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2,865,088

REFRACTORY METAL BODIES

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This invention relates to refractory metal bodies and to other metal bodies which have been clad with a refractory metal and coated with a sintered skin containing silicon and chromium, with or without further quantities of boron to modify the effect thereof, these sintered skins serving to impart a high resistance to the refractory metal body to oxidation in air at high temperatures. More particularly, the invention relates to molybdenum, or metals which have been clad with molybdenum, to which substantial oxidation resistance in air at high temperatures has been imparted by a skin coating thereon of silicon and chromium, with or without further additions of boron, said skin being an alloy or intermetallic composition with the molybdenum, and to methods of forming these metallic products.

Refractory metals, particularly molybdenum, have highly desirable mechanical properties at elevated temperatures. One desirable use therefor has been as electrical furnace heating elements. Other desirable uses are in oil burner nozzles, artillery piece nozzles, rocket nozzles, turbine blades and buckets, component parts of jet engines, ignition coils for burners and valve seats for internal combustion engines. To obtain optimum utility for refractory metals in these several high temperature uses, it is usually necessary to exclude oxygen and it is common for this purpose to supply a continuous flow of hydrogen to the heated metal parts to avoid oxidation at the raised temperatures.

In copending applications of Campbell et al., Serial No. 150,398, Serial No. 150,543, Serial No. 150,544, filed March 18, 1950, methods are disclosed and claimed for the production of refractory bodies formed of molybdenum having a coating or skin which is resistant to oxidation in air at elevated temperatures, and thereby protects the metal base or core from oxidation. The coating therein is an integral coating or skin upon the molybdenum base, essentially of MoSi_2 , as alloys or intermetallic compositions having a silicon to refractory metal content in the molecular ratios of from about 1:1 to about 3:1, which correspond to alloys or intermetallic compositions containing from about 22.5% to about 47% silicon. Although the optimum protection of the molybdenum is obtained with coatings or skins having a molecular ratio of silicon to molybdenum or about 2:1, corresponding to a silicon content of about 37%, coatings or skins beyond this composition range also afford some protection for the molybdenum base or core. Thus, where it is indicated that the exterior skin layer comprises about 37% silicon and the balance molybdenum, this does not mean that the exterior layer consists entirely of the intermetallic compound of silicon and molybdenum having the approximate percentage named, namely MoSi_2 , but that the exterior layer consists largely or essentially of that pure intermetallic compound and may

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have associated with it the intermetallic compound of molybdenum and silicon consisting of about 22% silicon and the balance molybdenum, known as MoSi , and/or silicon in an amount in excess of that required to form the compound MoSi_2 .

These alloy coatings or skins on molybdenum furnish an exceedingly high resistance to oxidation at elevated temperatures. For example, molybdenum wire of very fine diameter of approximately 0.020 inch has a life of approximately 16 seconds when heated to a temperature of about 1500° C. in air. The same size molybdenum wire, when provided with a coating or skin as above described having a thickness of about 0.0032 inch, has a life of 4,000 seconds in air at the same temperature.

This thickness of coating does not represent the total thickness of an alloy layer. The total thickness of the alloy layer is roughly about double the thickness increase which is obtained during the coating operation. Throughout this application the term "thickness" is used to designate only the thickness increase effected by the coating.

In the copending application Serial No. 299,216, filed July 16, 1952 (Yntema et al. Case No. 1-C), improved resistance to high temperature oxidation of molybdenum wire was found by using a mixture of silicon and boron applied by vapor contact to form an alloy or intermetallic composition with the molybdenum, with the boron comprising about 2% to 10% of the coating.

In the copending application Serial No. 311,786 filed September 26, 1952 (Yntema et al. Case 2), improved resistance to high temperature oxidation in air of molybdenum was found by mechanically applying a mixture of silicon and boron wherein the mechanically applied coating in a ratio of about 1 to 4 parts of boron to 9 to 6 parts of silicon is sintered to the molybdenum as a skin alloy or intermetallic composition of the molybdenum, silicon and boron.

Molybdenum wire may fail at the point where it is maintained at highest temperature. For example, where molybdenum wire is secured between water cooled electrodes with passage of an electrical current therethrough, it may fail at its hottest point—about the center of the wire. A second type of failure is found at a point adjacent the cooler juncture of the wire with an electrode. Still another type of failure is at an intermediate point, neither the hottest nor the coolest. It is apparent that the life of molybdenum having a protective coating or skin is not necessarily and solely dependent upon the maximum temperature to which the body may be subjected.

Molybdenum-silicon-boron coatings are improved over molybdenum-silicon coatings in that the tendency of the wire to fail at a point of intermediate temperature is substantially reduced. However, such molybdenum-silicon-boron coatings, while having a long life up to about 250 hours at about 1700° C. in air, rapidly fail at a higher temperature, the life thereof being short at a temperature, for example, of about 2000° C. Moreover, while molybdenum-silicon-boron coatings are somewhat ductile, they do not have a particularly long life at a low or intermediate temperature, such as about 900° C., which is desirable for many uses.

As indicated above, the thickness of the coating does not represent the total thickness inasmuch as in the hot application, either sintering or by vapor deposition to effect the coating, there is substantial penetration of the molybdenum base. However, the thickness of the coating is measured as a thickness increase from the original

thickness of the metal coated and in the actual thickness of the alloy or intermetallic composition imparted as a skin to the molybdenum. Such thickness of coating usually exceeds about 0.5 mil and may range from about 1 to 5 mils, the thicker coatings usually having the greater protection.

According to the present invention, it is found that a coating of chromium, together with silicon, applied to the molybdenum as an alloy or intermediate composition therewith, will impart thereto such resistance to oxidation in air that it will withstand a temperature well exceeding 1700° C., such as about 2000° C., for periods long exceeding those available by the coatings of the prior applications above referred to. Moreover, at lower temperatures, such as a temperature as low as 900° C., a life exceeding 400 hours may be imparted to the molybdenum. In contrast, while a coating of molybdenum with silicon and boron is stable at 1700° C. in air for about 250 hours, the boron immediately begins to bubble and the coating is quickly destroyed by flaking and blistering at a temperature in the range of 1800 to 2000° C. However, in accordance with the present invention, when boron and chromium are used with silicon, the coating will not only withstand temperatures up to 1700° C. for a longer time, but the boron in combination therewith tends to inhibit the flaking and decrease a tendency of silicon and chromium alone to fail in a low temperature zone of heat, while increasing the life of the chromium-silicon coated molybdenum over the entire range of temperatures. For example, both chromium and boron with silicon impart to the molybdenum a life at 1700° C. of almost 600 hours, which is about double the life when the chromium is omitted. However, the boron, while inhibiting blistering and flaking of chromium-silicon coatings as well as preventing failures in a low temperature zone, causes the coating to fuse at about 2000° C., hence the boron-containing coatings with silicon and chromium are generally used at temperatures below 2000° C., such as about 1700° C., while the compositions wherein only silicon and chromium are present may be used at temperatures up to 2140° C. without fusion and for long periods of time.

Several procedures are available for applying the coatings hereof to the molybdenum. One useful procedure is to first electroplate or metallize the chromium upon the molybdenum and then deposit the boron and silicon by contacting the chromium-coated molybdenum with vapors of boron and silicon, such as vaporized halides of boron and silicon, in admixture with hydrogen. Where boron is to be included in the coating, vapors such as boron trichloride and silicon tetrachloride, in admixture with hydrogen and contacted with the metal, as described in the aforesaid application Serial No. 299,216 (Yntema et al. Case 1), or where the coating is to contain no boron, then halides of silicon only may be applied as vapors together with hydrogen, as described in copending applications Campbell et al. Serial Nos. 150,398, 150,543 and 150,544, filed March 18, 1950, to deposit the silicon upon the chromium-plated molybdenum.

Another useful method is to apply both the chromium and the silicon as vapors, the chromium being in the form of a volatile compound of chromium, such as chromium carbonyl, with or without vapors of boron halides, together with hydrogen, the molybdenum metal thus being coated with silicon and chromium or with silicon, chromium and boron, as desired, by a vapor contact at temperatures in the range of 1400 to 1800° C.

Another desirable method, which is generally preferred because of its simplicity, is to mechanically apply the elements silicon and chromium, with or without boron, as a slurry in a carrier liquid together with a temporary binder substance to be painted and dried as a temporary coating upon the molybdenum which is finally heated to volatilize and/or destroy the temporary binder, the elements being ultimately heated to sinter the same into the

molybdenum as an alloy or intermetallic composition therewith.

Other useful procedures are available in combinations of the procedures set forth above. For example, the molybdenum may be first metallized or plated with chromium metal and the silicon, with or without boron, may be further applied thereto either mechanically by painting as a slurry thereon or by a temporary binder which is finally sintered into the molybdenum coated with chromium metal. Thus, any combination of plating or mechanically applying one or more of the elements by painting and sintering or deposition of one or more elements from a vapor may be applied in any desired sequence to effect the coating.

Still other procedures are possible, particularly in effecting the chromium coating on the molybdenum. For example, the molybdenum may be prealloyed with the chromium to homogeneously contain a desired quantity of chromium; or the pure molybdenum or the molybdenum clad refractory metal may be suspended within a charge or bed of granular chromium and coarse alumina, the charge being then heated for several hours at about 1000 to 1100° C. while passing a mixture of hydrogen and hydrochloric acid gases through the coarse granular mixture. The chromiumized molybdenum body may then be siliconized by any desired procedure, with or without boron, either by vapor deposition or by mechanically applying the silicon, with or without boron, to the chromiumized molybdenum body. In any of these procedures, each of the elements may be coated as a separate step, or two of the elements may be first coated upon the molybdenum with the third coated as a separate step.

It is oftentimes useful when mechanical coating procedures are used to prealloy the silicon with the boron or the silicon with the chromium or the boron with the chromium, or all of these elements may be first prealloyed by sintering and then grinding to a powder which may be mechanically applied by painting with a temporary binder upon the molybdenum which is finally set as an integral skin upon the molybdenum either as an alloy or intermetallic composition therewith by sintering.

Substantial penetration and interaction of the coating elements takes place with the molybdenum variable somewhat with the time and the degree of heating as well as the method of application. The silicon, with respect to the elements chromium and boron, will vary from approximately 50 to 95 parts by weight thereof. The chromium will vary from about 25 to 5 parts by weight, and the boron, when used, will be in a generally similar proportion to that of the chromium, usually 25 to 5 parts by weight. Usually when chromium and silicon alone are applied, the proportions are preferably in the range of 10 to 15 parts of chromium to 90 to 85 parts of silicon, and the preferred ratio of boron, when used, is the same as the chromium so that in a ternary mixture a ratio of 70 to 80 parts of silicon to 15 to 10 parts of chromium to 15 to 10 parts of boron is a preferred ratio.

The actual composition of the skin formed with the molybdenum is one in which the quantity of molybdenum will vary with 50% to about 75%, increasing in molybdenum from the lowest to the highest in the region wherein the molybdenum is penetrated, the quantity of molybdenum increasing progressively to approach the pure molybdenum body. It is believed that the predominant molybdenum compound in the skin is molybdenum disilicide, MoSi_2 , but compounds which are analogous of chromium and boron will be present. Thus, the skin may also contain such compounds as chromium disilicide, chromium borosilicide, molybdenum borosilicide, molybdenum boride, chromium boride, silicon boride, and complex combinations of these whose identities have not been determined, as well as these several elements, molybdenum, chromium, silicon or boron as alloys.

The useful ratios of the coating elements are set forth in table form:

RATIO
(Parts by weight)

Silicon	Chromium	Boron	Preferred
95	5	---	-----
90	10	---	-----
85	15	---	-----
80	20	---	-----
75	25	---	-----
90	5	5	-----
85	10	5	-----
85	5	10	-----
80	10	10	-----
75	10	15	-----
75	15	10	-----
70	15	15	-----
60	20	20	-----
50	25	25	-----

Considered as an intermetallic composition or alloy with the molybdenum where chromium and silicon alone are used, the preferred composition for optimum stabilization effect is about 59% molybdenum, 37% silicon, and 4% chromium. Where the boron is also included as a component with the molybdenum, the preferred composition is approximately 59% molybdenum, 33% silicon, 4% chromium, and 4% boron.

In the several procedures mentioned above, where the molybdenum is first coated with chromium to effect a plating, this may be either by conventional electroplating procedure or by heating the molybdenum in the presence of granular chromium in a bed of coarse alumina while passing reducing gases, such as hydrogen, together with an acid gas, such as hydrochloric acid gas, through the bed while heating the bed to a temperature in the range of 1000 to 1100° C., preferably about 1050° C. Thereafter, the chromiumized molybdenum is subjected to vapors of silicon tetrachloride or other volatilizable silicon halide at temperatures in the range of about 1400 to 1800° C. while maintaining a reducing atmosphere, such as by volatilizing the silicon halide in an atmosphere of hydrogen. The chromiumized and the siliconized molybdenum body may thereafter be again treated by a similar vapor contact comprising a volatile halide of boron, such as boron trichloride in admixture with hydrogen. The vapor contact of the chromized molybdenum metal may be by a mixture of vapors of both silicon halide and boron halide and hydrogen, as described in the aforesaid application, Serial No. 299,216 (Yntema et al. Case 1-C).

Alternatively, molybdenum metal which has not been coated with chromium is exposed to vapors comprising volatile compounds of chromium such as chromium carbonyl, a silicon halide such as silicon tetrachloride, in sequence or in admixture, in the presence of a carrier gas such as hydrogen, at a temperature of about 1400 to 1800° C. These gases may be further admixed with a volatile compound of boron, such as boron trichloride, or the boron compound may be applied as a vapor in admixture with hydrogen as a subsequent treatment when the presence of boron is desired. A desirable means for heating the molybdenum, either before or after being coated with chromium, is by electric resistance or by suspending molybdenum metal, such as wire, between electrodes and passing an electric current therethrough while exposing the same to vapors of the metal compounds to be coated thereupon, the temperature of the wire being regulated by the quantity of current passed therethrough.

A much simpler and thereby preferred procedure for coating the molybdenum is to apply thereto the metal powders—silicon, chromium and, if desired, boron—as a mixture of these elements or in sequence in finely powdered form, as a slurry in a liquid carrier comprising a solution of a temporary binder substance which may be subsequently removed by heating to effect evaporation or

decomposition without leaving a carbonaceous residue in any significant quantity. The slurry is painted, such as by hand brushing, dipping, or spraying upon the molybdenum base, dried at ordinary or raised temperatures, such as in an oven at a temperature which merely evaporates the solvent, the temperature usually not exceeding about 100° C. The coated product is then slowly heated over a period of about 1 to 4 minutes to a temperature in the range of about 1300 to 1800° C., usually about 1400 to 1600° C., whereby the temporary binder substance is volatilized and/or decomposed to leave substantially no carbonaceous residue, and the thus coated molybdenum wire is then maintained for a further period of about 1 to 4 minutes, usually about 2 or 3 minutes, which is sufficient to sinter the particles into the molybdenum as an integral skin thereof, comprising an alloy or intermetallic composition with the molybdenum.

According to the preferred mechanical application procedure, both silicon and chromium are applied in proportions of 75 to 95 parts of silicon to 25 to 5 parts of chromium, preferably in proportions of 85 to 90 parts of silicon to 15 to 10 parts of chromium. Where the three elements are applied, the proportions are 50 to 90 parts of silicon, 25 to 5 parts of chromium and 25 to 5 parts of boron. The preferred range is 70 to 80 parts of silicon to 15 to 10 parts of chromium to 15 to 10 parts of boron. Powders of these elements separately or as presintered alloys are converted to a paint by suspending the finely powdered particles of a particle size of less than about 325 mesh in a liquid paint composition comprising a resin, preferably an alkyd resin such as Glyptal dissolved in a solvent. Coatings of the powders upon the molybdenum are mechanically applied by painting a slurry of the elements silicon and chromium as a binary mixture, or further with boron as a ternary mixture, upon the molybdenum base metal or upon a molybdenum-clad base metal such as steel, for example. The elements are temporarily bonded by the carrier to the molybdenum by drying the wet coatings, and are subsequently sintered to an alloy or intermetallic composition of the applied elements as a skin upon the molybdenum to form an alloy or intermetallic composition therewith. The molybdenum may be first coated with a liquid slurry of one element and dried and sintered, and then coated with a liquid slurry of the other element and dried and sintered. Alternatively, the molybdenum is coated with a slurry of mixed finely powdered elements of silicon and boron which are then dried and sintered. In a further alternative procedure, the silicon and chromium, with or without boron, may be sintered into an alloy mixture and the finely powdered sintered mixture is suspended as a liquid slurry and painted upon the molybdenum, the wet coating is then dried and finally sintered to the molybdenum. All of these procedures are possible, but the sintering of the finely powdered mixture of elements after application to the molybdenum and temporarily bonded thereto by drying is preferred.

In each case the coating procedure is repeated to produce a sintered intermetallic composition or alloy skin upon the molybdenum exceeding about 0.05 mil in thickness, such as in the range of 1 to 5 mils in thickness, preferably about 1.5 to 3 mils. The desired thickness is obtained by successive applications of painted coatings with or without intermediate sinterings. It is preferred to sinter each coating until the desired thickness of sintered coating is obtained. There is some variation in the life of the coating with respect to oxidation resistance in air at high temperatures, depending upon the method of sintering, the fineness of the elemental powders applied as a slurry in the wet coating to the molybdenum, and the character of the carrier liquid. Obviously it is desirable in any case that the coating be uniformly applied in even thickness over the molybdenum to obtain a uniformly thick sintered coating.

The paint resin

The resin of this paint is selected to be a thermoplastic resin because of its superior property to be volatilized and/or decomposed at high temperatures upon sintering to leave no substantial carbonaceous residue, and for imparting fluidity and even thickness to this paint. Any typical thermoplastic paint resin which leaves no substantial carbonaceous residue when heated to temperatures far exceeding its decomposition temperature, such as above 1300° C., may be used herein. Such resin will be understood to be a typical temporary bonding resin to firmly adhere the powdered elements silicon, chromium and boron to the molybdenum and maintain the adhesion until the resin is completely volatilized and/or decomposed. Alkyd resins are superior in this respect since they may be applied as a smooth coating and leave no carbonaceous residue when heated. Thermosetting resins such as Bakelite are generally unsuitable. Typical alkyds are such as are formed by reaction of a polybasic organic acid such as phthalic acid, succinic acid, adipic acid, etc., with a polyhydroxy aliphatic alcohol such as glycerin, ethylene glycol, etc., of which the reaction product of phthalic anhydride with glycerin, i. e., Glyptal resin, is preferred. The resin is applied in proportions of from 5% to 15%, usually about 10% by weight of the liquid carrier.

The solvent

Desirable solvents, particularly for Glyptal resins, are ketones. Thus we may use acetone, methyl ethyl ketone, diethyl ketone, diacetone alcohol, and preferably for a Glyptal, a mixture of diacetone alcohol and acetone in a ratio of about 7:3 by volume may be used.

Silicon

The silicon is preferably fine commercial elemental silicon, usually about 97% pure, used as a very finely powdered fraction which will pass a 325 mesh sieve or even finer. A desirable form of silicon is obtained by further classifying 325 mesh silicon by stirring a slurry thereof in water and pipetting off successive portions near the upper surface to obtain an extremely fine elutriated silicon in this manner.

Chromium

Substantially pure chromium is available in particle size, generally about 325 mesh. Extremely fine particle sized chromium may be obtained by elutriating a finely powdered suspension of 325 mesh chromium powder in water by agitating the suspension and pipetting off portions of the suspension near the surface of the agitated liquid. The chromium powder thus obtained is considerably finer than 325 mesh as commercially available and gives improved coatings when suspended as a slurry together with the other elements in a paint composition which is ultimately sintered as described.

Boron

The boron used may be a commercial grade comprising about 91% of elemental boron, the major impurity of which is magnesia. The boron is used as a finely powdered product, all particles of which are screened to pass a 325 mesh screen or even finer.

Presintering and mixing

As indicated above, the chromium and the silicon or the ternary elements chromium-silicon-boron may be applied as successive coatings, either element coated first, but it is preferred to mix the powders of the several elements with the carrier in the desired proportions and then paint the liquid slurry as a coating composition suspended in resinous solution in the solvent as a paint upon the molybdenum. Superior results are obtained when the elements are applied in extremely fine particle size, say less than about 325 mesh. Preferably the silicon is the extremely fine elutriated fraction obtained as above de-

scribed, wherein the particle size is considerably less than 325 mesh. Improved results, however, are obtainable where the fine powders, homogeneously mixed dry, are presintered at a temperature ranging from 1300° to 1800° C. in an inert atmosphere such as hydrogen and then finely ground to a powder less than 325 mesh, which is suspended as a slurry in the carrier liquid as a coating composition.

Coating composition

The resin is first dissolved in a high boiling solvent as above identified, preferably Glyptal resin in a solvent comprising a 7:3 volumetric mixture of diacetone alcohol and acetone. The powders are then stirred into the Glyptal resin in the ketone solvent in the desired ratio to form a paint slurry. The molybdenum or molybdenum-clad metal as wire rod or flat sheet is then coated either by hand brushing, dipping, or spraying with an air brush type sprayer. The wet coated metal is then placed in an air drying oven and dried at moderate temperatures, usually not exceeding 100° C., to evaporate the solvent and produce an empirically dry adherent coating of powder temporarily bonded to the molybdenum with the alkyd resin.

Sintering

The coated molybdenum has its coating sintered by heating for a short period of time in an inert or reducing atmosphere in the temperature range of about 1300° C. to 1800° C., whereby the Glyptal resin binder is volatilized and/or decomposed, leaving substantially no residue of carbon, and simultaneously when heated in this range, the chromium and silicon, as well as boron when present, become sintered to a substantially penetrated and sintered alloy or intermetallic composition skin upon the molybdenum.

Several types of furnaces may be used for effecting the sintering. Heating may be in a muffle furnace, or an induction heated furnace, or the molybdenum metal base may form the resistance of an electrical circuit whereby it becomes heated to the desired temperature range. This latter is herein termed "electrical resistance heating." If desired, the dried coated molybdenum may be preheated to more firmly set and partially or entirely decompose or volatilize the binder. In any case, the coated molybdenum is heated relatively slowly over a period of 1 to 4 minutes to reach the optimum sintering temperature in the range of 1300° to 1800° C., preferably about 1500° C. For sintering, after reaching the sintering temperature, the coated molybdenum is maintained at the sintering temperature for about 1 to 4 minutes, preferably about 2 to 3 minutes. It will be understood that substantial variation in the time of heating the molybdenum or molybdenum-clad metal is possible depending upon the size and the regularity, i. e., shape of the metallic article being heated, the objective being to relatively slowly heat the article at a rate which is not so rapid that the temporarily bonded and incompletely set coating will blister or flake off.

As indicated, a desirable coating should be at least one mil in thickness, and a single coat may be approximately this or even less, depending upon how thick the slurry was originally applied. For this purpose it is usually desirable to obtain the proper thickness of the coating by applying several coats in sequence. This repeated application of coatings may be merely after preliminarily drying the first coat, but it is most desirable and preferred to sinter each coating prior to application of the next.

EXAMPLE 1

Molybdenum wire having a thickness of approximately 20 mils is electroplated with chromium by conventional procedures to a plate thickness of approximately 0.5 mil. The wire is then suspended between electrodes within a chamber which is first purged of air by passing hydrogen gas therethrough and then through which is passed vapors

of silicon tetrachloride and hydrogen which has been freed of water vapor and oxygen, the wire being heated by the passage of electrical current therethrough to a temperature of approximately 1600° C. The atmosphere of hydrogen and silicon tetrachloride may be produced by passing the hydrogen gas through liquid silicon tetrachloride maintained at a temperature of about 0° C. at a rate of about 800 cc. of hydrogen gas per minute, and passed into contact with the hot molybdenum wire over a period of about 8 minutes and then terminating the heating of the filament while continuing to pass hydrogen gas alone through the chamber while the wire is cooling. Where boron is desired to be included in the coating, the same method is followed except that both boron and silicon halide vapors are obtained by bubbling hydrogen gas separately through the silicon and boron compounds at separate rates to obtain the desired proportions, after which both vapors and hydrogen are combined before passing into the chamber for contact with the hot filament. Further control of proportions of halide vaporized into the hydrogen is obtainable by varying the temperature of the liquid halide of silicon or boron such as between 0 and 30° C.

EXAMPLE 2

The method of Example 1 is repeated except that the molybdenum wire is heated as such without a coating of chromium, the chromium being supplied as a chromium carbonyl vaporized similarly by passing hydrogen gas through the liquid at room temperature, the hydrogen gas-vapor mixtures of chromium carbonyl and silicon tetrachloride, with or without boron chloride, being combined for simultaneous depositions on the hot molybdenum wire.

EXAMPLE 3

The following table illustrates a substantial number of sample coatings, each of which was obtained by sintering a mixture of silicon and chromium in alternate ratios of 90 silicon to 10 of chromium, and 80 silicon to 20 chromium, all sintering being at 1500° C., but the several samples further differ in the thickness of the coating imparted and the temperature at which they were tested to destruction by heating in air. Each of the chromium-silicon coatings of this table were prepared from powders of these elements of less than 325 mesh, obtained by water elutriation as described above. The powders in these proportions were suspended in a 10% solution of Glyptal resin dissolved in diacetone alcohol and acetone in volume ratio of 7:3. The molybdenum rod was painted by hand brushing with the slurry and dried in an oven at 100° C. The coated rod was then

slowly heated in hydrogen over a period of 3 or 4 minutes to a temperature of about 1500° C., and then sintered at that temperature by heating further for 2 or 3 minutes. The coated rods as described were repeatedly coated with several coatings and sinterings until the desired coating thickness was obtained.

TABLE I

Fabrication and testing of the oxidation resistance of Si-Cr coatings on 80-mil molybdenum rod

Sample No.	Ratio of Metals Applied, Parts by Weight		Sintering Temp., ° C.	Coating Thickness, Mils	Testing Temp., ° C.	Life Hours
	Si	Cr				
88	90	10	1,500	2.5	1,700	147.0
93	90	10	1,500	2.5	1,700	1248.2
83	90	10	1,700	3.0	2,000	2.2
85	90	10	1,500	4.0	2,000	64.8
86	90	10	1,500	3.0	2,000	75.9
87	90	10	1,500	2.0	2,100	11.4
89	80	20	1,500	2.0	2,150	Fused
90	90	10	1,500	2.5	2,150	Fused
91	80	20	1,500	2.5	2,000	1.4
92	80	20	1,500	2.0	2,000	1.3

¹ Failed in a low-temperature zone, below red heat.

It will be noted that the coating of silicon and chromium fused at a temperature of about 2150° C. Surprisingly, the longest lasting sample of this table, No. 93, failed in the low temperature zone, i. e., the zone of the heated coated molybdenum rod which is below red heat. However, the sample did not bubble or blister at temperatures increased substantially above 1700° C., which is a characteristic of coatings containing boron.

EXAMPLE 4

A second table is presented illustrating results secured when coatings containing silicon and chromium, varied in ratios from 95 to 5 of silicon to chromium down to 80 to 20, are heated in air at 2000° C. It will be noted that the range of 85 to 90 of silicon to 15 to 10 of chromium gave the best results. These coatings again were made in the same manner as Example 3, the silicon and chromium being finely elutriated powder suspended in a 10% Glyptal resin solution of diacetone alcohol and acetone in the ratio of 7:3 by volume. The coatings were obtained by wet coating the molybdenum rod, drying it at about 100° C., and then slowly heating to about 1500° C. to destroy the binder and then to sinter, the operation being repeated for about 3 to 5 coats to obtain a thickness of approximately 3 mils.

TABLE II

Life in hours of samples of 80-mil molybdenum rod coated with Si-Cr in different ratios and tested at 2000° C.

RATIO OF SILICON TO CHROMIUM

80 to 20		85 to 15		90 to 10		95 to 5	
Sample No.	Life, Hours	Sample No.	Life, Hours	Sample No.	Life, Hours	Sample No.	Life, Hours
91	1.4	98	6.3	83	2.2	97	0.8
92	1.3	101	0.2	85	64.8	102	0.4
112	4.7	104	8.3	86	75.9	103	1.7
113	7.4	105	80.3	94	2.6	106	30.3
116	8.4	108	5.5	95	8.3	107	0.1
117	62.2	109	1.0	96	76.3	114	0.1
		118	3.4	110	10.5	115	3.5
		119	1.6	111	63.0		
				120	6.0		
Max.	62.2	Max.	80.3	Max.	76.3	Max.	30.3
Ave.	13.4	Ave.	13.4	Ave.	33.9	Ave.	5.3

Both Tables I and II illustrate a characteristic pattern of chromium and silicon coated molybdenum rod to give coatings which last a considerable period of time at temperatures up to 2150° C. in air, the pattern being characterized by the fact that the coating either lasted a very long period of time, such as up to 76 hours at 2000° C., or up to 248 hours at 1700° C., failing at a low temperature zone, or failing completely in a very short period of time due to flaking or imperfections in the setting of the coating.

EXAMPLE 5

All of these types of failures are substantially overcome by inclusion of a quantity of boron in approximately the same range as the chromium. The boron coatings were generally smoother and gave substantially improved life at temperatures up to 1700° C. A sample which was coated with 80 parts of silicon to 10 parts of chromium to 10 parts of boron lasted 595 hours when heated in air at 1700° C. and failed only in the high temperature zone. However, this coating fused and failed immediately when heated to 2000° C.

As thus shown, a very desirable coating composition and method of coating is taught by addition of chromium in quantities of 5% to 25% and silicon in quantities of 95% to 75%, provides as an integral skin in combination with molybdenum upon a base metal. Such coating upon molybdenum is capable of imparting a long life to the molybdenum when heated in air at extremely high temperatures or at intermediate temperatures, failures being only in a low temperature zone. Such low temperature zone failures may be overcome by the further addition of boron to the molybdenum-chromium-silicon coating upon the molybdenum. Additionally, the boron provides a smoother and longer lasting coating; however, the coatings including boron are serviceable for protection in air only at temperatures not substantially exceeding 1700° C.

Our invention is not to be limited to the in situ formation of molybdenum-silicon-chromium, with or without boron, skin on a molybdenum base, since the said skin may be preformed and applied either to a molybdenum base or a base of another metal or alloy, such as steel, nickel, titanium, etc., which is to be protected from high temperature oxidation such as by having a skin of molybdenum first applied thereto as by cladding or electroplating the same, or by other known means for obtaining a molybdenum coating upon a refractory metal, the said molybdenum coated metal then having a skin applied thereto according to the procedures taught herein.

We claim:

1. As an article of manufacture, a refractory metal

body resistant to oxidation at elevated temperatures comprising a molybdenum base having an exterior layer composed predominantly of an alloy or intermetallic composition of molybdenum, silicon and chromium in the approximate proportions of 59% molybdenum, 37% silicon and 4% chromium.

2. As an article of manufacture, a refractory metal body resistant to oxidation at elevated temperatures comprising a molybdenum base having an exterior layer composed predominantly of an alloy or intermetallic composition of molybdenum, silicon, chromium and boron in the approximate proportions of 59% molybdenum, 33% silicon, 4% chromium and 4% boron.

3. As an article of manufacture, a metal base having thereon a protective skin resistant to oxidation at elevated temperatures, said skin being composed predominantly of an alloy or intermetallic composition of molybdenum, silicon and chromium, there being from about 50% to 75% by weight of molybdenum in said alloy or intermetallic composition and the balance being substantially silicon and chromium, the silicon to chromium ratio being in the range of from about 75 to 95 parts by weight of silicon to 25 to 5 parts by weight of chromium.

4. As an article of manufacture, a metal base having thereon a protective skin resistant to oxidation at elevated temperatures, said skin being composed predominantly of an alloy or intermetallic composition of molybdenum, silicon, chromium and boron, there being from about 50% to 75% by weight of molybdenum in said alloy or intermetallic composition and the balance being substantially silicon, chromium and boron, the silicon to chromium to boron ratio being in the range of from about 50 to 90 parts by weight of silicon to 25 to 5 parts by weight of chromium to 25 to 5 parts by weight of boron.

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