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OXIDATION PROTECTED TUNGSTEN AND MOLYBDENUM BODIES AND METHOD OF PRODUCING SAME

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Fig. 1

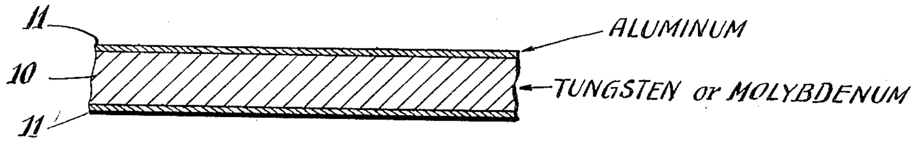


Fig. 2

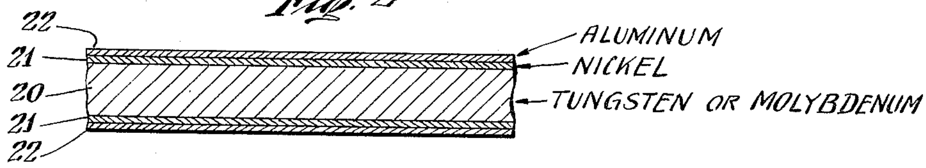
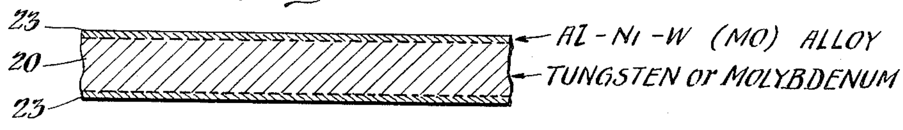


Fig. 3



INVENTORS
Marshall G. Whitfield
Victor Sheshunoff

BY Nicholas Lang Jr.

ATTORNEY

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OXIDATION PROTECTED TUNGSTEN AND MOLYBDENUM BODIES AND METHOD OF PRODUCING SAME

Marshall G. Whitfield and Victor Sheshunoff, Garden City, N. Y., assignors to Whitfield & Sheshunoff, Incorporated, Garden City, N. Y., a corporation of New York

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5 Claims. (Cl. 29—196)

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The present invention relates to improved metal bodies constituted of tungsten or molybdenum and ferrous alloys thereof, and, more particularly, to metal bodies containing substantial percentages of tungsten and molybdenum protected against deterioration in oxidizing atmospheres at high operating temperatures.

At the present time there are various industrial developments where alloys of special character are necessary, capable of retaining their high mechanical strength at high operating temperatures. Examples of such applications are particularly parts for jet engines and gas turbines in which the demands made on the structural parts with respect to their strength at elevated operating temperatures are extremely exacting. Materials now employed for these purposes generally comprise alloys of iron and of nickel, in many cases with additions of cobalt, chromium, tungsten and molybdenum. Even the alloys of tungsten and molybdenum, while theoretically promising, proved very disappointing in actual practice. In general, few, if any of these alloys had a useful life over 300 hours, necessitating frequent replacement of critically important structural elements at great trouble and expense.

As is known, tungsten and molybdenum are unstable when heated in air or in any other oxidizing atmosphere at temperatures in the range of 800° C., or above. The oxides formed on the surface of the tungsten and molybdenum bodies under such conditions sublime or boil away continuously to such a pronounced degree that these metals can only be used in a pure reducing atmosphere of hydrogen, or of an inert gas, such as argon, or in vacuum. The same difficulty is present with respect to alloys containing more than 15% of tungsten and molybdenum. Of course, this circumstance greatly restricted or even negatived the usefulness of such metal bodies and, as a matter of fact, those skilled in the art strongly advised against the use of alloys containing tungsten and molybdenum in excess of 15% for high temperature applications. Although the outstanding problem was well known in the art and from time to time various suggestions and proposals were made to provide a solution therefor, none, as far as we are aware, of these suggestions and proposals was completely satisfactory and successful on a practical and industrial scale.

We have found that the problem may be solved in a remarkably simple and unique manner.

It is an object of the present invention to pro-

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vide a method of preventing the detrimental effect of oxidizing atmospheres at elevated temperatures upon refractory metal bodies containing tungsten and molybdenum.

It is another object of the invention to provide a novel and improved method of preventing the surface sublimation and resulting deterioration of metal bodies constituted of tungsen, molybdenum, and alloys thereof when exposed to oxidizing atmosphres at elevated temperatures in the range of 800° C. and thereover.

It is a further object of the invention to provide a protective layer on the surface of tungsten and molybdenum bodies, said protective layer being essentially composed of an aluminum base material.

It is also within the contemplation of the invention to provide a novel method of protecting tungsten and molybdenum bodies against surface sublimation at high operating temperatures while exposed to oxidizing atmospheres which is simple in character and which may be readily carried out on a practical and industrial scale at a low cost.

The invention also contemplates a new article of manufacture in the form of a refractory metal body protected from oxidic surface deterioration comprising a core of tungsten and molybdenum, or alloys thereof with each other or with other metals, and a protective layer of aluminum base material having a relatively high aluminum content coated on said core.

Other and further objects and advantages of the invention will become apparent from the following description, taken in conjunction with the accompanying drawing, in which:

Figure 1 is a fragmentary sectional view of a metal body embodying the principles of the invention during the process of its manufacture;

Figure 2 is a similar view of an oxidation protected tungsten or molybdenum body having a bonding layer of nickel and a protective layer of aluminum applied thereto; and

Figure 3 is a longitudinal sectional view of a refractory metal body comprising a core of tungsten or molybdenum and having a partially diffused protective layer thereon constituted of an alloy of aluminum, nickel and molybdenum or tungsten.

Broadly stated, according to the principles of the invention, the tungsten or molybdenum bodies to be protected are coated with an aluminum base material which may be pure aluminum or alloys rich in aluminum. This coating may be carried out by various procedures but best results are obtained by a hot dip method in which the metal bodies to be protected are immersed in a bath of molten aluminum base material for a predetermined length of time sufficient to provide a coating of the aluminum base material thereon. We have found that by this method there is formed a thin protective layer on the surface of the tungsten or molybdenum body which layer is essentially constituted of an alloy of aluminum with the base metal. Experimental work with tungsten and molybdenum bodies treated in accordance with the invention has indicated that these materials do not exhibit their normal oxide forming characteristics even at temperatures approximating the boiling point of aluminum and in many cases even at temperatuures as high as 2000° C.

The bath of molten aluminum base material may be composed of high purity aluminum, commercially pure aluminum and of aluminum alloys having a relatively high aluminum content. Examples of such aluminum alloys are alloys containing 5% to 15% by weight of at least one of the elements selected from the group consisting of iron, nickel, chromium, cobalt and beryllium, the balance being substantially all aluminum. In addition, various other aluminum base materials containing other and further constituents may be used.

If desired, the bodies to be treated with the bath of molten aluminum base material may be subjected to a preliminary cleaning by sandblasting, burnishing and similar mechanical procedures. In most cases, however, such preliminary cleaning is not necessary. For example, rolled molybdenum sheet may be subjected to treatment by the bath of aluminum base material without any preliminary cleaning.

The temperature of the bath of molten aluminum base material may be subject to considerable variations in accordance with its composition. Thus, in the case of a bath of commercially pure aluminum, temperatures in the range of 700° to 800° C. provide satisfactory results.

The aluminum coating treatment may be carried out continuously or by means of a batch type process. Particularly in case of a continuous treatment, it is desirable to preheat the bodies to be coated. The period of treatment in the molten bath of aluminum base material may vary from a few seconds to several minutes depending on the initial temperature of the bodies to be treated, on their thickness or mass and to some extent also on the operating temperature of the bath. The thickness of the coating of aluminum base material is not critical but may be in the order of 0.002″ to 0.004″.

Examination of wire and sheet samples of tungsten and molybdenum, which have been treated with aluminum and exposed to high temperatures in oxidizing atmospheres, indicates that a high melting compound of aluminum with the tungsten or molybdenum core has been formed and that this alloy is free from the weakness of either the tungsten or molybdenum with regard to oxidizing to form a compound of low boiling or sublimation point on the surface. For example, samples treated by the method of the invention have been heated to temperatures a hundred degrees C. above the normal boiling point of aluminum before the aluminum boiled away, indicating that the alloys of aluminum with tungsten or molybdenum have extremely high boiling or sublimation points. Likewise, it has been found that the presence of aluminum on

the surface of these metals will permit their use for applications requiring substantial strength at elevated temperatures. The method of the invention is applicable with equal or similar results also to alloys of at least one of the metals iron, nickel, cobalt with tungsten or molybdenum, or both, containing substantial quantities of tungsten or molybdenum, such as at least 15% by weight, and also to alloys of tungsten and molybdenum.

Preferably, the aluminum coated tungsten and molybdenum containing bodies are heat treated to assure the formation of a high melting compound of aluminum with the tungsten or molybdenum core and thereby to obtain a completely stable product. It is also possible, however, to omit such heat treatment and to rely on the diffusion of the aluminum coating into the refractory core during the actual operation at elevated temperature. If heat treatment is resorted to, the heat treating temperature may be in the order of 1300° C., although it is not restricted to such temperature.

While the method of the invention provides excellent results in protecting and stabilizing tungsten and molybdenum bodies, when treating these metals with aluminum or its alloy, occasionally small spots or areas are found which are alloyed only with extreme difficulty. We have found that this difficulty may be completely avoided by electrodepositing a thin film or layer of nickel on the surface of the tungsten or molybdenum and diffusing or at least heating the nickel plated sections in a non-oxidizing or reducing atmosphere at approximately 1000° C. before treating the sections of tungsten or molybdenum with aluminum. This modification of the method of the invention provides in most cases more uniform protection or alloying of the aluminum with the base metals.

The thickness of the electrodeposited nickel layer is not critical and may be subject to considerable variations. In this connection, it may be observed that diffusion of the nickel layer may be accomplished not only by heating under non-oxidizing conditions but also by heating in an oxidizing atmosphere provided that sufficient nickel is present. As a matter of fact, electroplating with nickel may be immediately followed by the aluminum coating treatment. In this case, diffusion of the nickel layer is accomplished by the heating effect of the bath of aluminum base material, and the bath at the same time provides the non-oxidizing or protective environment.

It has been found that nickel is not the only metal which is capable of providing this additional protection, but that in general iron group metals such as nickel, iron, cobalt, chromium and manganese will accomplish substantially the same result. Moreover, we have found that in many cases copper and silver plates may provide equal or similar results.

While the exact reason for the beneficial effect of the preliminary deposit of nickel or other iron group metal is not fully understood, it is believed that there metals form alloys with aluminum more quickly than do tungsten and molybdenum and that these electrodeposited films act as temporary protectors until the aluminum can form its alloy with the tungsten or molybdenum which have a tendency to oxidize even at relatively low temperatures, such as red heat.

Referring now to the drawing, in Figure 1 there is shown a metal body embodying the principles of the invention which comprises a base or core 10 of tungsten or molybdenum. Upon both faces of the core there is provided a thin coating 11 of aluminum or aluminum base material constituting a protective layer for the core. Of course, in actual manufacture, layer 11 is initially a coating of aluminum containing some tungsten or molybdenum and is bonded to the core by an aluminum rich alloy of these refractory metals caused by partial diffusion of the aluminum into the core. In service, or in the final stage of manufacture, the excess aluminum is partly oxidized and partly diffused to produce the alloy surface layer which is referred to in the foregoing.

Figure 2 illustrates an example of the modification of the invention in which the tungsten or molybdenum core 20 is first coated with a thin film of nickel or other iron base metal 21 and thereafter is exposed to the effect of a molten bath of aluminum base material, such as, for example, commercially pure aluminum, thereby forming a protective layer 22 on the exterior of the core. As a result of the interaction of the core material with that of the layers 21 and 22 during the heat and coating treatments and subsequent service operation, the metal body is converted into the one shown in Figure 3 wherein the individual existence of layers 21 and 22 has practically disappeared, such layers being combined into a layer 23 which is composed of an alloy rich in aluminum and containing appreciable amounts of nickel and tungsten or molybdenum.

While in the drawing fragmentary sectional views of refractory metal strips are shown which are coated with a layer of aluminum base material on both faces thereof, in actual practice, the refractory metal bodies are provided with a protective layer of the described character throughout their entire surface, including their ends and edges. In this manner, the said metal bodies are fully protected from deterioration at elevated operating temperatures.

In order to facilitate understanding of the invention by those skilled in the art, the following illustrative examples may be given:

Example I

A molybdenum sheet 0.015″ thick, mill finish, was immersed in a bath of molten commercially pure aluminum having a temperature of 720° C., for 6 minutes. After removal from the bath and cooling, the material was tested by heating it to 1400–1500° C. in an oxidizing atmosphere for 4 hours, without noting any appreciable deterioration.

Example II

A molybdenum sheet about 0.020″ thick was cleaned and a light coating of nickel was electrodeposited thereon. The plated sheet was heated for a few minutes in a reducing atmosphere at approximately 1000° C. The sheet was cooled and then treated by immersing in a bath of molten commercially pure aluminum, having a temperature of 740° C. for 3 minutes.

Although the present invention has been described in connection with a few preferred embodiments thereof, variations and modification may be resorted to by those skilled in the art without departing from the principles of the invention. Thus, as it has been indicated in the foregoing, the principles of the invention are not restricted to the treatment of tungsten and molybdenum bodies but may be applied with equal or similar results to metal bodies composed of alloys of tungsten and molybdenum with each other or with other metals. The advantages of the invention in the case of tungsten and molybdenum alloys are particularly accentuated when such alloys contain at least 15% by weight of tungsten or molybdenum, or tungsten and molybdenum combined. All of these variations and modifications are considered to be within the true spirit and scope of the present invention, as disclosed in the foregoing description and defined by the appended claims.

What is claimed is:

1. The method of protecting metal bodies chosen from the class consisting of tungsten, molybdenum, alloys of tungsten and molybdenum, and alloys containing at least 15% of any of the foregoing, against surface deterioration at elevated temperatures which comprises electrodepositing a thin coating of nickel on the surface of said bodies, heat treating said coated bodies under non-oxidizing conditions to cause at least partial diffusion of said nickel coating, and immersing the bodies thus treated in a bath of molten aluminum to form an aluminum-rich protective layer thereon.

2. The method of protecting refractory metal bodies chosen from the class consisting of tungsten, molybdenum, alloys of tungsten and molybdenum, and alloys containing at least 15% of any of the foregoing, from surface sublimation at elevated temperatures in oxidizing atmospheres which comprises electroplating said bodies with a thin coating of a metal selected from the group consisting of nickel, iron, cobalt, chromium and manganese, heat treating said coated bodies under non-oxidizing conditions to cause at least partial diffusion of the coating, and then immersing the bodies thus treated in a bath of molten aluminum base material to form a protective layer thereon.

3. The method of stabilizing refractory metal bodies chosen from the class consisting of tungsten, molybdenum, alloys of tungsten and molybdenum, and alloys containing at least 15% of any of the foregoing, in oxidizing atmospheres at temperatures in the range of 800° C. and thereover, which comprises electrodepositing on the surface of the metal body a thin plating of an iron group metal, heating the plated body in a reducing atmosphere to a temperature of about 1000° C. for a period of time to cause at least partial diffusion of the iron group metal, and then immersing the body thus treated in a bath of molten aluminum thereby to form a protective layer thereon, said protective layer being substantially constituted of an alloy rich in aluminum and containing appreciable amounts of iron group metal and of the refractory metal.

4. As a new article of manufacture, a refractory metal body protected from surface deterioration at elevated operating temperatures comprising a core constituted of a refractory metal selected from the group consisting of tungsten, molybdenum, alloys of tungsten and molybdenum, and alloys containing at least 15% of any of the foregoing with at least one of the metals iron, nickel and cobalt, and a protective layer on said core essentially composed of an alloy of aluminum with the material of said core.

5. A method for preventing appreciable high temperature deterioration in an oxidizing atmosphere of bodies chosen from the class con-

sisting of tungsten, molybdenum, alloys of tungsten and molybdenum, and alloys containing at least 15% of any of the foregoing, which comprises plating such bodies with a thin layer of a metal selected from the group consisting of an iron group metal, copper, and silver, heating such plated material under non-oxidizing conditions to a temperature up to about 1000° C., and applying a molten coating of a metal selected from the group consisting of aluminum and alloys rich in aluminum at a temperature sufficient to form an intimate alloy bond with said tungsten and molybdenum bodies, said alloy bond being resistant to oxidizing conditions at temperatures above 800° C.

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