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METHOD OF MAKING REFRACTORY METAL BODIES

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This invention relates to metal bodies which are of a refractory character, or which have been clad with a refractory metal, and coated with a sintered skin of silicon and boron to impart thereto a high resistance to oxidation at high temperatures. More particularly, the invention relates to coated molybdenum, or metals which have been clad with molybdenum, to which oxidation resistance at high temperatures has been imparted by a skin coating on the molybdenum of silicon and boron as an alloy or intermetallic composition with the molybdenum, and to mechanical 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, now United States Patent No. 2,665,475; Serial No. 150,543, now United States Patent No. 2,665,997; and Serial No. 150,544, now United States Patent No. 2,665,998; filed March 18, 1950 and issued January 12, 1954, methods are disclosed and claimed for the production of refractory bodies formed of molybdenum having a coating or skin which is resistant to oxidation at elevated temperatures, thereby protecting the metal base or core from oxidation. The coating described therein is an integral coating or skin upon the molybdenum base comprising $MoSi_2$ as alloys or intermetallic compositions having a silicon to refractory metal content in the molecular ratio 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 of about 2:1, corresponding to a silicon content of about 37%, coatings 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 have associated with it the intermetallic compound of molybdenum and silicon consisting of about 22½% 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 such coating 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 the 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.

As described in copending application Serial No. 299,216, filed July 16, 1952, Yntema et al., improved resistance to high temperature oxidation of molybdenum wire was obtained by using a mixture of silicon and boron to from a skin or coating in the form of an alloy or intermetallic composition with the molybdenum, using both of these elements, with the boron comprising about 2% to 10% of the weight of the coating.

Molybdenum wire may fail at the point where it is maintained at highest temperature. For example, when molybdenum wire is secured between electrodes with passage of electric current therethrough, it may fail at its hottest point, about the center of the wire. A second type of failure is found at an intermediate point between the hottest point and the cooler juncture with the electrode. An outstanding advantage of the coating containing both silicon and boron is in its greater resistance to failure of this second type.

All the coatings of these prior applications hereinabove mentioned were obtained by maintaining the heated molybdenum in a reducing atmosphere of hydrogen containing vapors of a metal salt of one of these metals, such as silicon tetrachloride or other halide, where silicon alone is coated, or a mixture of vapors of silicon and boron salts where both are coated, such as silicon tetrachloride or other silicon halide, and boron chloride or other boron halide, the molybdenum being exposed to a mixture of such vapors and hydrogen in the temperature range of 1400 to 1800° C. The vapor deposition process has been difficult to apply commercially under certain conditions, and particularly to large metal bodies.

According to the present invention we have found that highly simplified procedures are possible for mechanically applying a coating of boron and silicon upon a molybdenum base to substantially enhance the useful life of the molybdenum at high temperatures in the presence of air or other oxidizing medium.

Moreover, according to this invention it is found that the mechanical coating of molybdenum with silicon and boron imparts different characteristics as to the depth of the penetration and the ductility of the coating by having a reduced brittleness, and resistance to oxidation in air at high temperatures.

Coatings of boron alone, however applied, impart only a minor improvement in resistance of the molybdenum to oxidation, approximately 6 hours. Silicon, while greatly increasing the life, of the order of hundreds of hours, when coated upon molybdenum by vapor deposition according to the prior applications above referred to, will increase the life of the molybdenum in air at 1700° C. only about 35 hours when coated by the simplified mechanical application procedures herein disclosed.

We have discovered that the presence of boron in the molybdenum-silicon coatings as exterior layers, mechanically applied as a paint or slurry of these elements in a carrier medium which is subsequently removed to leave the boron and silicon superficially bonded to the molyb-

denum, and finally sintered into the molybdenum as a coating comprising a skin thereon, comprising an alloy or intermetallic composition of molybdenum with both the boron and silicon, has outstanding advantages both in the simplification of applying the oxidation resistant coating and in the superiority of the coated product so obtained. The composition by present coating procedures consists of ternary alloy coatings or intermetallic compounds, or any other type of alloy or composition including molybdenum, silicon and boron in the proportion ranges hereinafter stated.

The exact chemical nature of the skin or coating is unknown. It may consist largely of molybdenum silicides, molybdenum borides, molybdenum borosilicides, or some or all of these in admixture with silicon boride or with the free elements silicon and boron, the critical properties of which are imparted when the elements are mechanically applied in the desired proportions.

According to the procedure of the present invention, both boron and silicon are applied desirably in the proportions of 1 to 4 parts of boron to 9 to 6 parts of silicon, preferably about 2 parts of boron to 8 parts of silicon, all parts being by weight. Powders of these elements, separately or as alloys with each other, are converted to a paint by suspending the finely powdered particles in a liquid paint composition comprising a thermoplastic resin or a thermosetting resin, preferably an alkyd resin, such as Glyptal, dissolved in a solvent. Coatings of the powders upon the molybdenum are mechanically applied herein by painting a slurry of both of these elements, silicon and boron, upon the molybdenum base metal or upon a molybdenum clad base metal. The elements silicon and boron are temporarily bonded by the carrier resin to the molybdenum, and are subsequently sintered to an alloy or intermetallic composition of silicon and boron as a skin upon the molybdenum to form a ternary alloy or intermetallic composition therewith.

Several specific mechanical procedures are possible. The molybdenum may be first coated with a liquid slurry of one element, 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 boron may be presintered into an alloy mixture and the finely powdered sintered mixture suspended as a liquid slurry and painted upon the molybdenum, the coating dried and finally sintered to the molybdenum. All of these procedures are desirable, 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 .05 mil in thickness, such as in the range of 1 to 3 mils in thickness, preferably about 1.5 to 2.5 mils. The desired coating may be obtained by successive applications of painted and dried coatings with or without intermediate sinterings. It is preferred to coat, dry and sinter each coating in a series of cycles until the desired thickness of composite 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 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 volatized 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 about 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 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 give good adhesion, good flow, and hold the coating while heating and leave no carbonaceous residue. Thermosetting resins, such as Bakelite, which leave a substantial deposit of carbon are unsuitable; others are typical alkyd resins such as are formed by reaction of polybasic organic acids such as phthalic acid, succinic acid, adipic acid, etc., with polyhydroxy aliphatic alcohols 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, and the quantity of resin related to powdered elements may range from about 1.5 to 3.5:1, usually about 2 to 3:1.

THE SOLVENT

Desirable solvents, particularly for alkyd resins, are ketones. We may use any volatile ketone, such as acetone, methyl ethyl ketone, diethyl ketone, diacetone alcohol, and preferably, for a Glyptal resin, a mixture of diacetone alcohol and acetone in a ratio of about 7:3 parts by volume may be used.

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, and may be even finer. It is used in proportion, as indicated above, of 1 to 4 parts by weight of boron for each 9 to 6 parts of silicon, preferably about 2 parts of boron to about 8 parts of silicon.

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 and preferably 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 liquid surface to obtain an extremely fine elutriated silicon in this manner.

PRESINTERING AND MIXING

As indicated above, the boron and the silicon may be applied as successive coatings, either element coated first, but it is preferred to mix both of the powders with the carrier in the desired proportions and then paint the liquid slurry as a coating composition suspended in the resinous solution in the solvent as a paint upon the molybdenum. Superior results are obtained when extremely fine particle size, in any case less than 325 mesh, is applied, and preferably the silicon is the extremely fine elutriated fraction obtained, as above described, wherein the particle size is considerably less than 325 mesh. Improved results, however, are obtainable where fine silicon and boron 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 coating composition in the desired ratio, i. e., 1 to 4 parts of boron and 9 to 6 parts of silicon, 1 part of Glyptal resin and sufficient solvent to form a fluid mixture, the solids being by weight. The molybdenum or molybdenum clad metal as wire rod or flat sheet is then coated either by hand brushing or spraying with an air brush type sprayer. Other methods, including dipping, may be resorted to for rapid coating with some sacrifice of the desired even thickness of coating. 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 a substantially dry adherent coating of the boron and silicon powder temporarily bonded to the molybdenum with the substantially dry alkyd resin.

SINTERING

The coated and dried molybdenum then has its coating sintered by heating for a short period of time in an inert or reducing atmosphere in the temperature range of 1300° to 1800° C., whereby the Glyptal resin binder is volatilized and/or decomposed, leaving substantially no residue of carbon. Simultaneously when heated in this range the boron and silicon 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, an induction heated furnace, or the coated molybdenum metal base may form the resistance of an electrical circuit whereby it becomes heated by passage of electric current therethrough to the desired temperature range, herein termed "electrical resistance heating." If desired, the dried, coated molybdenum may be preheated to more firmly set and to partially or entirely decompose or volatilize the binder. In any case, the coated molybdenum is heated relatively slowly over a period of about 2 to 5 minutes to raise the temperature thereof to destroy the binder and to obtain the optimum sintering temperature in the range of about 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 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 as originally applied. For this purpose it is usually desirable, to obtain the proper thickness of the coating, to apply 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 both dry and sinter each coating prior to application of the next.

EXAMPLES

The following table illustrates results obtained from several experimental coatings. The several examples of the table illustrate the effects of one and several coatings dried and sintered in alternate cycles. The single coating, usually from 0.5 to 1 mil in thickness, is considerably less effective than the thicker coatings of 2.5 mils or more. The thickness of each coating was measured as an increase in the absolute thickness of the rod, the depth of penetration of the molybdenum as an alloy or intermetallic composition with the boron and silicon being unknown. The sintering was usually effected by electrical resistance heating, although in some instances a muffle furnace was used.

Fabrication and testing of the oxidation resistance of Mo-Si-B *painted coatings on 80-mil molybdenum rod in lengths of 4½ inches*

Sample Number	Ratio of Metals Applied (Parts by Weight)		Sintering Temperature (° C.)	Sintering Time (Minutes)	Coating Thickness (Mils) [1]	Life at 1,700° C. in Air (Hours)
	Si	B				
1	10		1,640	1		35.2
3	9	1	1,640	3	1	50.3
10	7	3	1,820	3	0.5	0.2
15	9	1	1,525	3	1	53.2
16	9	1	1,410	3	0.5	17.7
17	8	2	1,525	3	1	47.8
18	7	3	1,525	3	1	11.6
19	9	1	1,525	3	1	
19	Recoated once under same conditions				1.5	52.1
20	8	2	1,525	3	1	
20	Recoated once under same conditions				1.5	106.7
21	[2] 8	2	1,525	3	0.5	
21	Recoated once under same conditions				1	111.9
24	[2] 8	2	1,525	1	0.5	
24	Recoated once under same conditions				2.5	252.3
27	[2] 8	2	[3] 1,450	1	0.5	
27	Recoated once under same conditions				2.5	183.8
30	8	[4] 2	1,525	1	1	
30	Recoated twice under same conditions				2	156.0

[1] Radial increase in dimension.
[2] Very fine silicon separated by elutriation.
[3] Sintered in muffle furnace. Temperature registered by thermocouple.
[4] Prealloyed silicon and boron (minus 325 mesh).

Sample numbers 15, 17 and 18 illustrate variation in ratios of silicon to boron of 9:1, 8:2 and 7:3, respectively. Samples 15 and 17, coated to 1 mil thickness, lasted about 50 hours when heated at 1700° C. in air, but sample 18, with 7:3 silicon-boron coating, lasted only 12 hours under the same conditions. The 9:1 and 8:2 ratios were repeated in samples 19 and 20, which were coated twice to produce coatings of 1.5 mils thickness. The 8:2 ratio of sample 20, is indicated to be substantially better since it lasted 107 hours as compared to the 9:1 ratio of sample 19, which showed a life of only about 52 hours under the same conditions. The extremely fine elutriated silicon in the 8:2 ratio with boron, according to sample 21, gave a coating only 1 mil in thickness but which lasted approximately 112 hours, indicating superiority for this type of silicon, better than twice that of sample 17. Maximum life is illustrated in these samples, as sample 24, wherein a coating of 2.5 mils of very fine silicon and boron had a useful life of approximately 252 hours. The sintering of these samples was effected in an atmosphere of hydrogen but other inert gases, such as argon, may be used.

Other shapes, such as flat sheets of molybdenum, may be coated by the present method in an analogous manner. Protection is available where molybdenum is merely a cladding, such as a welded sheet of molybdenum, upon the metal to be protected, or a plating or metalizing of molybdenum upon some other metal.

The foregoing description illustrates that molybdenum or molybdenum coated bases may be protected from air oxidation at temperatures up to about 1700° C. for long periods of time, and at temperatures even exceeding 1700° C. for lesser periods, but it will be understood that the protective effect is longer lasting at much lower temperatures, such as at 900° C., which is a desirable temperature limit when some of the mechanical properties of the molybdenum or metal coated therewith are desirably retained.

It is apparent from the foregoing that the coating method described herein is one which may be rapidly applied to molybdenum in a highly commercial manner to produce skins or coatings having comparably high portective characteristics with respect to the more difficultly applied methods described in the companion applications, referred to herein. Many base metals, such as

steel, nickel, titanium, etc., which are to be protected from high temperature oxidation in air may be first coated or clad with a thin film of molybdenum, and may thereafter have sintered thereto by painting and then sintering the silicon and boron.

We claim:

1. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures, comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron in a liquid carrier containing a fugitive binder substance, there being from about 1 to 4 parts by weight of boron for each 9 to 6 parts by weight of silicon, and slowly heating the coated molybdenum body in a non-oxidizing atmosphere to a temperature in the range of 1300° to 1800° C. to remove the binder substance and sinter the silicon and boron to an integral film coating upon the molybdenum.

2. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron as powders of a particle size not exceeding 325 mesh in a liquid carrier containing a fugitive organic binder substance, there being from about 1 to 4 parts by weight of boron for each 9 to 6 parts by weight of silicon, and slowly heating the coated molybdenum base in a non-oxidizing atmosphere to a temperature in the range of 1300° to 1800° C. to remove the binder substance and sinter the silicon and boron to an integral film coating upon the molybdenum.

3. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron as powders of a particle size not exceeding 325 mesh in a liquid carrier containing a fugitive organic binder substance, there being from about 1 to 4 parts by weight of boron for each 9 to 6 parts by weight of silicon, and slowly heating the coated molybdenum body in a non-oxidizing atmosphere to a temperature in the range of 1300° to 1800° C. to remove the binder substance and sinter the silicon and boron as an integral film coating upon the molybdenum.

4. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron in a liquid carrier comprising a thermoplastic resin decomposable at high temperatures with substantially no carbonaceous residue dissolved in a volatile solvent, there being from about 1 to 4 parts by weight of boron for each 9 to 6 parts by weight of silicon, and slowly heating the coated molybdenum base in a non-oxidizing atmosphere to a temperature in the range of 1300° to 1800° C. to remove the binder substance and sinter the silicon and boron as an integral film coating upon the molybdenum.

5. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron in a liquid carrier comprising an alkyd resin dissolved in a volatile solvent, there being from about 1 to 4 parts by weight of boron for each 9 to 6 parts by weight of silicon, and slowly heating the coated molybdenum base in a non-oxidizing atmosphere to a temperature in the range of 1300° to 1800° C. to remove the binder substance and sinter the silicon and boron as an integral film coating upon the molybdenum.

6. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron in finely powdered form of a particle size not exceeding 325 mesh in a liquid carrier comprising a thermoplastic resin decomposable at high temperatures with substantially no carbonaceous residue dissolved in a volatile solvent, said elements being present in a ratio of about 1 to 4 parts of boron to about 9 to 6 parts of silicon by weight, and said thermoplastic resin being present in a ratio of 1.5 to about 3.5 parts of resin to each part of powdered coating element, drying the wet coated molybdenum base and slowly heating the same to a temperature in the range of 1300° to 1800° C. to remove the thermoplastic resin, and continuing the heating in said range for a period sufficient to sinter the silicon and boron as an integral film upon the molybdenum having a thickness exceeding about 0.5 mils.

7. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a suspension of the elements silicon and boron in finely powdered form of a particle size not exceeding 325 mesh in a liquid carrier comprising a thermoplastic resin decomposable at high temperatures with substantially no carbonaceous residue dissolved in a volatile solvent, said elements being present in a ratio of about 1 to 4 parts of boron to about 9 to 6 parts of silicon by weight, and said thermoplastic resin being present in a ratio of 1.5 to about 3.5 parts of resin to each part of powdered coating element, drying the wet coated molybdenum base, slowly heating the same to a temperature in the range of 1300° to 1800° C. to remove the thermoplastic resin, continuing the heating in said range for a period sufficient to sinter the silicon and boron as an integral film upon the molybdenum having a thickness exceeding about 0.5 mils, and applying at least one additional coating in the same manner to produce a sintered coating upon the molybdenum base of silicon and boron having a thickness in the range of 1 to 3 mils.

8. The method as defined in claim 6 wherein the silicon and boron are applied in a ratio of about 8:2.

9. The method as defined in claim 6 wherein the liquid carrier is a solution of an alkyd resin dissolved in a volatile ketone.

10. The method as defined in claim 4 wherein the non-oxidizing atmosphere comprises hydrogen.

11. The method as defined in claim 4 wherein the silicon and boron are commercial powders having usual commercial impurities, said elements having a particle size not exceeding 325 mesh, the silicon of which is obtained by elutriating a suspension in water of the finely powdered commercial silicon.

12. The method of forming refractory metal bodies resistant to oxidation in air at elevated temperatures comprising coating a molybdenum metal base with a liquid coating composition comprising a carrier liquid having dissolved therein a temporary organic binder substance and having suspended therein a finely powdered presintered mixture of silicon and boron in the ratio of about 1 to 4 parts of boron to about 9 to 6 parts of silicon by weight, drying said coated molybdenum base and then slowly heating the same at a temperature in the range of 1300° to 1800° C. to remove the binder substance and sinter the silicon and boron into the base metal as an integral film coating thereon having a thickness exceeding about 0.5 mils.

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