

1

3,081,530

COATED COLUMBIUM

Stanley T. Wlodek, Niagara Falls, N.Y., assignor to Union Carbide Corporation, a corporation of New York
No Drawing. Filed Aug. 3, 1960, Ser. No. 47,136
7 Claims. (Cl. 29—194)

This application is a continuation-in-part of application Ser. No. 781,839 filed December 22, 1958.

The present invention relates to coated columbium and to a method for coating columbium to obtain columbium articles characterized by high-temperature oxidation resistance and resistance to thermal and mechanical shock.

Jet aircraft, rockets, missiles and the like require high-temperature materials of construction which have good oxidation resistance and good thermal and shock resistance at elevated temperatures. The number of materials which are characterized by these properties and which are suitable for the rigorous treatment to which these materials will be subjected are very few. Among the most promising are the refractory metals and alloys thereof such as tungsten, molybdenum, tantalum and columbium. Without exception, however, these materials are rapidly oxidized far below the elevated temperatures required in service, i.e., about 1700° F. to 2000° F. and above.

These refractory materials and alloys to be useable must also be workable. However, it is a well established fact that workability and oxidation resistance do not generally occur simultaneously, i.e., the higher the oxidation resistance the lower is the workability of the material in most cases.

One method which has been employed to overcome these problems is to apply a protective coating to these materials. The requirements for turbine buckets to operate around 2000° F. illustrate the nature of the problems encountered. The coating must withstand oxidation in combustion gases. It must be free of defects and/or be self-healing before destructive oxidation occurs, i.e., it must be able to provide its own protective coating in the oxidizing atmosphere in the event any defects do occur in the coating. The coating must withstand the stress induced with thermal gradients. It must have high resistance to thermal shock as temperatures may vary as much as 1000° F. in a matter of seconds. The coating must resist severe fatigue stresses and possess sufficient ductility to elongate without failure. It must resist mechanical shock and especially foreign particles entrained in a gas stream. It must withstand the corrosive and erosive action of the gas stream itself. While these problems were stated to exist with coated turbine buckets equivalent or similar problems and exacting requirements are present in other components of jet engines, missiles, rockets, etc.

Many prior compositions have been tried as coating materials for refractory metals, for example, molybdenum disilicide, ceramic-type coatings, enamels, chrome coatings, nickel-chrome alloys, alloys of aluminum, nickel and silicon and nickel-boron. All are known to fail when subjected to severe tests requiring the performances described above. In general, the more ductile tough coatings are not sufficiently oxidation resistant or have too low melting points to be useful whereas those possessing good oxidation resistance do not possess self-healing properties and/or are too brittle and sensitive to impact.

One of the most common causes of failure occurs when the coating obtains pin-point defects and cracks as a result of thermal stresses. If the coatings exhibited self-healing characteristics prior to the destructive oxidation of the base metal such failures could be prevented. Many of the known coatings described above exhibit self-healing but like molybdenum disilicide will not self-heal at low temperatures. Molybdenum disilicide, MoSi_2 , does not

2

effectively heal below 2200° F. to 2500° F. It is, therefore, obvious that such a coating would not be suitable below such a temperature as small defects develop. A coating that self-heals at relatively low temperatures, 1200° F. to 1700° F., has many advantages and is, therefore, desirable.

Accordingly, it is an object of the present invention to provide a coated refractory metal, which coated material is able to withstand severe thermal and mechanical stresses under oxidizing conditions.

Another object of the invention is to provide a coated refractory metal having thermal shock resistance, mechanical shock resistance and exhibiting self-healing characteristics.

Still another object of the present invention is to provide a process for improving the properties of columbium and columbium alloys.

The objects are achieved by coating columbium metal and columbium-base alloys with a plurality of coatings at least one of which is characterized by high-resistance to thermal and mechanical shock and the second being characterized by oxidation resistance.

The internal layer which is contiguous to the metal being coated must be the coating exhibiting thermal and mechanical shock resistance and must be miscible with the metal being protected. This coating should be plastic, and should exhibit a coefficient of expansion and a modulus of elasticity substantially the same as that of the base metal being protected. The exterior coating must be oxidation resistant and exhibit self-healing characteristics.

It is possible to employ more than a single coating of each of the oxidation resistant and shock resistant materials but in any case the shock resistant layer should be contiguous to the material being coated and the exterior coating must be an oxidation resistant coating. The physical properties of the exterior coating and the interior coating should correspond so that residual strains that would normally exist at the interface between a coating and the metal being coated are substantially eliminated or at least greatly alleviated by the presence of an intermediate or inner layer.

An outer and oxidation resistant coating which is suitable for use in the present invention comprises an alloy of molybdenum, silicon, chromium, boron and aluminum. This alloy more specifically comprises between 10 and 40 atom percent of at least one metal selected from the group consisting of molybdenum, tungsten, tantalum, columbium, and vanadium, between 20 and 65 atom percent silicon, between 2 and 16 atom percent of at least one metal selected from the group consisting of chromium, titanium and zirconium, between 2 and 25 atom percent boron and between 3 and 30 atom percent aluminum. The remainder of the composition is oxygen and other impurities such as carbon.

It has been found that a boron constituent and the constituent of the second metal grouping above (chromium, titanium or zirconium) can exist in the composition of the invention in the form of a metal boride, as a mixture of metal borides or as a mixture of elemental metals and boron.

A very suitable composition has been prepared from 40 percent by weight of molybdenum, 40 percent by weight silicon, 10 percent by weight chromium boride, which may be represented by Cr_2B_3 , and 10 percent by weight of aluminum. In atomic percentages this is 18.3 percent Mo, 62.3 percent Si, 3.2 percent Cr_2B_3 and 16.3 percent Al. This composition may be made as a blend of powders, or preferably as a prealloyed powder. The alloy offers greater uniformity when it is used for coating purposes. The optimum raw material composition appears to be noted above, namely 18.3 percent Mo—62.3 percent Si—3.2 percent Cr_2B_3 —16.3 percent Al, in atomic

percentages, although protective coatings have been made from compositions in the range of 30-65 percent Si, 10-35 percent Mo, 2-16 percent Cr, 2-25 percent B and 5-30 percent Al.

This composition of matter may be applied by the detonation coating method described in U.S. Patent 2,714,563 issued to R. M. Poorman et al. on August 2, 1955. In that process, a powdered composition to be coated is suspended in a body of detonatable gas in an elongated barrel capable of sustaining a detonation, and, upon ignition of the body of detonatable gas, the suspended powder is ejected from the barrel under the impetus of the detonation and directed against the surface of the body to be coated.

Coatings may be provided utilizing the composition of matter in conjunction with other known flame spraying processes such as the Wall-Colmonoy process.

A spray gun employing an oxy-acetylene flame as the heat source may be used in this coating process. The fuel-gas mixture is adjusted to produce essentially a chemically neutral flame. Powder consisting in composition of 40 weight percent Mo, 40 weight percent Si, 10 weight percent Cr_2B_3 and 10 weight percent Al is aspirated into the flame zone of the spray gun by means of an argon stream passing through a powder dispenser. The outlet of the spray gun is held about 6 inches from the workpiece. The workpiece is rotated and the spray gun is traversed along the axis of the workpiece so as to apply a coating 0.008-inch thick. The coating produced by this method is characteristically porous and further heat treatment is necessary in order to obtain a satisfactory coating. The coated workpiece may be placed in a furnace and heated to 1100° C. for 3 hours in a hydrogen atmosphere.

In addition, dipping, painting, or spraying the refractory body with a slurry of the suspended alloy or blended powder followed by heat treatment in an inert or reducing atmosphere may be employed to provide coatings from the novel composition of the invention.

It has been found that the detonation process of applying the novel composition of matter as a coating for surfacing bodies offers many advantages.

Suitable inner coatings are composed of columbium-base alloys with at least one of the metals of the group consisting of titanium, chromium, vanadium, aluminum, nickel and iron. Fair examples of suitable inner coating alloys can be specified.

The first of the aforementioned suitable inner alloy coating is a composition consisting essentially of from 1 to 40 weight percent of titanium, 8 to 30 weight percent iron, 3 to 35 weight percent chromium, up to 10 weight percent vanadium, up to 30 weight percent tungsten, up to 30 weight percent tantalum, the aggregate of said vanadium, tungsten and tantalum not exceeding 50 weight percent, up to 20 weight percent in the aggregate of at least one metal selected from the group consisting of nickel and cobalt, up to 5 weight percent in the aggregate of at least one alloying element selected from the group consisting of barium, silicon, beryllium, yttrium, boron and the rare earth metals, the remainder being columbium in a minimum amount of at least 30 weight percent.

The second of the aforementioned suitable inner alloy coating is a composition consisting essentially of from 1 to 40 weight percent titanium, 1 to 30 weight percent chromium, 1 to 40 weight percent aluminum, 0.5 to 10 weight percent vanadium, up to 30 weight percent in the aggregate of at least one metal selected from the group consisting of tungsten and tantalum, up to 10 weight percent in the aggregate of at least one metal selected from the group consisting of manganese, nickel, iron, cobalt, zirconium and hafnium, up to 5 weight percent in the aggregate of at least one alloying element selected from the group consisting of barium, silicon, beryllium, yttrium, boron, and the rare earth metals,

and the remainder being columbium in an amount of at least 30 weight percent.

The third of the aforementioned suitable inner alloy coating a composition consisting essentially of a minimum of 27 weight percent columbium, 10 to 50 weight percent tungsten, 5 to 40 weight percent tantalum, about 0 to 20 weight percent titanium, about 0 to 20 weight percent chromium, about 0 to 7 weight percent vanadium, about 0 to 5 weight percent iron, about 0 to 5 weight percent nickel, about 0 to 7 weight percent aluminum, about 0 to 5 weight percent cobalt, about 0 to 2 weight percent beryllium, about 0 to 5 weight percent zirconium, about 0 to 5 weight percent hafnium, about 0 to 2 weight percent barium, about 0 to 2 weight percent thorium, about 0 to 2 weight percent yttrium, about 0 to 2 weight percent of at least one rare earth metal, the sum total of titanium, chromium, aluminum, iron, nickel cobalt and vanadium not exceeding 50 weight percent and the sum total of zirconium, hafnium, barium, beryllium, yttrium, thorium and the rare earth metals not exceeding 6 weight percent; and incidental impurities.

The fourth of the aforementioned suitable inner alloy coating a composition consisting essentially of a minimum of 35 weight percent columbium, about 0 to 60 weight percent zirconium, about 0 to 10 weight percent of aluminum, about 0 to 10 weight percent vanadium, about 0 to 20 weight percent titanium, about 0 to 5 weight percent beryllium, about 0 to 5 weight percent magnesium, about 0 to 5 weight percent silicon, about 0 to 5 weight percent barium, about 0 to 5 weight percent tin, about 0 to 5 weight percent of at least one rare earth metal and incidental impurities.

Other suitable coatings are described in U.S. Patent No. 2,822,268 to Hix, U.S. Patent No. 2,838,395 to Rhodin and U.S. Patent No. 2,838,396 to Rhodin. An inner coating which has been found to be quite suitable comprises from 30 percent to 60 percent columbium, 10 percent to 40 percent titanium, 5 percent to 15 percent chromium, 2 percent to 10 percent aluminum, up to 10 percent vanadium, up to 20 percent nickel and up to 20 percent iron and preferably from 40 to 50 percent columbium, 20 percent to 40 percent titanium, 8 percent to 15 percent chromium, 3 percent to 7 percent aluminum, up to 7 percent vanadium, up to 15 percent nickel and up to 15 percent iron.

The various coatings may be applied to the columbium metal being coated by a method such as that described in U.S. Patent No. 2,714,563 to Poorman et al. However, other methods, e.g., spraying, flame spraying, flame plating, pressure bonding, etc., may be utilized to obtain these coatings.

The inner alloy may be applied in substantially the same manner as that described above for the preparation of the outer coating. To obtain the powdered material the alloy composition for the inner coating may be prepared by non-consumable arc-melting procedures after which the ingots so obtained may be embrittled by treatment in pure hydrogen at 600° F. The embrittled ingots may be crushed to through 325 mesh. The powder may be dehydrogenated by vacuum annealing.

To illustrate the advantages obtained by employing the multiple coating of the present invention rods of pure columbium metal 2 inches long and 1/4 inch in diameter having hemispherical ends were coated either with the oxidation resistant coating alone, or the oxidation resistant coating with the inner shock resistant coating, both being coated by the methods described previously. The specimens were employed in tests to determine their self-healing and shock resistant properties. The properties of the single coated materials were compared to those of the dual coated materials. The results are described in the following examples.

Example I

A pure columbium metal rod, prepared in the manner described previously, was coated by flame-plating tech-

5

niques with a 0.008-inch layer of an alloy consisting of 40 percent molybdenum by weight, 40 percent silicon, 7.6 percent chromium, 2.4 percent boron, and 10 percent aluminum. An identical rod was coated in the same manner first with an 0.005-inch layer of an alloy consisting of 46 percent by weight columbium, 30 percent titanium, 15 percent chromium, 5 percent vanadium, 4 percent aluminum, and, subsequently, with an 0.0035-inch layer of an alloy consisting of 40 percent by weight molybdenum, 40 percent silicon, 7.6 percent chromium, 2.4 percent boron, and 10 percent aluminum. Both specimens withstood 1000 hours exposure in air at 1150° C. without failure. After this preliminary test, four holes, 0.040, 0.031, 0.02 and 0.0135 inch in diameter and 1/2 of an inch deep were drilled in each specimen. The two specimens were then exposed to the atmosphere at 1050° C. with the result that the specimen which had been protected by the singly molybdenum-silicon-chromium-boron-aluminum coating suffered progressive oxidation and failure at the points where the coating had been damaged by drilling, while the specimen treated with the duplex coating showed remarkable self-healing tendency to the point that little visible attack occurred after 120 hours of exposure at 1050° C.

Example II

Four pure columbium metal rods, prepared in the manner described previously, were used in this experiment. Two of the rods were coated by flame-plating techniques with an 0.008-inch layer of an alloy consisting of 40 percent by weight molybdenum, 40 percent silicon, 7.6 percent chromium, 2.4 percent boron, and 10 percent aluminum, and the other two rods were coated by the same method with a first layer, 0.004 inch thick, of an alloy consisting of 47 percent by weight columbium, 30 percent titanium, 10 percent chromium, 10 percent nickel, 3 percent aluminum, and, subsequently, with a second layer, 0.003 inch thick, of an alloy consisting of 40 percent by weight molybdenum, 40 percent silicon, 7.6 percent chromium, 2.4 percent boron, and 10 percent aluminum. The four specimens were exposed to an oxidizing atmosphere (air) at 1150° C. and periodically removed from said hot environment and immediately quenched in water. The two specimens coated with a single layer were able to withstand only 3 and 5 water quenches, respectively, during a total exposure of 140 and 150 hours, respectively, while the remaining specimens protected by the duplex coating withstood 30 and 24 water quenches, respectively, during a total exposure of 267 and 188 hours, respectively.

Example III

A columbium rod was flame coated with a first coating comprising 32.3 weight percent titanium, 14.9 weight percent chromium, 4.84 weight percent vanadium, 4.24 weight percent aluminum, balance columbium and remainder incidental impurities and a second exterior coating comprising 40 atomic percent molybdenum, 40 atomic percent silicon, 8 atomic percent chromium, 2 atomic percent boron and 10 atomic percent aluminum. The resultant coated columbium exhibited an oxidation resistance of 1050 hours at a temperature of 1150° C. and withstood 7 water quenches from a temperature of 1150° C. before failure.

Example IV

A columbium rod was flame coated with a first coating comprising 31.1 weight percent titanium, 10.2 weight percent chromium, 9.9 weight percent nickel, 3.2 weight percent aluminum, balance columbium and remainder incidental impurities including iron and a second exterior coating comprising 40 atomic percent molybdenum, 40 atomic percent silicon, 8 atomic percent chromium, 2 atomic percent boron and 10 atomic percent aluminum. The resultant coated columbium withstood 30 water quenches from a temperature of 1150° C. before failure.

6

Example V

A columbium rod was flame coated with a first coating comprising 30.4 weight percent titanium, 9.8 weight percent chromium, 11.5 weight percent iron, 3.1 weight percent aluminum, balance columbium and remainder incidental impurities and a second exterior coating comprising 40 atomic percent molybdenum, 40 atomic percent silicon, 8 atomic percent chromium, 2 atomic percent boron and 10 atomic percent aluminum. The resultant coated columbium withstood 21 water quenches from a temperature of 1150° C. before failure.

Example VI

A columbium rod was flame coated with a first coating comprising 28.7 weight percent titanium, 11.1 weight percent chromium, 9.3 weight percent nickel, 3.4 weight percent aluminum, balance columbium remainder incidental impurities and a second exterior coating comprising 40 atomic percent molybdenum, 40 atomic percent silicon, 8 atomic percent chromium, 2 atomic percent boron and 10 atomic percent aluminum. The resultant coated columbium exhibited an oxidation resistance of 672 hours at a temperature of 1250° C.

As may be seen from the foregoing examples, the dual coated materials exhibit far greater self-healing characteristics and shock resistance than the single coated materials.

What is claimed is:

1. A process for the production of duplex-coated refractory metals comprising selecting at least one refractory-metal base from the group consisting of columbium and columbium alloys; providing and applying to said refractory-metal base a first coating contiguous to and miscible in said base, said first coating and said base exhibiting substantially similar coefficients of expansion and moduli of elasticity, said first coating comprising from 30 to 60 weight percent columbium, 10 to 40 weight percent titanium, 5 to 15 weight percent chromium, 2 to 10 weight percent aluminum, up to 10 weight percent vanadium, up to 20 weight percent nickel, up to 20 weight percent iron, and incidental impurities; and providing and applying a second coating, said second coating comprising between 10 and 40 atom percent of at least one metal selected from the group consisting of molybdenum, tungsten, tantalum, columbium and vanadium, between 20 and 65 atom percent silicon, between 2 and 16 atom percent of at least one metal selected from the group consisting of chromium, titanium and zirconium, between 2 and 25 atom percent boron, between 3 and 30 atom percent aluminum, the remainder being incidental impurities; said second coating being characterized by self healing properties and oxidation resistance.

2. A duplex coated columbium-base metal product characterized by resistance to severe thermal and mechanical stresses, oxidation-resistance, and self-healing, which comprises; a refractory-metal base selected from the group consisting of columbium and columbium-base alloys; a first coating contiguous to said base comprising 30 to 60 weight percent columbium, 10 to 40 weight percent titanium, 5 to 15 weight percent chromium, 2 to 10 weight percent aluminum, up to 10 weight percent vanadium, up to 20 weight percent nickel, up to 20 weight percent iron, and the remainder incidental impurities, said first coating being miscible in said refractory-metal base and having substantially similar coefficients of expansion and moduli of elasticity as said refractory-metal base; and a second coating comprising between 10 and 40 atomic percent of at least one metal selected from the group consisting of molybdenum, tungsten, tantalum, columbium and vanadium, between 20 and 65 atomic percent silicon, between 2 and 16 atomic percent of at least one metal selected from the group consisting of chromium, titanium and zirconium, between 2 and 25 atomic percent boron, between 3 and 30 atomic percent aluminum and the remainder incidental impurities.

3. A duplex coated columbium-base metal product in accordance with claim 2 wherein said refractory-metal base is essentially columbium.

4. A duplex coated columbium-base metal product in accordance with claim 2 wherein the first coating contiguous to said base is composed of 40 to 50 weight percent columbium, 20 to 40 weight percent titanium, 8 to 15 weight percent chromium, 3 to 7 weight percent aluminum, up to 7 weight percent vanadium, up to 15 weight percent nickel, up to 15 weight percent iron and the remainder incidental impurities.

5. A duplex coated columbium-base metal product characterized by resistance to severe thermal and mechanical stresses, oxidation-resistant and self-healing, which comprises; an essentially columbium refractory-metal base; a first coating contiguous to said base consisting essentially of 46 weight percent columbium, 30 weight percent titanium, 15 weight percent chromium, 4 weight percent aluminum and 5 weight percent vanadium, wherein said first coating is miscible in said refractory metal base; and a second exterior coating consisting essentially of 40 atomic percent molybdenum, 40 atomic percent silicon, 7.6 atomic percent chromium, 2.4 atomic percent boron and 10 atomic percent aluminum, said first coating and said columbium refractory-metal base exhibit substantially similar coefficients of expansion and moduli of elasticity.

6. A duplex coated columbium-base metal product characterized by resistance to severe thermal and mechanical stresses, oxidation resistant and self-healing, which comprises; an essentially columbium refractory-metal base; a first coating contiguous to said base consisting essentially

of 47 weight percent columbium, 30 weight percent titanium, 10 weight percent chromium, 3 weight percent aluminum and 10 weight percent nickel; and a second exterior coating consisting essentially of 40 atomic percent molybdenum, 40 atomic percent silicon, 7.6 atomic percent chromium, 2.4 atomic percent boron and 10 atomic percent aluminum, wherein said first coating and said columbium refractory-metal base exhibit substantially similar coefficients of expansion and moduli of elasticity.

7. A duplex coated columbium-base metal product characterized by resistance to severe thermal and mechanical stresses, oxidation resistant and self-healing, which comprises; an essentially columbium refractory-metal base; a first coating contiguous to said base consisting essentially of 44 weight percent columbium, 30 weight percent titanium, 10 weight percent chromium, 4 weight percent aluminum and 12 weight percent iron; and a second exterior coating consisting essentially of 40 atomic percent molybdenum, 40 atomic percent silicon, 8 atomic percent chromium, 2.0 atomic percent boron and 10 atomic percent aluminum, wherein said first coating and said columbium refractory-metal base exhibit substantially similar coefficients of expansion and moduli of elasticity.

References Cited in the file of this patent

UNITED STATES PATENTS

2,472,930	Wilkes	June 14, 1949
2,690,409	Wainer	Sept. 28, 1954
2,763,919	Kempe	Sept. 25, 1956
2,871,150	Fraser	Jan. 27, 1959