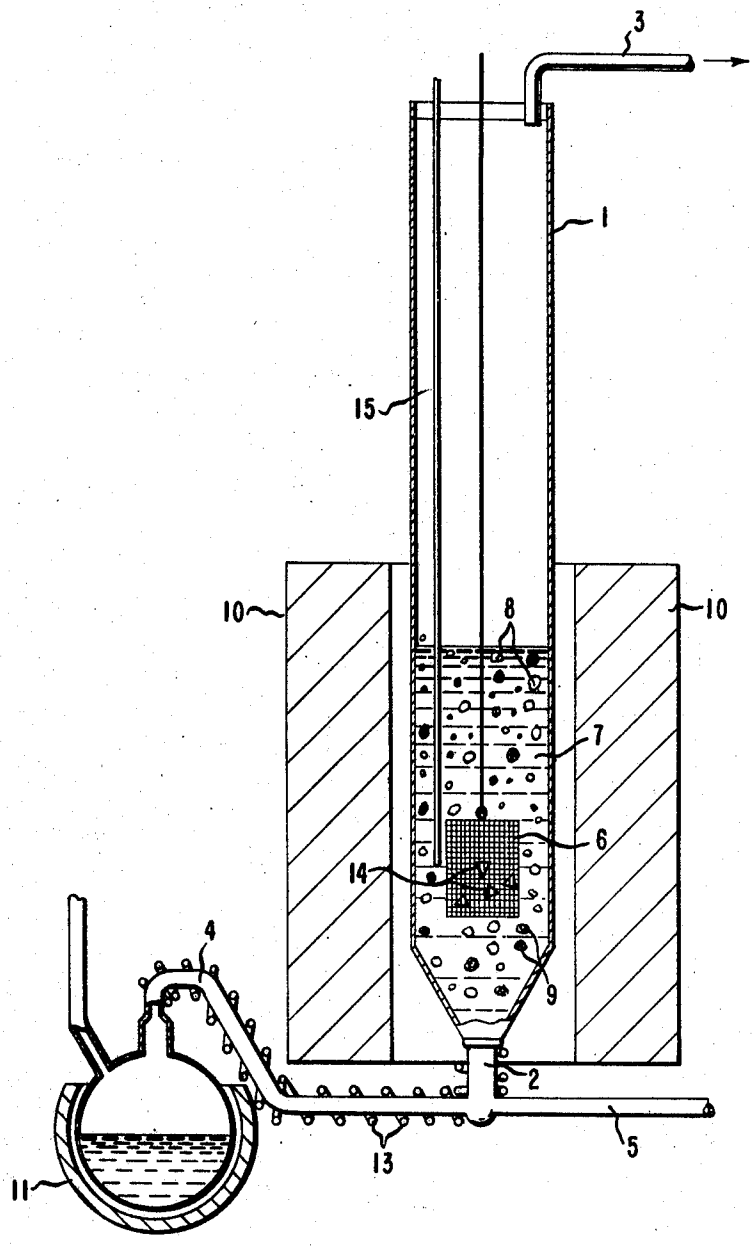
Oct. 28, 1969 H. W. JACOBSON ET AL 3,475,233

CHROMIUM-CONTAINING SILICIDE COATINGS
ON REFRACTORY-METAL-BASE ARTICLES

Filed Oct. 7, 1965 2 Sheets-Sheet 1

FIG. 1



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FIG. 2

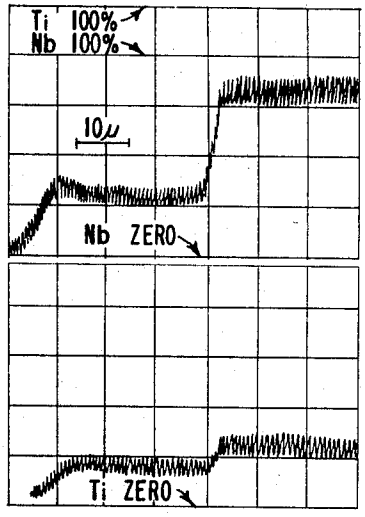


FIG. 2A

FIG. 3

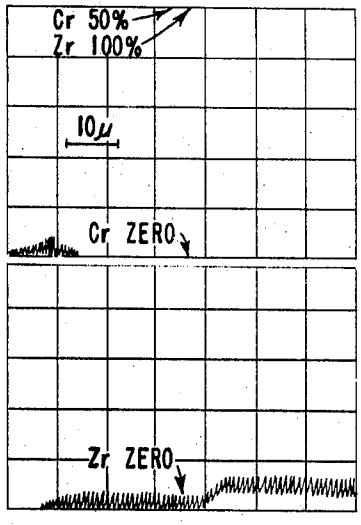


FIG. 3A

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CHROMIUM-CONTAINING SILICIDE COATINGS ON REFRACTORY-METAL-BASE ARTICLES

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ABSTRACT OF THE DISCLOSURE

A process for applying a chromium-containing silicide coating to a refractory metal article is provided by effecting contact between the refractory metal article and a fluidized bed of inert particles, silicon, iodine, and a chromium-bearing alloy. The product is a refractory metal article of columbium or tantalum, with a coating of a silicide and from about 1% to about 5% by weight chromium based on the total weight of the coating, the major portion of the chromium being present in the outer periphery of the coating.

This invention relates to processes for the application of protective coatings to refractory-metal-base articles as an integral part thereof, and to the coated articles produced, and is more particularly directed to such processes comprising effecting contact between said refractory metal article at a temperature of about from 850° F. to 1,150° F. in a fluidized bed of inert particles, said bed comprising also silicon iodine, and a chromium-bearing alloy in which the chromium content is about from 5 to 25% by weight until a silicide coating containing about from 1 to 5% by weight of chromium based on the weight of the coating has formed on said article at least the major portion of said chromium being present in about from 10 to 20% of the depth of the coating as measured from the outer periphery thereof. The invention relates also to refractory metal articles coated according to the described processes, said articles comprising (1) an underlying base comprising columbium, tantalum, or a combination of them, in an amount not less than 50% by weight and firmly adherent thereto, as an integral part of the article, (2) a coating comprising (a) a major portion of a silicide of the columbium, tantalum, or combination thereof of (1), and (b) chromium in an amount of about from 1 to 5 weight percent of said coating (2) at least the major portion of said chromium being present at from about 10 to about 20% of the depth of the coating as measured from the outer periphery thereof.

In the drawings:

FIGURE 1 shows diagrammatically an apparatus useful in carrying out a process of the invention, and

FIGURES 2 and 2*a* show line drawings simulating a microprobe tracing for columbium and titanium respectively through the depth of a coating of the invention.

FIGURES 3 and 3*a* show similar line drawings for chromium and an zirconium respectively.

The invention provides processes for the application of a protective alloy coating to refractory-metal-base articles by means of halogen-transport reactions in a fluidized-bed process in which silicon is caused to combine with the refractory metal which is the major constituent of the article to be coated, to form a refractory-metal silicide, and in which said silicide coating is modified by the presence of a small amount of chromium deposited simultaneously with said silicide, from a chromium-comprising alloy source.

The processes of the invention have been found to be particularly valuable for applying chromium-modified silicide coatings to articles comprising columbium or an alloy of columbium. Although tantalum and tantalum-base alloys can be coated very satisfactorily by the novel processes and although this metal and its alloys exhibit some outstanding properties which make them exceptionally useful at high temperatures columbium and its alloys have a distant advantage in aerospace applications because of their much lower density.

Columbium-base alloys exhibit good strength at elevated temperatures, however, their relatively poor resistance to oxidation at the temperatures of 2,000° F. to 3,000° F. often attained in aerospace applications makes the use of protective coatings very desirable. To be effective, the protective coatings on these alloys must meet very stringent requirements. The coating must be completely compatible with the base material not only in chemical reactivity but also in physical properties; it must provide excellent resistance to oxidation and must prevent erosion from gases; it must be impervious to high speed particles or exhibit the property of self-healing; it must resist thermal shock; and it must have sufficient ductility to withstand stresses and strains that may be encountered by the base alloy. Also the coating must be easily applied by a reproducible process which will result in complete coverage of the underlying refractory metal. Additional advantage will be found if the coating process is one which is adaptable to coating of large as well as small parts, and will be particularly advantageous if large parts formed of foilgage material can be coated thereby.

It is therefore an object of this invention to provide metal-coating processes which will yield products extremely resistant to oxidation and corrosion at high temperatures. A further object is to provide processes applicable to the coating of metal pieces of large or small size and of intricate design. Another object is to produce metal-coated articles in which the oxidation- and corrosion-resistant coating is completely compatible with the underlying metal at any temperature. A still further object is to provide processes for coating articles of columbium or columbium-base alloys or tantalum or taltanum-base alloys in which the coating is applied to the alloy under conditions such that there is no degradation of properties of the underlying metal comprising the article. A specific object of the invention is to apply oxidation- and corrosion-resistant coatings to articles of columbium and columbium-base alloys or of tantalum and tantalum-base alloys in which the coating comprises a silicide of columbium or of tantalum, which silicide coating is modified by a small amount of chromium.

These and other desirable objects are attained by the herein-described processes in which refractory-metal articles are treated in a fluidized bed operation in which the reactants comprise the metal or metals of the article to be coated, silicon, a halogen—preferably iodine—and an alloy of which chromium is a minor constituent.

To attain satisfactory uniform coating on the refractory metal articles, the reaction is carried out in a reactor having inlet and outlet connections and containing a bed comprising inert particles fluidized by the upward flow of gases. In a preferred embodiment of the invention a quartz reactor is used, the articles to be coated are suspended within the reactor, and the fluidized bed comprises silica as the inert material, and particles of silicon and a superalloy in which the chromium content is from 5 to 25% by weight of the alloy. Instead of silica, particles of alumina, thoria, zirconia, or magnesia can be used as the inert. The bed is fluidized by upward flow of an inert gas comprising a small amount of iodine vapor which acts as a transport agent in the coating reaction.

In an especially preferred embodiment of the inven-

tion, the refractory metal articles comprise columbium or columbium-base alloys; the transport agent is iodine; the inert particles are silica; the inert gas to effect fluidization is argon; and the chromium-bearing alloy is a superalloy comprising about from 15 to 25 weight percent chromium. The base metal of the superalloy can be either cobalt or nickel.

In another specific embodiment of the invention, a reactor of a chromium-bearing superalloy can be used in place of the quartz reactor and particles of chromium-bearing alloy. Such operation is advantageous in that the reactor is stronger and much less subject to breakage than is a quartz reactor; but thereactor itself will, of course, be attacked to the extent that chromium is removed for deposition as a constituent of the coating.

In any metal-coating process, a problem is encountered in obtaining a coating which completely covers the underlying metal. Where the articles to be coated are of such size and shape that they must be supported within the reactor, it is often very difficult to achieve complete coating. A fluidized bed operation is advantageous in obtaining an even and complete coating on metal articles of all shapes and sizes, and particularly on articles in which inner surfaces are to be coated. Where the parts to be coated are small, complete coating of all surfaces of these articles can be effected if the articles are placed in a basket of wire or perforated metal suspended within the reactor, and the articles to be coated are lifted, along with the bed particles, by the upward flow of the fluidizing gases.

There is shown diagrammatically in FIGURE 1 the apparatus which is preferred for the operation of this invention. A quartz reactor **1** has an inlet connection **2** at its base for the introduction of gases, and an outlet connection **3** for exhaust of gases and entrained solid particles. A thermocouple **15** is positioned in thereactor so as to indicate the temperature of the fluidized bed therein. Two gas feed lines are shown, line **4** from a reservoir of iodine, the vapor of which is carried into the reactor by a flow of inert gas through the reservoir, and line **5** which carries additional inert gas to the reactor. The means of introduction of these gases can be varied; for example, all of the fluidizing gas may be introduced through a single line which carries the iodine vapor as well. A tantalum wire basket **6** containing the refractory metal articles **14** to be coated is suspended within the reactor at such depth as to be completely below the surface of the bed particles when fluidization is effected by the upward flow of gas. The bed **7** comprises inert particles, preferably silica; silicon chips or powder **8**; and chips of a superalloy comprising chromium **9**. There is also supplied external furnacing **10** and means **11** for heating the iodine reservoir and **13**, for heating the inlet line. The exhaust gases are passed through a solids trap and bubbler (not shown) to a vent.

FIGURES 2 and 3, show tracings made by electron microprobe through the depth of a coating applied to a columbium-base alloy article by a process of this invention. In this case, the columbium-base alloy was one known commercially as "D–36," a product of E. I. du Pont de Nemours & Company, and comprising 10 weight percent titanium, 5 weight percent zirconium, the balance columbium. The chromium-bearing alloy used in the preparation of this specimen was a nickel-base alloy known commercially as "Hastelloy X," produced by Union Carbide Co. FIGURE 2 shows the microprobe tracings for columbium and titanium through the depth of the coating the external surface of the coated article being at the left of the figure. FIGURE 3 shows the microprobe tracing for chromium and zirconium through the depth of the coating, again the external surface being at the left side of the figure. It will be seen in FIGURES 2 and 3 that the chromium content in the coating is at a maximum level of about 3 to 5% and occurs

only in the outer 10–20% of the depth of the coating. "Hastelloy X" nickel base alloy contains the metals cobalt, molybdenum, tungsten, iron, silicon and manganese in addition to nickel and chromium. The only one of these elements detected in the coating was chromium; all of the other elements gave no signal. The columbium, zirconium, and titanium in the coating came, of course, from the base alloy D–36.

To illustrate in detail the operation of this invention, the following example is given. This is to be considered as illustrative only and is not to be held as in limitation of the invention.

EXAMPLE

In a quartz reactor and associated apparatus of the type shown in FIGURE 1, was suspended a tantalum wire basket containing 5 crimped columbium-base alloy coupons of 2 mil foil, each coupon measuring 1 inch by 1 inch. The bed particles consisted of 90 volume percent sand having a particle size of −20 +40 mesh (U.S. standard sieve scale), 8 volume percent of particulate silicon of −10 +20 mesh size, and two volume percent of chips of a chromium-bearing alloy, "Hastelloy X" having a particle size of −10 +20 mesh. The alloy coupons were formed of columbium-base alloy D–36.

A flow of nitrogen to the reactor was commenced at a rate which was sufficient to fluidize the bed. Heating of the reactor was begun and continued until the temperature of the bed was 500° F. At this temperature the inert gas was changed from nitrogen to argon, and introduction of iodine vapor was effected by flow of argon through the iodine reservoir. The gas feed to the reactor was adjusted to 98 volume percent argon and 2 volume percent iodine vapor, and the reaction in the fluidized bed was continued under these conditions for 30 minutes. At the conclusion of this time the heating was stopped, the flow of iodine was discontinued, and the basket containing the alloy coupons was removed from the reactor.

Using the same reactor and conditions of operation except that no chromium-bearing alloy chips were included in the fluidized bed, 5 additional coupons were coated, these being of the same dimensions and composed of the same alloy as were the coupons described above.

The depth of coating on each of these two series of samples was measured and found to average 0.3 mil for both series. For the process in which chips of chromium-bearing alloy were present, the coated coupons were found by electron-microprobe analysis to have a small amount of chromium (3–5%) deposited in the outer 10 to 20% of thickness of the columbium silicide coating.

Using the same procedure, but allowing the coating process to continue for longer periods of time, other series of samples were prepared in which the coating thicknesses averaged 0.55 mil to 1.67 mils.

Coupons from each of these runs were tested in cyclic oxidation tests and in thermal shock tests, and the results are given in Tables 1 and 2.

For testing thermal shock, the coupons are heated in a continuous flame to a temperature of from 2,200° F. to 2,500° F. in an oxidizing atmosphere and are cooled to room temperature once every hour. For oxidation testing the coupons being tested are heated in an electrically-heated furnace, with air flowing through at such a rate that the volume of the furnace is displaced every minute. The coated coupons are inspected and weighed every hour. The thermal shock test is much more severe than a static oxidation test, since it combines periodic thermal shock with static exposure. Results of this test give an evaluation of oxidation resistance, sensitivity to thermal shock, and degree of self-healing.

The test indicated as thermal shock test is a much more severe test in that coated coupons are heated in an oxidizing oxyacetylene flame to a temperature of from 2,500° F. to 3,000° F., held for a short period, and then cooled to a temperature in the range of room temperature to

200° F. by means of a blast of cold air. One cycle including heating and cooling takes about one minute. It will be seen that such a thermal shock test imposes severe stresses between the coating and the base metal. If the coating-base bond is not compatible, rapid failure occurs. Also, this is a severe test for integrity in the coating itself.

TABLE 1.—CYCLIC OXIDATION TESTS—COLUMBIUM-BASE ALLOY COATED SAMPLES

Chromium-modified $NbSi_2$ coating

[2,700° F.]

Coating thickness (mils)	Cycles to failure
0.55	75
1.38	426
1.44	398
1.50	295

[3,000° F.]

1.26	55
1.29	42

$NbSi_2$ coating, not chromium modified

[2,700° F.]

Coating thickness (mils)	Cycles to failure
0.43	83
0.95	66
1.10	23
1.30	28
1.50	96

[3,000° F.]

0.95	33
1.07	9
1.52	7

TABLE 2.—THERMAL SHOCK TESTS—COLUMBIUM-BASE ALLOY COATED SAMPLES

Chromium modified $NbSi_2$ coating

Coating thickness (mils)	Number of thermal shock cycles [1]
0.56	223
1.58	380
1.67	380

$NbSi_2$ coating, not chromium-modified

0.46	137
0.47	146
0.78	105
1.05	49
1.42	190

[1] To failure. (2,700° F. to room temp.).

Although in the illustrative examples given above, chips of the superalloy "Hastelloy X" were used as the source of chromium in the modified silicide coatings, other chromium-bearing alloys have been found to be equally useful. The chromium content of the alloy should be not over about 25% by weight, however, for it has been found that if an alloy of higher chromium content or if a very small amount of elemental chromium is substituted for the alloys of preference, chromium is deposited throughout the depth of the coating rather than being concentrated in a relatively narrow band as is shown by the X-ray probe traces of FIGURES 2 and 3. Such coatings have shown less resistance to oxidation and poorer properties in general than have the coatings formed using alloys of the chromium content specified.

Although the process of this invention has been described principally as a means of applying a protective alloy coating to columbium base alloys, it will be found equally effective when tantalum or tantalum-base alloys are used as the underlying metal.

We claim:

1. A process for applying a chromium-containing silicide coating to a refractory-metal article as an integral part thereof, the refractory metal comprising said article containing more than 50% by weight of a columbium, tantalum, or a combination of them, which process comprises effecting contact at a temperature of about from 850° F. to 1,150° F. between said refractory metal article and a fluidized bed of inert particles, said bed comprising also silicon, iodine, and a chromium-bearing alloy in which the chromium content is about from 5 to 25% by weight until a silicide coating having a chromium content of about from 1 to 5% by weight has formed on said article, at least the major portion of said chromium being present in about from 10 to 20% of the depth of the coating as measured from the outer periphery thereof.

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