreased markedly in the reservoir layer. There was little effect in the diffusion layer where the molybdenum concentration was low, and none was present at the interface of substrate and diffusion layer.

Titanium also decreases significantly in the reservoir layer as a result of oxidation (see Figure 19). There was a slight increase of titanium in the diffusion layer and only very small amounts were present at the substrate-diffusion layer interface. At 2700 F, the titanium clusters at the interface between the diffusion and reservoir layers. Figure 20 shows that vanadium behaved similarly to titanium.

In the as-coated condition, tungsten is concentrated in the reservoir layer close to the diffusion layer, also in the diffusion layer and, of course, it constitutes 10% of the substrate alloy (see Figure 21). Oxidation causes the tungsten to be more uniformly dispersed in the reservoir layer (55%), while the amount of tungsten in the diffusion layer decreases. Therefore, tungsten is diffusing from the diffusion layer into and throughout the reservoir layer.

Figure 22 shows that tantalum, in the as-coated and under oxidizing conditions clusters mainly at the substrate/diffusion layer interface, and in the diffusion layer. At 2700 F, there is some diffusion of tantalum (0.9 wt %) up to 225μ from the substrate into the reservoir layer. Diffusion of tantalum from the substrate into the diffusion layer contributes to the broadening of the diffusion layer noted at 2700 F.

EFFECT OF HEATING RATE ON THE OXIDATION OF THE COATED ALLOY

Since we reported[1] that the complex disilicide coatings are susceptible to pesting in the temperature range 1400 to 1600 F it seemed advisable to establish the minimum heating rate at which the coating could safely traverse the pesting range without deleterious effects. Accordingly, oxidation runs were made at heating rates of 1, 6, 10, and 25 C rise per minute from ambient to 2800 F. The results were plotted in Figure 23. Failure of the coating occurred only at the slowest heating rate of 1 C rise/minute. In the temperature range 800 to 1300 F where the slope of the curves is greatest, low temperature oxides are forming, whereas high temperature oxides are forming between 1500 and 2100 F. Since the exposure time is longer at a 1 C rise/minute heating rate at a given temperature, the opportunity for the formation of the lower temperature oxides is optimized, but failure occurs due to pesting. Therefore, higher temperature oxides must be present to alleviate pesting. Although high temperature oxides have formed to some extent during this run, it appears that damage to the intercrystalline structure of the coating during its exposure in the pesting range has progressed beyond the point where self-healing by the high temperature oxides formed can repair the damage.

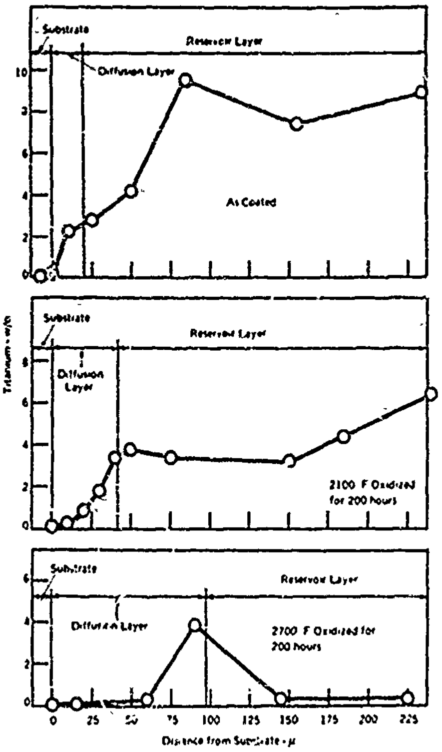


Figure 19. DIFFUSION OF TITANIUM IN THE COATING SYSTEM

19-066-1018/AMC-71

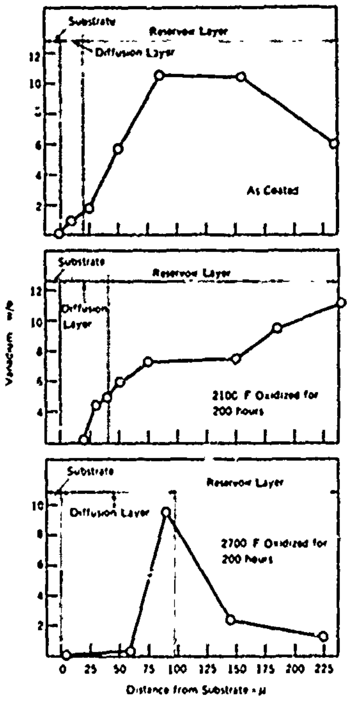


Figure 20. DIFFUSION OF VANADIUM IN THE COATING SYSTEM

19-066-1017/AMC-71

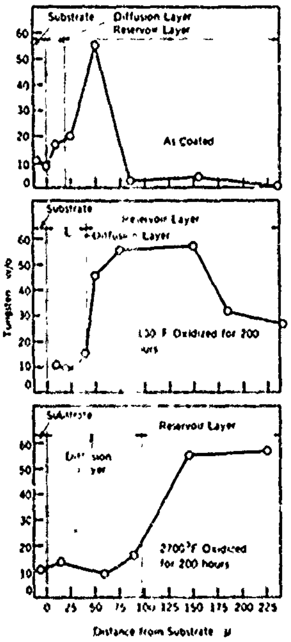


Figure 21. DIFFUSION OF TUNGSTEN IN THE COATING SYSTEM

19-066-1016/AMC-71

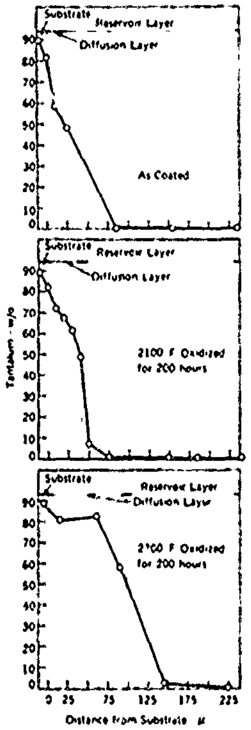


Figure 22. DIFFUSION OF TANTALUM IN THE COATING SYSTEM

19-066-1015/AMC-71

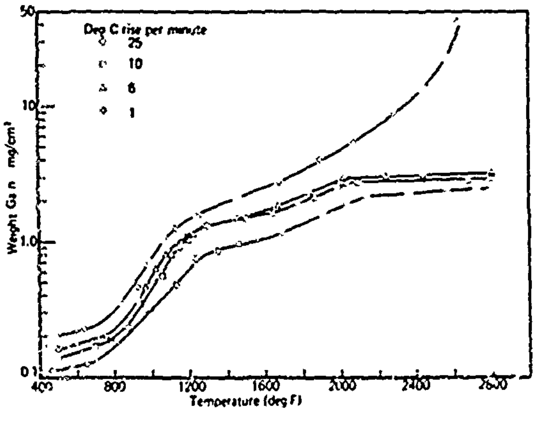


Figure 23. EFFECT OF HEATING RATES ON THE OXIDATION OF A COATED REFRACTORY ALLOY FROM ROOM TEMPERATURE TO 2800 F.
19-066-176/AMC-70

High temperature oxides are completely formed at 2100 F, suggesting that this would be the most advantageous temperature to preoxidize the coating system before subjecting it to pesting temperatures. A coated specimen which was preoxidized at 2100 F for 5 hours and then subjected to pesting conditions afforded excellent protection for 200 hours. After 200 hours of oxidation, the coating had a uniform glazed appearance which is preferred over the specimen preoxidation treatment at 1900 F reported previously by the authors.

CONCLUSIONS

The modified complex silicide coating afforded the 90Ta-10W alloy complete protection against static oxidation for at least 200 hours at temperatures between 1700 and 2700 F. The excellent oxidation resistance of the coating system is due to the formation of a protective layer which consists mainly of SiO_2 with some Ti, V, and W in solution and a second dispersed phase of TiO_2. While the oxide layer at and above 2100 F is glassy, the reaction products become increasingly crystalline with decreasing temperature between 1700 and 2000 F. After the glassy layer is formed, silicon and titanium are preferentially oxidized. The oxidation rate curves suggest that the parabolic growth law is applicable, indicating that oxide growth is controlled by solid state diffusion through the scale. During oxidation, the disilicide is partially consumed both by oxidation and an inward diffusion of silicon. At 2300 F the $(Ta, W) Si_2$ in the diffusion layer thus becomes converted to $(Ta, W)_5 Si_3$ and $(Ta, W)_2 Si$. The lower silicides in turn would not exhibit as good oxidation resistance as the disilicides, and performance could be reduced. Since the glassy protective layer was formed at 2100 F, it appears that the preoxidation treatment to alleviate pesting would more advantageously be carried out at 2100 F rather than the 1900 F previously reported. Without a preoxidation treatment, pesting failures can occur at heating rates below a 10 C rise per minute as the temperature is increased from ambient to 2800 F.

FUTURE WORK

We plan to carry out similar studies with SU31 and FS85 columbium alloys — disilicide coating systems and to investigate the use of barrier layers and element additives to the disilicides to reduce the thermodynamic activities of diffusing species.

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