

1

2,920,006

HIGHLY REFRACTIVE MOLYBDENUM BODIES AND METHOD OF PREPARING SAME

Leonard F. Yntema, Waukegan, Ill., and Edward A. Beidler, Columbus, and Ivor E. Campbell, Gahanna, Ohio

No Drawing. Application December 13, 1957
Serial No. 710,831

9 Claims. (Cl. 148—6.3)

This invention relates to metal bodies resistant to oxidation at high temperatures and more particularly to such bodies formed of molybdenum which is provided with a coating or skin to render the base metal resistant to oxidation at high temperatures.

This application is a continuation-in-part of our co-pending application, Serial No. 299,216, filed July 16, 1952 now abandoned, which application is a continuation-in-part of application Serial No. 202,412, filed December 22, 1950, now abandoned.

The refractory metal molybdenum has highly desirable properties and characteristics for many purposes. For example, it retains its mechanical properties at elevated temperatures and is very desirable for use in forming electrical furnace heating elements. However, in order to prevent oxidation of the metal at elevated temperatures it is necessary to exclude oxygen and a continuous flow of hydrogen is maintained over the heated resistance elements. Molybdenum, of course, is desirable for many other applications, such as oil burner nozzles, artillery piece nozzles, rocket nozzles, turbine blades or buckets and other component parts of jet engines, ignition coils for gas and oil burners and valve seats for internal combustion engines, the foregoing use being merely the best known.

The present invention makes possible the protection of all metals, steel, for example, but particularly molybdenum, which are designed for use in products which in use are exposed to high temperature, air and erosion.

In the co-pending applications of Campbell et al., Serial No. 150,543, now Patent No. 2,665,997; Serial No. 150,544, now Patent No. 2,665,998; and Serial No. 150,398, now Patent No. 2,665,475, 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 at elevated temperatures and which protects the base or core from oxidation at such temperatures. The molybdenum bodies formed in accordance with these methods consist of a molybdenum base or core having an integral coating or skin of molybdenum-silicon alloys or intermetallic compounds. The silicon content of the protective coatings or skins varies in the molecular ratio of silicon to refractory metal of from about 1:1 to about 3:1, which corresponds to alloys or intermetallic compounds 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 or skins beyond the composition range also afford some protection for the molybdenum base or core.

The coating or skin is formed on the molybdenum base by passing a mixture of hydrogen and vapors of a silicon halide such as silicon tetrachloride or silicon tetrabromide over the heated molybdenum base. Where the molybdenum base is maintained at a temperature appreciably below the melting point of silicon during the

2

deposition, the deposited silicon does not alloy or diffuse into the molybdenum to any appreciable degree, the degree of alloying or diffusion being directly proportional to the specific temperature employed. The silicon coated molybdenum is then heated to a higher temperature and maintained at such higher temperature to effect a substantially complete alloying of the silicon and the surface portions of the molybdenum base to form the protective coating or skin.

Where the temperature of the molybdenum body is maintained at a temperature at least as high as the melting point of silicon during the deposition of the silicon, there is an immediate alloying of the silicon and the surface portions of the molybdenum.

These alloyed coatings or skins on molybdenum furnish an exceedingly high resistance to oxidation at elevated temperatures. For example, molybdenum wire having a diameter of approximately 0.020" 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 having a thickness of about 0.00032" has a life of 4,000 seconds at the same temperature.

The thickness of the 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 operation.

The protection afforded the molybdenum by the alloy coatings may be further illustrated by reference to the lives of coated molybdenum bars having dimensions of about 0.5" x 0.05" x 6" and having coatings of the order of 0.0015" to 0.002" in thickness. The lives were measured by maintaining the coated bars at the designated temperatures in air.

Temperature		Life
° C.	° F.	
815	1,500	In excess of 8,000 hours.
1,090	2,000	In excess of 3,000 hours.
1,370	2,500	Average about 100 hours.
1,650	3,000	Average about 70 hours.
1,760	3,200	(1 specimen) 77 hours.
1,850	3,360	Average about 24 hours.

Molybdenum bodies provided with this protective molybdenum-silicon coating or skin, while being a tremendous advance in the art, can be made to exhibit two types of failures. The first type of failure is that which is commonly encountered at lower temperatures and occurs at that portion of the body which is maintained at the highest temperature. For example, a molybdenum wire secured at opposite ends to electrodes and heated by the passage of an electrical current therethrough will fail, in general, near its mid-point when maintained at a relatively low temperature. In such instances the center portion of the wire will attain a higher temperature because of the greater heat loss at the ends of the wire which are secured to terminals.

The second type of failure which is most commonly encountered at the higher temperatures is a failure which occurs at a point intermediate an area of maximum temperature and an area of minimum temperature. It is thus apparent that the life of the molybdenum having the protective coating or skin is not necessarily and solely dependent upon the maximum temperature to which the body will be subjected.

The principal purpose of the present invention is to

provide molybdenum bodies and other metal bodies having a coating or an exterior layer which has an appreciably greater resistance to oxidation at high temperatures than the resistance exhibited by molybdenum-silicon alloy coatings.

A further object of this invention is to provide a highly resistant coating or skin which does not exhibit a failure at the intermediate temperature zones.

Another object of our invention is to provide a method of applying to or forming on molybdenum an integrally bonded, highly protective coating or exterior layer which will protect the molybdenum against oxidation at high temperatures.

Other objects and advantages of this invention will become apparent from the description and claims which follow.

The present invention contemplates, in particular, bodies of the refractory metal molybdenum having a coating or exterior layer of molybdenum-silicon-boron alloys or intermetallic compounds, but it includes other metal bodies to which the high temperature, oxidation-resistant coating of the present invention is either formed thereon in situ, as by plating the metal base with molybdenum and then reacting it with silicon and boron, or applied thereto by mechanical means, as by welding, for example. Although we have designated the coatings of the present invention as molybdenum-silicon-boron alloys or intermetallic compounds, the precise nature of the coatings or skins has not been determined. It has been established that in accordance with the methods as described in the aforementioned Campbell et al. applications, alloys or intermetallic compounds are formed between the molybdenum and the deposited silicon. The inclusion of small amounts of boron increases the complexity of the coatings and it appears that the precise nature of the coatings is dependent upon the method employed in preparing the bodies. Successive deposition of silicon and boron or boron and silicon produces a coating or exterior layer having a more complex structure than the coating or skin produced by simultaneous deposition of silicon and boron. We therefore do not intend to limit our invention to a coating consisting solely of true alloys or intermetallic compounds of molybdenum-silicon-boron. Our invention contemplates compositions which may consist of such true tertiary alloys or intermetallic compounds or any other type of alloy or composition including molybdenum, silicon and boron in the approximate proportions stated.

We have discovered that the presence of boron in the molybdenum-silicon coatings or exterior layers as described in the aforementioned co-pending applications vastly increases the protective qualities of the alloy coating and also substantially eliminates the second type of failure described hereinbefore; namely, the failure of the coating at an intermediate temperature zone. The coatings contemplated by our invention contain a small amount of boron, that is, an amount of from about 2% up to about 10% by weight, preferably between about 3% and about 7.5%, based on the weight of the skin or coating.

Boron may be incorporated in our coatings by any desired method. The boron and silicon may be applied to and alloyed with the molybdenum either independently or simultaneously.

The boron may be applied to or alloyed with the molybdenum followed by the application of the silicon in accordance with the aforementioned co-pending applications.

Molybdenum wire having a diameter of about 0.080" and provided with a molybdenum-silicon-boron skin or coating by the deposition of boron on the molybdenum followed by the deposition of silicon has an average life of about 95 hours when maintained at 1700° C. in air. The maximum life exhibited by one of a series of such specimens was 416 hours. Of 20 specimens provided with the boron-containing exterior layer, only two ex-

hibited a failure at an intermediate temperature zone when maintained at 1700° C. in air.

Molybdenum-boron compositions in themselves are of little protective value, the life of such coating or skin having a thickness of 0.003" being about 6 hours at a temperature of 1000° C.

The same size molybdenum wire provided with a molybdenum-silicon alloy skin of about 0.001" in thickness has an average life of about 24 hours when maintained at a temperature of 1700° C. in air. The maximum life exhibited by one of a series of such specimens was as great as 47 hours.

The simultaneous deposition of boron and silicon produces a coating or exterior layer which possesses greater protective qualities. Coatings produced by the simultaneous deposition have exhibited lives in excess of 1,000 hours when maintained at a temperature of 1700° C. in air.

The application or deposition of the boron and silicon may be effected by a vapor deposition process and the temperature of the molybdenum body may be such as to promote the alloying action simultaneously with the deposition. A boron halide or a silicon halide, or a boron halide and a silicon halide, such as the bromides or chlorides, are volatilized and mixed with hydrogen. The halide-hydrogen mixture is then brought into contact with the heated molybdenum body. The body is maintained at a temperature sufficiently high to cause a reaction between the halide and the hydrogen allowing the boron or silicon, or boron and silicon to plate out on the molybdenum body. Since it is desired to produce what we have termed an alloy coating of molybdenum, boron and silicon, we prefer to maintain the molybdenum body at a temperature sufficiently high so as to effect an alloying of or a reaction between the deposited materials and the surface portions of the molybdenum simultaneously with the deposition of the boron and silicon. Temperatures from about 1400° C. to about 1800° C. are satisfactory. In the independent deposition and alloying of boron and silicon, the boron may be deposited on and alloyed with the molybdenum surface by maintaining the molybdenum at a temperature of about 1600° C. The silicon is subsequently deposited on and alloyed with the molybdenum-boron surface at a temperature of about 1800° C. In the simultaneous deposition of boron and silicon a temperature of about 1600° C. is satisfactory.

The protective qualities of the alloy coatings or skins are dependent upon the composition of the coatings or skins. The composition of the coating or skin is in turn dependent upon the composition of the halide hydrogen mixture from which the boron and silicon are derived. As in the case of the molybdenum-silicon alloys, the proportion of silicon in the coatings of this invention also determines the protective qualities of the coatings or skins. Coatings or skins which exhibit the high protective qualities contain combinations of silicon and molybdenum containing from about 22.5% to about 47% silicon, particularly about 37% silicon, and combined boron in amounts of about 2 to 10% of the total weight of the coatings. Calculated on a composition basis, the coatings or skins contain from about 15% to about 40% silicon, from about 2% to 10% boron, and the balance molybdenum. The preferred coatings contain about 22% silicon, about 5.5% boron, and the balance molybdenum. The amount of boron in the coatings has a direct bearing upon the resistance of the coatings of this invention. In turn, the amount of boron deposited is dependent upon the amount of boron in the halide-hydrogen mixture. The presence of boron in the coatings or skins in amounts exceeding about 10% decreases the life of the coatings. The hydrogen which is employed should be substantially free of water vapor or oxygen. The amount of hydrogen present in the gaseous mixture should be at least sufficient to react with the halides and an excess amount is preferably pro-

vided to aid in the removal of the acid vapors which are formed.

We have discovered that satisfactory coatings may be prepared from atmospheres of gaseous mixtures having molar ratios between silicon tetrachloride and boron trichloride of from about 2.5:1 to about 18:1 and containing from about 1.5 to 6.0 times the amount of hydrogen theoretically required to reduce the halides. Coatings which have exhibited optimum resistance to oxidation have been obtained from gaseous mixtures wherein the ratio of silicon tetrachloride to boron trichloride is about 4.6:1 by volume and having a silicon to boron ratio of about 11.9:1 by weight. The ratio of the amount of hydrogen in the gaseous mixture to the amount of hydrogen theoretically required to reduce the halides or react with the halides was about 3.6:1.

In the independent deposition and alloying of boron and silicon with molybdenum, the molybdenum body is positioned in a suitable chamber which is purged with hydrogen. The molybdenum body is then heated to the desired plating temperature by any suitable means. For example, in the coating of wire or rod the wire may be heated to a temperature of about 1600° C., by passing an electric current therethrough. The hydrogen is passed through a boron halide such as boron tribromide. The boron tribromide may be maintained at room temperature and the hydrogen passed through the liquid at the rate of about 800 cc. per minute. The resulting gaseous mixture is then brought into contact with the heated molybdenum wire or rod. Such gaseous flow is maintained for about 5 seconds. The flow of gas is then interrupted and the molybdenum body heated to a temperature of about 1800° C. Hydrogen is passed through a silicon halide such as silicon tetrachloride maintained at room temperature at about the same rate of flow and the flow continued for about 8 minutes. The gas flow is then interrupted and hydrogen may be slowly passed through the chamber while the coated molybdenum is cooling.

In the simultaneous deposition, the coating atmosphere is prepared by passing hydrogen through a silicon halide such as silicon tetrachloride which may be maintained at about 0° C. at the rate of about 800 cc. per minute, and by passing hydrogen through a boron halide such as boron tribromide maintained at room temperature at the rate of about 20 cc. per minute. The two gas streams are then merged and brought into contact with the heated molybdenum which may be at a temperature of about 1600° C. This gas flow is maintained for about 8 minutes. The gas-vapor mixture is then interrupted and hydrogen passed through the container until the coated molybdenum has cooled.

The maintenance of such flow rates and temperatures for the stated period will produce a coating having a thickness of the order of 0.002" on a molybdenum wire having a diameter of about 0.080". Molybdenum wire of this size provided with the exterior layer containing silicon and boron by such simultaneous deposition and alloying has exhibited a life of 1415 hours at 1700° C. (3100° F.) in air and as high as 134 hours at a temperature of about 1900° C. (3450° F.).

Increasing appreciably the boron content of the vapor-hydrogen atmosphere and thereby increasing appreciably the boron content of the coating substantially decreases the life of the coating. For example, by doubling the amount of boron trichloride vapors added to the hydrogen-silicon tetrachloride mixture produces a coating on 0.080" molybdenum wire which has a life of about 0.05 hour at 1700° C.

It is apparent from the foregoing description that the presence of boron effects a substantial increase in the life of the molybdenum-silicon alloy coatings or layers. The boron-containing coating substantially eliminates the common failure of molybdenum-silicon coatings which

occurs at intermediate temperature zones. This type of failure is in general the type of failure encountered where the coated molybdenum body is maintained at temperatures of about 1200° C. to about 1400° C. and higher.

The failure generally occurs at a zone where the temperature of the body remains in the neighborhood of 1200° C. to 1400° C., although the maximum temperature of other portions of the body may be appreciably higher. The presence of boron thus permits the coated body to be utilized under conditions whereby the body attains higher temperatures and protects the body from failure at the zones maintained in the neighborhood of about 1300° C. to 1500° C. where the body is employed under conditions which result in temperature gradients. Our invention is not to be limited to the deposition of boron and silicon on a molybdenum base by a chemical reaction, i.e., the reduction of the halides of boron and silicon by hydrogen, since in accordance with our invention the boron and silicon may be deposited by mechanical means, as by brushing or spraying a suspension of silicon and boron powders on the molybdenum base, or by a metallizing operation with the aid of a metal spray gun. No matter how the silicon and boron are deposited, they are caused to react with the molybdenum base by a heat treatment, as described.

Nor is our invention to be limited to the in situ formation of a molybdenum-silicon-boron skin (layer) on a molybdenum base, since the said skin may be preformed and applied either to a molybdenum base or to a base of another metal or alloy such as steel, nickel, titanium, etc., which is to be protected from high temperature oxidation, as by mechanical means such as welding and bonding with a metal.

We claim:

1. The method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature exceeding about 1400° C., simultaneously depositing boron and silicon on the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and vapors of a boron halide and a silicon halide over the heated body, and maintaining the deposited boron and silicon in contact with said heated body until they react with the surface portions of the body, the molar ratio of silicon halide to boron halide in said mixture being from about 2.5:1 to about 18:1, the said mixture containing hydrogen in an amount of from about 1.5 to about 6 times the amount theoretically required to reduce the halides.

2. The method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature between about 1600° C. and about 1800° C., simultaneously depositing boron and silicon on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and vapors of boron trichloride and silicon tetrachloride over the heated body, and maintaining the deposited boron and silicon in contact with said heated body until they react with the surface portions of the body, the molar ratio of silicon tetrachloride to boron trichloride in said mixture being from about 2.5:1 to about 18:1, the said mixture containing hydrogen in an amount of from about 1.5 to about 6 times the amount theoretically required to reduce the chlorides.

3. The method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature between about 1600° C. and about 1800° C., simultaneously depositing boron and silicon on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and vapors of boron trichloride and silicon tetrachloride over the heated body, and maintaining the deposited boron and silicon in contact with said heated body until they react with the surface portions of the body, the molar ratio of silicon tetrachloride to

boron trichloride in said mixture being about 11.9:1, the said mixture containing hydrogen in an amount at least corresponding to that theoretically required to reduce the chlorides.

4. A method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature of at least about 1400° C., depositing boron on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and of vapors of a boron halide over the heated body, depositing silicon on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and of vapors of a silicon halide over the heated body, the amount of hydrogen present in said mixtures being at least sufficient to reduce the said halides and the molar ratios between said silicon halide and said boron halide varying from about 2.5:1 to about 18:1, and maintaining the deposited materials in contact with said heated body until they react with the surface portions of the said body.

5. A method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature of at least about 1400° C., depositing boron on the surface of the body by passing a mixture of hydrogen and of vapors of a boron halide over the heated body, depositing silicon on the surface of the body by passing a mixture of hydrogen and of vapors of a silicon halide over the heated body, the amount of hydrogen present in said mixtures being at least sufficient to reduce the said halides and the molar ratios between said silicon halide and said boron halide varying from about 2.5:1 to about 18:1, and maintaining the deposited materials in contact with said heated body until they react with the surface portions of the said body.

6. A method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature of at least about 1400° C., depositing boron on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and of vapors of boron trichloride over the heated body, depositing silicon on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and of vapors of silicon tetrachloride over the heated body, the amount of hydrogen present in said mixtures being at least sufficient to reduce the said halides and the molar ratios between said silicon halide and said boron halide varying from about 2.5:1 to about 18:1, and

maintaining the deposited materials in contact with said heated body until they react with the surface portions of the said body.

7. A method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature of at least about 1400° C., simultaneously depositing boron and silicon on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and of vapors of a boron halide and a silicon halide over the heated body, the amount of hydrogen present in said mixtures being at least sufficient to reduce the said halides and the molar ratios between said silicon halide and said boron halide varying from about 2.5:1 to about 18:1, and maintaining the deposited materials in contact with said heated body until they react with the surface portions of the said body.

8. A method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature of at least about 1400° C., simultaneously depositing boron and silicon on the surface of the body by passing a mixture of hydrogen and of vapors of a boron halide and a silicon halide over the heated body, the amount of hydrogen present in said mixture being at least sufficient to reduce the said halides and the molar ratios between said silicon halide and said boron halide varying from about 2.5:1 to about 18:1, and maintaining the deposited materials in contact with said heated body until they react with the surface portions of the said body.

9. A method of forming refractory metal bodies resistant to oxidation at elevated temperatures which comprises heating a molybdenum body to a temperature of at least about 1400° C., simultaneously depositing boron and silicon on the surface of the body by passing a mixture of hydrogen substantially free from water vapor and oxygen and of vapors of boron trichloride and silicon tetrachloride over the heated body, the amount of hydrogen present in said mixtures being at least sufficient to reduce the said halides and the molar ratios between said silicon halide and said boron halide varying from about 2.5:1 to about 18:1, and maintaining the deposited materials in contact with said heated body until they react with the surface portions of the said body.

References Cited in the file of this patent

UNITED STATES PATENTS

2,313,410	Walther	Mar. 31, 1939
2,665,998	Campbell et al.	Jan. 12, 1954