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SILICIDE COATINGS FOR REFRACTORY METALS

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20 Claims

ABSTRACT OF THE DISCLOSURE

A silicide coating process in which a modifier alloy is slurry applied and vacuum sintered onto a substrate preparatory to siliciding.

STATEMENT OF GOVERNMENT OWNERSHIP

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

BACKGROUND OF THE INVENTION

This invention relates to a coating process and composition for the protection of refractory metals from oxidation. The invention is particularly directed to forming a complex metal silicide coating on tantalum and columbium alloys.

Coatings have been proposed for refractory metals to raise the temperature at which mechanical components made from these metals can be operated. Aerospace hardware systems, such as rocket nozzles, skins of re-entry vehicles, and leading edges and nose caps of hypersonic vehicles, can withstand higher temperatures when coated. Furnaces can be operated at higher temperatures in the range between 2000° to 3500° F. when coated refractory metal elements are used instead of conventional heating elements which are very fragile. The efficiency of a gas turbine engine can be increased by substituting coated refractory metal components for superalloys.

It has been proposed that a silicide coating prepared from a pack of pure silicon be used to protect refractory metals from oxidation at high temperatures. Brittleness, pest behavior, low pressure deterioration, active oxidation and craze cracking due to differential expansion have been encountered in utilizing these silicide coatings. Because of these problems the coating life is not predictable.

It was also proposed that various desirable elements be added to the silicon in the pack to modify the silicide. It was found that while the pack technique is useful for the deposition of silicon alone, it is severely lacking for the deposition of other elements in controlled quantities. Careful analysis revealed that little, if any, of the modifying material actually entered the silicide coating. Severe problems with reproducibility were encountered in the silicide coatings formed by prior surface alloying of columbium with packs containing chromium and titanium. A fluidized bed containing vanadium was also used to prealloy columbium alloy surfaces prior to siliciding. However, the coating chemistries had to be kept simple with this process. Also, it is essentially impossible to deposit any appreciable amount of tungsten or molybdenum in conventional pack cementation processes. Molybdenum and tungsten form disilicides having the lowest thermal expansion of all known disilicides. Such coatings have a closer expansion match to the substrate than other silicide coatings. The melting point of these disilicides in combination with

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titanium is much higher than that for the silicide coatings containing chromium and titanium.

SUMMARY OF THE INVENTION

These problems have been solved by the present invention in which a slurry is sprayed onto a metal surface. This slurry contains controlled amounts of powdered metal modifiers. The sprayed surface is vacuum sintered to produce a very porous alloy coating of controlled chemistry. This coated surface is then exposed to silicon to form disilicides of the modifier metals in the porous coating.

It is, therefore, an object of the present invention to provide an improved duplex silicide coating process wherein the control of the coating chemistry is greatly improved because both the type and the amount of modifier material contained in the coating are very carefully controlled.

Another object of the invention is to improve a silicide coating process by forming a very porous coating of modifier metals on a substrate by vacuum sintering with accurate control of both the heating time and temperature prior to siliciding.

Still another object of the invention is to provide an improved coating process in which the surface to be coated is prealloyed prior to siliciding so that only the desired alloying material is placed on the substrate.

A further object of the invention is to provide an improved duplex silicide coating by improving the control of the chemistry at the start of the coating process as well as by accurately controlling the coating process itself.

A still further object of the invention is to utilize a porous modifier layer to provide a greater accumulation of silicon than has heretofore been realized.

Yet another object of the invention is to alleviate growth stress developed when a metal is converted to a disilicide by the presence of pores in the modified layer resulting from a substantial volume expansion during the conversion.

Yet a further object of the invention is to alleviate impact and thermal stress induced cracking of a silicide coating by utilizing residual pores which serve to terminate cracks.

These and other objects will be apparent from the specification which follows.

DESCRIPTION OF THE INVENTION

The surface of a refractory metal part, such as a turbine vane, is prepared for coating. This is accomplished by sandblasting and etching the substrate alloy for about 40 to 50 seconds in 45HNO₃-45H₂SO₄-10HF.

A slurry is prepared by mixing elemental powders or hydrides thereof in an organic vehicle by ball milling. One such organic vehicle is a composition of ethyl cellulose dissolved in a mixture of secondary-butyl alcohol, xylene, and Stoddard solvent. The Stoddard solvent is added after the ethyl cellulose dissolves. Another suitable organic vehicle is polyisobutylene and polymethylmethacrylate dissolved in trichlorethylene, ethyl acetate, and xylene. The polyisobutylene dissolves in the trichlorethylene and polymethylmethacrylate dissolves in the ethyl acetate before addition to xylene.

The preferable fluid-to-solid volume ratio is in the range of between 2.5 to 3.0. Table 1 shows various selected modifier alloy powders used in the slurry.

The modifier alloy compositions shown in Table 1 produce, upon siliciding, oxidation-resistant coatings. Of the disilicides having melting points exceeding 2400° F., tungsten disilicide has the lowest coefficient of expansion. Molybdenum disilicide has excellent oxidation resistance which is superior to that of the tungsten disilicide at lower temperatures. However, the thermal expansion coefficient

of molybdenum disilicide is slightly greater than that of tungsten disilicide.

Titanium is utilized as a sintering aid, and titanium disilicide has good oxidation resistance. Titanium also enhances the oxidation resistance of tantalum and columbium in the absence of silicon, and this would be beneficial in any unsilicided area at the interface between the substrate and the modifier alloy.

TABLE 1.—MODIFIER ALLOYS

Coating designation	Composition (wt. percent)					
	W	Mo	Ti	V	Cr	Fe
1.....	10	-----	90	-----	-----	-----
2.....	40	-----	60	-----	-----	-----
3.....	70	-----	30	-----	-----	-----
4.....	-----	40	60	-----	-----	-----
5.....	35	35	30	-----	-----	-----
6.....	40	-----	30	30	-----	-----
7.....	35	35	15	15	-----	-----
8.....	35	-----	30	-----	35	-----
9.....	-----	35	30	-----	35	-----
10.....	-----	-----	30	30	40	-----
11.....	97.5	-----	2.5	-----	-----	-----
12.....	-----	95.3	4.7	-----	-----	-----
13.....	95	-----	5	-----	-----	-----
14.....	65	15	10	10	-----	-----
15.....	65	15	15	5	-----	-----
16.....	65	15	15	-----	-----	5
17.....	42	28	15	15	-----	-----
18.....	50	20	20	10	-----	-----

Vanadium and chromium also act as sintering aids. These elements are added primarily to improve the low temperature oxidation resistance of the silicide layer.

According to the present invention, the slurry is sprayed onto the surface to be coated. The coated object is then given a preheat treatment to drive off the organic vehicle.

After drying the object is then sintered at temperatures from 2300° F. to 2800° F. This produces a coating which is quite porous. The as-sintered coating thickness is a minimum of 0.002 inch to provide a satisfactory base for siliciding. A thickness range between 0.003 to 0.006 inch is preferred for optimum results. However, satisfactory results have been obtained using an as-sintered coating thickness of 0.010 inch.

Sintering temperatures and times are shown in Table 2.

TABLE 2.—EXPERIMENTAL RESULTS FOR COATINGS ON T222 TANTALUM ALLOY

Coating	Sintering conditions			Siliconization conditions			Range of cyclic oxidation lives	
	Temp.	Time, hrs.	Weight gain, mg./cm. ²	Temp., ° F.	Time, hrs.	Weight gain, mg./cm. ²	Hours at 1,600° F.	Hours at 2,400° F.
1.....	2,435	15	59	2,000	7	14	As-silicided coating spalled	
2.....	2,435	15	48	2,150	7.5	21	16-31	62-332
3.....	2,435	15	79	2,150	7.5	23	16-111	126->626
4.....	2,760	15	51	2,150	7	24	16	16
5.....	2,760	15	71	2,150	7	37	16-31	31->206
6.....	2,760	15	43	2,150	7	31	>206->653	95->206
7.....	2,760	15	75	2,150	7	43	206->630	206-1,080
8.....	2,610	0.5	50	2,150	7	29	16	95
9.....	2,610	0.5	43	2,150	7	31	16	95->252
10.....	2,610	0.5	42	2,150	7	23	16	16

The majority, and in some cases all, of the sintered metal coating is converted to a disilicide by exposing the coated object to silicon. A high pressure pack cementation process has been satisfactory. This step is carried out within an outer stainless steel or Inconel retort with a double-walled inner box of a columbium alloy. The two walls of the inner box are separated by titanium sponge to assure an extremely clean coating environment. The silicon and the parts to be coated are contained in the

inner box. The silicon used is of reasonably high purity, i.e. 99% plus, and is of minus -200 mesh in particle size. The silicon particle size is not critical, but the fine grain size is preferred because the large surface area increases the amount of silicon vapor generated per unit of time in the pack.

The retort is vacuum cycle-purged using an inert gas, argon or helium, and maintained at a pressure slightly above atmospheric, i.e. 770-850 torr. The preferred deposition temperature is in the range of 2000° F. to 2200° F. for 2 to 15 hours. The time and temperature selection depends on the amount of silicon required, usually 20 to 45 mg./cm.².

It may be desirable to spray or dip the as-silicided coatings in a finely milled slip of a barium borosilicate glass. The coatings are dried before they are brushed to remove all the glass except that which is contained in surface defects such as thermal expansion cracks. Before subjecting the coatings to an oxidizing service environment, the coated parts are fired at approximately 1800° F. for about 10 to 14 minutes.

EXAMPLE

The corners and edges of 1-inch by 2-inch by 1/16-inch T222 tantalum alloy samples (Ta-9.6W-2.4Hf-0.01C) were rounded by tumbling in a ball mill charged with arrowhead-shaped deburring media. Sandblasting and acid etching the substrate preceded application of the slurry using a conventional paint spray gun. After drying, the sprayed coatings were sintered at 2435 to 2760° F. for either 30 minutes or 15 hours in a vacuum of 10⁻⁵ torr as shown in Table 2. The coatings containing chromium experienced liquid-phase sintering and were sintered for 30 minutes, while the balance of the compositions involved solid state (and vaporization-condensation) sintering and were sintered for 15 hours. The resultant 0.003 to 0.006-inch thick sintered coatings were silicided by packing the samples in minus -200-mesh silicon without activator, and heating to 2150 to 2250° F. in gettered argon (800 torr) for a period of 7 to 8 hours. Although no activator was added to the silicon, trace

amounts of halide impurities may have been present and promoted silicon transfer. Siliciding resulted in weight gains in the range of 20 to 48 mg./cm.² for the different coatings.

Table 2 shows the superior results obtained from coating No. 7 whose composition is 15Ti-35W-15V-35Mo as illustrated in Table 1. Additional test results for this coating are shown in Table 3. Test results for coatings 14 to 18 are likewise shown in Table 3.

TABLE 3.—COATING APPLICATION AND FURNACE OXIDATION TEST RESULTS FOR COATINGS ON T222 TANTALUM ALLOY

Coating	Sintered wt. gain (mg./cm. ²) and thickness (10 ⁻³ in.)	Siliciding wt. gain (mg./cm. ²) and thickness (10 ⁻³ in.)	Oxidation lives			
			Hours at 1,600° F.	Avg. wt. gain (mg./cm. ²)	Hours at 2,400° F.	Avg. wt. gain (mg./cm. ²)
7.....	60.0	44.0	3 at >209.....	1.4	3 at >209.....	3.5
14.....	4.5	3.2	3 at >209.....	2.2	3 at >209.....	3.3
15.....	73.1	48.3	3 at >209.....	1.3	2 at >209.....	3.4
16.....	5.1	4.1	3 at 60.....	8.1	189, 2 at >209...	3.5
17.....	72.5	41.6	189, 2 at >209...	2.5	3 at >209.....	2.9
18.....	4.3	3.6	3 at >209.....	1.7	3 at >209.....	2.8
19.....	74.4	50.3				
20.....	3.3	5.9				
21.....	54.0	40.6				
22.....	4.5	3.6				
23.....	57.7	38.1				
24.....	4.0	3.4				

Titanium was added as titanium hydride to the coatings listed in Table 3. Also vanadium having approximately 0.5% oxygen was used in the coatings listed in Table 3.

While a preferred embodiment of the invention has been described, it is contemplated that various modifications may be made to the process and composition described without departing from the spirit of the invention or the scope of the subjoined claims. For example, both titanium and titanium hydride, TiH_2 , can be used in the coating. Likewise, partially or completely hydrided vanadium can be utilized.

What is claimed is:

1. A method of protecting a refractory metal selected from the group consisting of tantalum and columbium from oxidation comprising the steps of

sintering powdered metals selected from the group consisting of tungsten, molybdenum, titanium, vanadium, chromium, and iron on the refractory metal to form a porous coating, and

converting said porous metal coating to a disilicide by exposing said sintered metal to silicon.

2. A method of protecting a refractory metal from oxidation as claimed in claim 1 including the step of mixing the powdered metals in a fluid to form a slurry

3. A method of protecting a refractory metal from oxidation as claimed in claim 2 including the step of spraying the slurry onto the refractory metal.

4. A method of protecting a refractory metal from oxidation as claimed in claim 3 including the steps of sandblasting and etching the surface of the refractory metal prior to spraying the slurry.

5. A method of protecting a refractory metal from oxidation as claimed in claim 3 including the step of preheating refractory metal with the sprayed slurry thereon to drive off the organic vehicle prior to siliciding.

6. A method of protecting a refractory metal from oxidation as claimed in claim 2 including the step of ball milling elemental powdered metal modifiers in an organic vehicle with a fluid-to-solid volume ratio in the range of about 2.5 to 3.

7. A method of protecting a refractory metal from oxidation as claimed in claim 6 including the step of dissolving ethyl cellulose in a mixture of secondary-butyl alcohol, xylene, and Stoddard solvent to form the organic vehicle of the slurry.

8. A method of protecting a refractory metal from oxidation as claimed in claim 6 including the step of dissolving polyisobutylene and polymethylmethacrylate in trichlorethylene, ethyl acetate, and xylene to form the organic vehicle of the slurry.

9. A method as claimed in claim 1 including the step of sintering the powdered metal at a temperature between 2300° and 2800° F.

10. A method as claimed in claim 1 wherein the porous coating has a thickness in the range between about 0.003 inch and about 0.006 inch.

11. A method as claimed in claim 1 including the step of converting the sintered metal layer to a disilicide by pack cementation.

12. A method as claimed in claim 1 including the steps of

covering the as-silicided coating with a finely milled slip of barium borosilicate glass, and

firing said covered coating.

13. An article comprising a refractory metal selected from the group consisting of tantalum and columbium having thereon a coating for protecting the refractory metal from oxidation comprising a disilicide of an alloy consisting essentially of from 15% to 35% molybdenum, 10% to 20% titanium, and 5% to 15% vanadium or 5% iron, and the remainder tungsten.

14. An article as claimed in claim 13 having thereon a coating consisting essentially of 35% tungsten, 35% molybdenum, 15% titanium, and 15% vanadium.

15. An article as claimed in claim 13 having thereon a coating comprising a disilicide of an alloy consisting essentially of 65% tungsten, 15% molybdenum, 10% titanium, and 10% vanadium.

16. An article as claimed in claim 13 having thereon a coating comprising a disilicide of an alloy consisting essentially of 65% tungsten, 15% molybdenum, 15% titanium, and 5% vanadium.

17. An article as claimed in claim 13 having thereon a coating comprising a disilicide of an alloy consisting essentially of 65% tungsten, 15% molybdenum, 15% titanium, and 5% iron.

18. An article as claimed in claim 13 having thereon a coating comprising a disilicide of an alloy consisting essentially of 42% tungsten, 28% molybdenum, 15% titanium, and 15% vanadium.

19. An article as claimed in claim 13 having thereon a coating comprising a disilicide of an alloy consisting essentially of 50% tungsten, 20% molybdenum, 20% titanium, and 10% vanadium.

20. An article comprising a refractory metal selected from the group consisting of tantalum and columbium having thereon a coating for protecting the refractory metal from oxidation comprising a disilicide of an alloy consisting essentially of about 5% titanium and the remainder tungsten or molybdenum.

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