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METHOD OF PREPARING HIGHLY REFRACTORY BODIES

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This invention relates to a method of preparing metal bodies resistant to oxidation at elevated temperatures and more particularly to such bodies formed of the refractory metals, molybdenum, tungsten, tantalum and columbium, which are provided with a coating or skin so as to render the metal base resistant to oxidation at elevated temperatures.

The refractory metals, molybdenum, tungsten, tantalum and columbium, have highly desirable properties and characteristics for many purposes. Molybdenum and tungsten, for example, retain their mechanical properties at elevated temperatures. Molybdenum, tungsten and tantalum are very desirable for use in electrical furnace heating elements. However, in order to prevent oxidation of these metals it is necessary to exclude oxygen. In the use of molybdenum and tungsten elements for such purpose, a continuous flow of hydrogen is maintained over the heated resistance elements. Tantalum and columbium are highly resistant to chemical attack, particularly acids; however, they must be handled cautiously at higher temperatures to prevent the absorption of gases. Heating of tantalum and columbium in the atmosphere or in gases results in an embrittlement of the metal.

The principal purpose of the present invention is to provide a method for producing refractory metal bodies formed of these metals 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.

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

The present invention contemplates a method for providing these refractory metals normally oxidizable at high temperatures with an integral coating or skin of the refractory metal-silicon alloy or intermetallic compound.

Methods are known whereby silicon may be deposited on refractory metals. The protection afforded by the silicon coating is of course limited somewhat by the relatively low melting point of silicon and its tendency to alloy with the base metal. Although silicon itself has excellent oxidation resistance and protective silicon coatings may be formed on these metals, it is impossible to maintain the silicon coating, as such, over extended periods at high temperatures because the silicon is gradually consumed in the formation of alloys or intermetallic compounds with the metal base. In the course of this alloying reaction, the continuity of the coating is

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frequently destroyed and the life of the coated body, particularly at higher temperatures, is generally much shorter than the life of the bodies coated with a skin of the alloys or intermetallic compounds as prepared by the method of this invention.

In contradistinction to these prior methods, whereby the base material is coated with silicon, our method provides a surface layer or coating which consists of alloys or intermetallic compounds of the metal base and silicon rather than merely a coating of silicon. This alloy or intermetallic compound coating or skin is formed by depositing silicon on the heated metal from a vapor phase while the metal is maintained at a temperature below the melting point of silicon and subsequently reacting the silicon with the metal to form the alloys or compounds. The metal may be heated by any desired means and is preferably raised to the deposition temperature in a reducing atmosphere before silicon containing vapors are brought into contact with the body.

We have discovered that the type of coating formed during the deposition operation is dependent upon the temperature of the body during plating. If the temperature of the body, at the time of deposition of the silicon is appreciably below the melting point of silicon, the coating consists almost entirely of silicon. When the temperature approaches the meltng point of silicon, some of the deposited silicon may alloy or interact with the metal; however, the protective qualities are not appreciably different from those of the substantially pure silicon coatings. In those instances where the temperature of the body is at least as high as the melting point of the silicon, the silicon as it is deposited on the metal body alloys or reacts with the metal body to form a skin or coating, as described and claimed in our copending application Serial No. 150,543, filed March 18, 1950, entitled Method of Preparing Highly Refractory Bodies. The nature or type of coating may be readily identified by an observation of the approximate melting point of the skin or coating, the silicon coating having a melting point of about 1400° C. while the alloy coating or skin has a melting point of about 1825° C.

The present invention is based upon our discovery that the highly protective skin or coating may be formed by depositing silicon on the metal body which is maintained at a temperature below the melting point of silicon and subsequently maintaining the coated body in a pro-

tective atmosphere for a period of time sufficient to allow the silicon to react or alloy with the metal to form the highly protective skin or coating.

In accordance with the method of this invention, the metal body to be coated is maintained at a temperature between about 950° C. and about 1400° C., preferably at a temperature of between about 1000° C. and about 1200° C., during the deposition of the silicon. The metal body is preferably raised to the deposition temperature in hydrogen or other inert gas before a mixture of hydrogen and the vapors of a silicon halide such as a silicon chloride, silicon bromide and the like, is passed over the heated body. This mixture may be formed by passing the hydrogen through silicon tetrachloride held at room temperature. As the mixture contacts the heated metal, the silicon tetrachloride decomposes thereby depositing or plating silicon on the metal body.

If the temperature of the body is appreciably below the melting point of silicon, the deposit does not alloy with the metal base or may alloy to only a slight extent. At the higher temperatures within the stated temperature range, some alloying or reaction occurs. It is apparent that the rate of deposition of the silicon and the rate or degree of alloying or reaction between the silicon and metal will vary directly with the temperature of the metal body during deposition. The influence of temperature on the rate of deposition and the nature of the coating or rate of reaction between the silicon and metal base may be illustrated by the following data obtained in the coating of molybdenum wire:

Wire Temperature, °C.	Plating Time, Min.	Thickness, Silicon	Thickness, Mo-Si Alloy
1,000	120	0.002	0.0009
1,200	60	0.008	0.00167
1,400	30		0.0038

The silicon coating thus formed has limited protective qualities because of the low melting point of silicon and the tendency of the silicon to alloy or react with the metal. In order to form the highly protective silicon-metal alloy coating or skin, the coated body is heated in the plating atmosphere or in an inert atmosphere to the incipient melting point of silicon and is maintained at this temperature or at a temperature just below the melting point of silicon for a brief period whereby the silicon and metal alloy or react without flowing of the silicon. As reaction proceeds, the temperature may be increased. For example, in the preparation of molybdenum wire, the silicon coated wire may be heated to a temperature between about 1400° C. and about 1470° C. and maintained at the temperature for from about 5 minutes to about 15 minutes; the precise time being dependent upon the thickness of the silicon coating. As alloying or reaction proceeds, the temperature may be increased gradually so that at the end of the period the wire has reached a temperature of about 1580° C. In those instances where the silicon coating is very thin, the formation of the silicon-metal alloy coating or skin may be effected by flashing the wire to a temperature above about 1400° C. while the wire is maintained in the plating atmosphere.

As an alternative, the alloy or intermetallic compound skin or coating may be formed without heating the wire or body to a temperature exceeding about 1400° C. or the melting point of silicon. Silicon exhibits the ability to react or alloy with the metal base throughout the temperature range set forth. The rate of alloying or reaction with the metal base or the rate of diffusion of the silicon varies directly with the temperature as in other chemical reactions. We have discovered that the alloys or intermetallic compounds may be formed by decreasing the rate of deposition of the silicon and conducting the deposition over a greater period of time. By such practice, the silicon deposits slowly and the silicon and metal base are retained at an elevated temperature for a sufficient period of time to permit the diffusion of the silicon into the metal base to form the alloy or intermetallic compound. As is obvious, the permissible rate of deposition of the silicon will vary directly with the temperature at which the metal base is maintained during the deposition period and the period required to form an alloy layer of unit thickness will vary inversely with the temperature at which the metal base is maintained during the deposition period. The deposition rate is regulated so that there is no appreciable layer of pure silicon covering the metal base. This alternative method appears to produce a coating of greater uniformity than that of the method described hereinbefore. Molybdenum filaments coated by the deposition of silicon at a low rate over a longer period of time wherein filaments have been maintained at temperatures of about 1200° C. and about 1400° C. have exhibited a life in air in excess of 2000 hours at 1000° C.

The alloys or intermetallic compounds formed by the foregoing methods will vary in the molecular ratio of silicon to refractory metal of from about 1:1 to about 2:1. The heat treatment of the silicon coated metal as described, either the treatment at temperatures between 1400° C. and about 1580° C. or the flashing at a temperature just above 1400° C., and the deposition of silicon at a low rate and formation of the alloy coating or skin, appears to promote the formation of an alloy or intermetallic compound having a composition corresponding to a molecular ratio of silicon to refractory metal of about 2:1 which exhibits maximum protective qualities.

The thickness of the silicon-metal coating or skin is dependent upon the thickness of the silicon deposit on the metal. The thickness of the silicon deposit may be controlled by regulation of the supply of silicon halide, of the plating period and of the plating temperature. The diffusion of the silicon into the metal base and the alloying of the silicon and metal is regulated or controlled by the period of heat treatment or by the plating period in the low rate of deposition method.

In the first of the specific methods described herein, after the desired thickness of silicon has been deposited, the hydrogen-vapor mixture or plating atmosphere may be arrested and purged from the plating chamber by passing hydrogen or an inert gas through the chamber or the heat treatment may proceed in this atmosphere. If the heat treatment has been conducted in the plating atmosphere, or if the low rate deposition method has been utilized, the atmosphere is purged from the chamber at the termination of the heat treatment or the deposition period and the body cooled in hydrogen or other inert gas. Care should be exercised in cooling the coated

body so as to insure a substantially complete conversion of all of the deposited silicon to the alloy or intermetallic compound.

The oxidation resistance of these metals at elevated temperatures may be further increased by forming the alloy coating or skin in successive layers with intermediate heat treating periods. The silicon is deposited upon the metal body as described herein. The flow of the mixture of hydrogen and vapors of the silicon halide is arrested and the temperature of the coated body is raised so as to allow the silicon to diffuse into and alloy or react with the metal. Although we have specifically illustrated the heat treating temperatures as lying within a range between about 1400° C. and about 1580° C., the maximum temperature is not critical providing all of the silicon has alloyed with the metal. For example, the maximum temperature may be as high as about 1750° C. if all of the silicon has alloyed with the metal because the melting point of the alloy exceeds 1800° C. The maximum temperature employed during this heat treatment should be sufficiently high to insure complete alloying of the silicon.

After the silicon has been alloyed with the metal base, the temperature of the metal body is reduced to the plating temperature, a temperature below about 1400° C. and the plating atmosphere again allowed to flow into the plating chamber. The heat treatment is then employed to alloy the added silicon with the metal.

It is to be understood that the foregoing description is merely illustrative of our invention and that the specific examples included above are not intended as limitations. Although the specific illustrations describe the methods as applied to molybdenum wire or rod, it is to be understood that the other refractory metals tungsten, tantalum and columbium may be provided with the highly protective alloy or intermetallic compound coatings by the use of these methods. The specific examples have described only the preparation of coated or alloyed wire. Bars, strips and other bodies have been similarly protected against oxidation at elevated temperatures. The description of the treatment of wire or rod and the testing or examination of wire affords a simple and ready illustration of the effectiveness of the coatings or skins.

We claim:

1. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating the refractory metal body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the metal body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated metal body, and heating the coated metal body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the metal body whereby a surface coating consisting essentially of said alloy is formed on said metal body.

2. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a molybdenum body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body and heating the coated molybdenum body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

3. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a tungsten body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated tungsten body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

4. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a tantalum body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated tantalum body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

5. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a columbium body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated columbium body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

6. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating the refractory metal body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the metal body while maintained at said temperature by passing a mixture of hydrogen and vapors of silicon tetrachloride over the heated metal body, and heating the coated metal body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the metal body whereby a surface coating consisting essentially of said alloy is formed on said metal body.

7. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating the refractory metal body in an inert atmosphere to a temperature between about 1000° C. and about 1200° C., depositing silicon on the metal body while maintained at said temperature by passing a mixture of hydrogen and vapors of silicon tetrachloride over the heated metal body, and heating the coated metal body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the metal body whereby a surface coating con-

sisting essentially of said alloy is formed on said metal body.

8. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C., which comprises heating a molybdenum body in an inert atmosphere to a temperature between about 1000° C. and about 1200° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated molybdenum body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said metal body.

9. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a tungsten body in an inert atmosphere to a temperature between about 1000° C. and about 1200° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated tungsten body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

10. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a tantalum body in an inert atmosphere to a temperature between about 1000° C. and about 1200° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated tantalum body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

11. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a columbium body in an inert atmosphere to a temperature between about 1000° C. and about 1200° C., depositing silicon on the body while maintained at said temperature by passing a mixture of hydrogen and vapors of a silicon halide over the heated body, and heating the coated columbium body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the body whereby a surface coating consisting essentially of said alloy is formed on said body.

12. The method of forming refractory metal bodies resistant to oxidation at temperatures above about 1000° C. which comprises heating a molybdenum body in an inert atmosphere to a temperature between about 950° C. and about 1400° C., depositing silicon on the metal body while maintained at said temperature by passing a mixture of hydrogen and vapors of silicon tetrachloride over the heated metal body, and heating the coated metal body to a temperature above about 1400° C. and for a time sufficient to alloy the silicon with the surface portions of the metal body whereby a surface coating consisting essentially of said alloy is formed on said metal body.

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