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## OXIDATION RESISTANT TUNGSTEN AND MOLYBDENUM ALLOY BODIES

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### ABSTRACT OF THE DISCLOSURE

A metal body which consists mainly of tungsten and/or molybdenum, and which is resistant to oxidation at elevated temperatures, includes, at least as a constituent of a surface layer of the body, a minor proportion of at least one metal, preferably chromium, which is preferentially oxidizable in relation to tungsten and molybdenum, and preferably also a minor proportion of at least one of the metals cobalt, nickel, ruthenium, rhodium, palladium, platinum, palladium being preferred, and the metal body has formed on its surface an adherent, oxidation-resistant, protective coating including an oxide of the preferentially oxidizable metal derived from the surface layer.

This invention relates to metal bodies of which the main constituent consists of tungsten, or of molybdenum, or of both tungsten and molybdenum, and more particularly is concerned with the provision of metal bodies of this kind which are resistant to oxidation at elevated temperatures. The invention also relates to the manufacture of such oxidation-resistant metal bodies.

Tungsten and molybdenum, and alloys of which these metals form the base, are, by virtue of their refractory nature and their mechanical properties, suitable for use in the construction of components which are subjected to high temperatures in operation; however, since tungsten and molybdenum are oxidisable by exposure to air at elevated temperatures, the surfaces of such components are liable to severe oxidation in use, resulting in curtailment of the useful life of the components or even in rapid failure of the components in operation. It has previously been proposed to coat the surfaces of such components with a substance, for example silicon, which is capable of forming with the base metal, a surface layer of an oxidation-resistant alloy. However, the presence of an alloy of this kind on the surface of a body consisting mainly of tungsten and/or molybdenum in some cases results in an undesirable modification of the mechanical properties of the body; moreover, if such a surface layer is damaged in use it is not "self-healing," that is to say it is not re-formed on further heating.

It is an object of the present invention to provide a metal body of the kind referred to, having an improved protective surface coating derived from the material of the body itself and capable of reducing the rate of atmospheric oxidation of the body at elevated temperatures while, at least in some cases, enabling the mechanical properties of the body to be maintained substantially unchanged. It is a further object of the invention to provide an improved method of manufacturing metal bodies of the kind referred to having enhanced resistance to oxidation.

According to the first aspect of the invention, a metal body of which the main constituent consists of tungsten, or of molybdenum, or of both tungsten and molybdenum, includes, at least as a constituent of a surface layer of the body, a minor proportion of at least one metal which is capable of being oxidised preferentially in relation to the said main constituent, and the metal body has formed on

its surface an adherent, protective coating consisting of or including a compound containing oxygen and the said preferentially oxidisable metal derived from a surface layer of the body, which compound has a greater resistance to oxidation than that of the metal body itself.

Usually the said compound containing oxygen and the preferentially oxidisable metal is an oxide of the said metal, but in some cases the compound may contain one or more other elements in addition to oxygen and the said metal.

Preferably the metal body also includes, at least as a constituent of a surface layer thereof, a small proportion of at least one of the metals of Group VIII of the Periodic Table of the elements consisting of cobalt, nickel, ruthenium, rhodium, palladium, platinum.

References herein to tungsten and/or molybdenum as the "main constituent" of the metal body are to be understood to mean that, apart from the presence of the preferentially oxidisable metal and optionally the Group VIII metal as aforesaid, the metal body either consists wholly of tungsten and/or molybdenum, or consists of a tungsten-and/or molybdenum-based alloy containing one or more additional constituents which may be required for modifying the mechanical or other properties of the body in known manner and which will not have any deleterious effect on the oxidation resistance of the protective coating. For example, the metal body may include one or more other refractory metals such as rhenium or tantalum, the total amount of such additional metals being about 10% to 20% by weight of the body, or less. The metal body may also, if desired, include an additive for influencing the grain structure of the base metal in known manner, such as thoria or potassium silicate, for example in a proportion of about 1-2% of the weight of the body.

If desired, the preferentially oxidisable metal or metals, and said Group VIII metal or metals if included, may be distributed throughout the whole of the metal body, so that the latter consists entirely of an alloy of substantially homogeneous composition, provided with a said protective surface coating. Alternatively, the preferentially oxidisable metal or metals and the Group VIII metal or metals may be confined to a surface layer of the metal body, this surface layer thus consisting of an alloy (hereinafter referred to as "durable alloy," of the preferentially oxidisable metal or metals and the Group VIII metal or metals, if present, with the base metal and possibly one or more additional constituents as aforesaid, and the surface layer having a said protective coating. Thus in the former alternative the whole metal body consists of durable alloy whereas in the latter alternative only the said surface layer consists of durable alloy. The latter alternative is in fact advantageous, for some applications, in that the metal body as a whole retains the mechanical properties which it would have in the absence of the preferentially oxidisable and Group VIII metals, while at the same time having improved resistance to oxidation on heating.

The preferentially oxidisable metal included in the durable alloy is preferably chromium, but other metals capable of preferential oxidation in relation to tungsten and molybdenum, and which can also suitably be employed in the durable alloy, include thorium, titanium, hafnium, zirconium, uranium, magnesium, cerium, aluminium beryllium. In some cases the preferentially oxidisable metal (for example when one of the refractory metals titanium, hafnium, or zirconium is employed), when distributed throughout the metal body may have a beneficial effect on the mechanical properties of the metal body as a whole. If desired, as implied above, two or more preferentially oxidisable metals may be included in the durable alloy composition. The proportion of such metal or metals

incorporated in the durable alloy is preferably at least 5% by weight of the weight of durable alloy present, and advantageously may be considerably higher in some cases, for example up to 15% by weight, preferably being at least 10% by weight when the main constituent of the metal body, which is also the main constituent of the durable alloy, is wholly or mainly molybdenum.

When a Group VIII metal as aforesaid is included in the metal body, the proportion of such metal present in the durable alloy may be from 0.01% to 10% by weight of the said alloy, and is preferably from 1% to 5% by weight of the durable alloy. The preferred Group VIII metal for use in accordance with the invention is palladium. The presence of a said Group VIII metal, especially palladium, in many cases promotes the formation of a satisfactory protective coating or improves the resistance of the coating to oxidation, and is apparently essential in metal bodies of which the main constituent consists wholly or mainly of molybdenum, for ensuring that an adequate protective coating is formed on the durable alloy surface.

It will be appreciated that the degree of resistance to oxidation required to be imparted to a metal body in any particular case may vary considerably, depending upon the expected conditions of use of the component formed from the metal body, especially upon the temperature to which the component will be heated in operation and the length of time for which the component will be required to be subjected to a high temperature. Thus in some cases, where the component is not expected to attain an exceptionally high temperature (say, not above 1200° C.), or is required to have only a short life (possibly not more than 15 minutes), a relatively thin protective coating will suffice, whereas a considerably thicker coating may be necessary in cases where the components will be required to operate at higher temperatures and/or for a prolonged period. It will of course also be understood that the oxygen-containing compound constituting or included in the protective coating must be stable under the conditions of use of the metal body, that is to say it must be a compound which will not undergo decomposition, or chemical reaction with any constituent of the metal body or surface layer thereof or with the surrounding atmosphere, under such conditions. Thus the choice of the preferentially oxidisable metal and the amount of such metal incorporated in the durable alloy part (which may be the whole) of the metal body, and the inclusion of a Group VIII metal as aforesaid and the amount of this metal included, will be determined by the degree of protection which will be acceptable and hence by the expected conditions of use of the metal body.

A preferred metal body in accordance with the first aspect of the invention either consists wholly of an alloy (being a said durable alloy) of tungsten, chromium and palladium, or consists of tungsten with a surface layer composed of such a durable alloy, and has formed on the surface of said durable alloy an adherent, protective coating consisting of or including chromium oxide produced by oxidation of the chromium content of a surface layer of the body. The preferred proportions of chromium and palladium present in the said durable alloy are from 5% to 10% of chromium, and from 1% to 5% of palladium, by weight of the weight of the durable alloy.

The initial metal body may be formed in a desired shape by any convenient known method. Thus a body composed wholly of a durable alloy as defined above can be formed, for example, by arc-melting and casting a mixture of the constituent metals, or by pressing and sintering a mixture of the powdered metals. Alternatively a shaped body may be formed from tungsten and/or molybdenum, with or without any desired additional metals as aforesaid for modifying the mechanical properties of the body, by arc-melting and casting the metal or metals, or by pressing and sintering the metal powder, and the required preferentially oxidisable metal, and Group VIII metal if de-

sired, may then be deposited upon the surface of the pre-fabricated metal body, for example by vapour deposition or electro-plating, in known manner, the body then being heated to cause the deposited metal or metals to diffuse into the surface layer of the underlying base metal or alloy and form a durable alloy region therewith. All of these procedures must, of course, be carried out in such a manner that oxidation of the tungsten and/or molybdenum is substantially avoided.

The protective coating is formed on the surface of the metal body by a suitable heat treatment in an oxidising atmosphere, for effecting oxidation of the preferentially oxidisable metal present in, or in the surface layer of, the metal body. The nature of the treatment required for forming a coating capable of giving adequate protection, having regard to the conditions of use of the metal body, depending upon the actual metals present in the durable alloy and the relative proportions of these metals in the durable alloy.

Thus according to a second aspect of the invention, a method of manufacturing a metal body of which the main constituent consists of tungsten, or of molybdenum, or of both tungsten and molybdenum, and which has enhanced resistance to oxidation at elevated temperatures, includes the steps of forming a metal body containing, at least in a surface layer thereof, in addition to said main constituent, at least one metal which is capable of being oxidised preferentially in relation to said main constituent, and optionally at least one of the metals cobalt, nickel, ruthenium, rhodium, palladium, platinum, and subjecting the metal body to heat treatment in an atmosphere which is capable of causing oxidation of the said preferentially oxidisable metal present in a surface layer of the body, the temperature and duration of the heat treatment being sufficient to effect the formation, on the surface of the body, of an adherent, protective coating consisting of or including an oxygen-containing compound of the preferentially oxidisable metal.

In some cases, especially in the cases of metal bodies of the preferred composition referred to above, that is to say metal bodies composed of durable alloy in the form of tungsten, chromium and palladium only, a satisfactory protective coating can be produced by carrying out the heat treatment step in the manufacture of the metal body in air. Moreover in some cases, where the durable alloy comprises tungsten only as the main constituent and contains a Group VIII metal as specified, especially palladium, and more particularly where the preferentially oxidisable metal used is chromium, preformation of a protective coating may not be necessary. Thus, such a metal body may be self-protective, that is to say the heat treatment required for forming the protective coating can be effected by the initial heating of the metal body under normal conditions of use, provided that the body is initially heated in use to a sufficiently high temperature to result in the oxidation of the preferentially oxidisable metal.

Durable alloys which are particularly advantageous in being self-protective in this way are again those consisting only of tungsten, chromium and palladium. Thus according to a third aspect of the invention, a metal body of which the main constituent is tungsten and which is resistant to oxidation at elevated temperatures either consists wholly of an alloy of tungsten, chromium and palladium, or consists of tungsten with a surface layer composed of such an alloy, the preferred proportions of chromium and palladium present in the said alloy being from 5% to 10% chromium, and from 1% to 5% palladium, by weight.

The temperatures to which a metal body as referred to in the preceding paragraph must be heated in air, either in initial use or in a heat treatment during manufacture, to achieve adequate protection depends upon the actual composition of the said alloy. For example, in the cases of alloys consisting of tungsten with 10% of chromium

and small proportions of palladium, satisfactory protective coatings can be formed by heating in air to temperatures in the ranges of 1200° C. to 1275° C., 1100° C. to 1500° C., and 1050° C. to 1600° C. for palladium contents of 0.1%, 1.0% and 2.0%, by weight, respectively: adequate protection is not obtained by heating in air at lower temperatures.

Self-protection is provided only up to a limited temperature and/or for a limited time, for example to a maximum temperature in the range of about 1200° C. to 1600° C. for tungsten-chromium-palladium alloys, the actual maximum temperature to which the body can be subjected, and the length of time for which the body can be subjected to a given elevated temperature, without failure of the protective coating, varying according to the chromium and palladium contents of the alloy. If the operating temperature of a component formed from the metal body, or the desired duration of exposure of the component to high temperatures, exceeds these limits, it is necessary for a protective coating to be pre-formed during the manufacture of the metal body, before the body is exposed to elevated temperatures in normal use.

In such cases it is preferable, and in the cases of alloys wherein the main constituent is wholly or mainly molybdenum and/or which do not contain a Group VIII metal it is essential, to carry out the heat treatment in an atmosphere of moist hydrogen.

In some cases, especially where the durable alloy treated contains a relatively high proportion of molybdenum, a two-stage heat treatment may be desirable for the production of a satisfactory protective coating.

Again in some cases, where the metal body is wholly composed of a durable alloy as aforesaid, and is formed by pressing and sintering a mixture of metal powders, the heat treatment for producing the protective coating may be carried out simultaneously with the sintering step, by sintering the metal compact in moist hydrogen or in any other atmosphere capable of effecting preferential oxidation of the said oxidisable metal, and by continuing the sintering process for a sufficient length of time to produce the requisite protective coating. This procedure is, of course, only applicable when the sintering temperature required for the alloy concerned is also suitable for the formation of a satisfactory protective coating, and in general when the sintering temperature is at least as high as the temperature to which the metal body will be subjected in operation. However if desired, especially if the sintering temperature used is lower than the operating temperature of the metal body, an additional heat treatment can be carried out after completion of the sintering step, such additional heat treatment preferably being at a higher temperature than the sintering. If, as may sometimes occur, a coating of a kind which does not give the desired protection against oxidation is formed during the sintering process, this coating can be removed prior to carrying out a suitable heat treatment for producing an adequate protective coating.

As examples of suitable methods of manufacturing metal bodies having enhanced resistance to oxidation, in accordance with the invention, from some particular types of alloys, a tungsten-chromium alloy body, formed by arc-melting and casting or by pressing and sintering the mixed metal powders, is preferably subjected to heat treatment in moist hydrogen for one hour at a temperature in the range of 1300° C. to 1500° C.; and a tungsten-chromium-palladium alloy body, formed by sintering a mixture of the constituent metal powders, may be provided with a protective coating by carrying out the sintering in moist hydrogen at a temperature of 1400° C. to 1450° C., the sintering if desired being followed by a further heat treatment in moist hydrogen, at a temperature in the range of 1400° C. to 1500° C. and preferably higher than the sintering temperature, for a period of 15 minutes to one hour.

In general, as indicated above, a metal body in ac-

cordance with the invention whose protecting coating has been formed by a special heat treatment procedure in manufacture of the body, especially in moist hydrogen, can subsequently be subjected to higher temperatures, without failure of the protective coating, than is the case with bodies whose protective coatings have been formed merely by an initial heating in air in use of the body. This is illustrated, for a series of tungsten-chromium-palladium alloys, in the following Table 1, which shows, for each alloy, the maximum temperature to which a body formed of, or having a surface layer of, the alloy can be exposed, with protection maintained for at least 15 minutes before the coating fails, after it has been provided with a protective coating by (a) heating in air during an initial period of use, and (b) heat treatment in moist hydrogen, for example for one hour at 1400° C. The corresponding maximum permissible temperatures for a tungsten-chromium alloy are also given, showing that an initial heating in air is not sufficient to provide satisfactory protection for such an alloy. Some molybdenum-containing alloys are also included in the table: although an initial heating in air does not provide an adequate protective coating on these alloys, and therefore no temperature figures are given for them in this column, the maximum permissible exposure temperatures after heat treatment in moist hydrogen are shown for comparison with the tungsten alloys. 15 minutes has been taken as the minimum time for maintenance of protection, for purposes of comparison, and also because, as already mentioned, there are some applications of metal bodies of the kind with which the invention is concerned for which this duration of resistance to oxidation is acceptable; protection for longer periods will be obtained at operating temperatures lower than those indicated in the table.

TABLE 1

| Composition of alloy, percent by weight | Maximum exposure temperature without failure: ° C. ± 25° C. |                                        |
|-----------------------------------------|-------------------------------------------------------------|----------------------------------------|
|                                         | After initial heating in air, in use                        | After heat treatment in moist hydrogen |
| 90 W, 10 Cr.....                        | <800                                                        | 1,450                                  |
| 94.9 W, 5 Cr, 0.1 Pd.....               | 1,225                                                       | 1,425                                  |
| 94 W, 5 Cr, 1.0 Pd.....                 | 1,375                                                       | 1,475                                  |
| 93 W, 5 Cr, 2.0 Pd.....                 | 1,425                                                       | 1,475                                  |
| 89.9 W, 10 Cr, 0.1 Pd.....              | 1,275                                                       | 1,475                                  |
| 89 W, 10 Cr, 1.0 Pd.....                | 1,500                                                       | 1,700                                  |
| 88 W, 10 Cr, 2.0 Pd.....                | 1,600                                                       | 1,800                                  |
| 84 W, 15 Cr, 1.0 Pd.....                | >1,300                                                      | >1,450                                 |
| 88 Mo, 10 Cr, 2.0 Pd.....               |                                                             | >1,300                                 |
| 58 W, 31 Mo, 10 Cr, 1 Pd.....           |                                                             | >1,400                                 |
| 36 W, 53 Mo, 10 Cr, 1 Pd.....           |                                                             | >1,400                                 |

It can be seen from the above table that the magnitude of the maximum operating temperature of these alloys, with protective coatings formed under similar conditions, is considerably affected by the proportion of palladium present in the alloy, and is also influenced by the content of preferentially oxidisable metal, namely chromium.

As has been shown above, the adherent coating formed on the surface of a metal body in accordance with the invention protects the tungsten and/or molybdenum of the underlying durable alloy, whether this constitutes the whole body or only a surface layer thereof, from oxidation at elevated temperatures, and thus prolongs the useful operational life of the body, the duration of the protective effect of the said coating, and hence the life of the metal body, depending to some extent upon the magnitude of the temperatures to which the body is exposed in use. The life of the metal body is also influenced by the concentration of the preferentially oxidisable metal in the durable alloy, a relatively high initial concentration of such metal, at least in the surface layer, usually being desirable.

The inclusion of a Group VIII metal such as palla-

dium, as aforesaid, in the durable alloy has the advantage of rendering the metal body oxidation-resistant up to higher temperatures than is the case with durable alloys not including such a metal, as shown in Table 1: we believe that, for example in the case of a tungsten-chromium alloy, the inclusion of palladium results in the formation of a tungsten-chromium-palladium alloy as a thin layer located between the tungsten base metal and the chromium oxide coating, this thin alloy layer thus providing additional protection for the tungsten.

The presence of a said Group VIII metal, at least in the surface layer of the metal body, also confers self-healing properties upon the protective coating, that is to say enables the protective coating to be re-formed rapidly on further heating if a portion of it is accidentally damaged or removed during use of the metal body. However, this self-healing property is only evident if such damage to the coating occurs when the body is at a temperature not higher than the maximum to which it can be exposed, without failure of the coating, when the coating has been formed by heating in air, that is to say at a temperature somewhat lower than the maximum to which it can safely be exposed after a protective coating has been produced by heat treatment in moist hydrogen. Furthermore, the property of self-healing is subject to the same temperature limitations as the ability of the same durable alloys to form an initial protective coating by heating in air, either on initially heating in use or as a result of heat treatment in manufacture: thus for each durable alloy capable of being self-healing there is a particular temperature range within which it must be heated to achieve re-formation of the protective coating, which range is the same as that which is effective for forming the initial protective coating in air, referred to above.

An additional advantage of the metal bodies of the invention is that the protective coatings formed thereon are resistant to thermal cycling, that is to say the coatings remain stable and adherent when they are subjected to rapid fluctuations of temperature within limits varying with different durable alloy compositions, the degree of resistance to thermal cycling of any given alloy depending to some extent upon the maximum temperature to which it is heated during the cycles. Thermal cycling tests have been carried out on a number of durable alloys of the kind employed in metal bodies according to the invention, and the results of such tests are given in Table 2, below, for a series of tungsten-chromium-palladium alloys tested after sintering the pressed metal powder compacts for 2 hours at 1400° C. in moist hydrogen. The thermal cycling test employed with the specimens listed in the table consisted in alternately heating the specimen for two minutes, to the test temperature as shown in the second column of the table, and cooling the specimen for one minute, the heating rate being about 75° C. per second, and the cooling rate, to room temperature, being about 150° C. per second: this cycle of operations was repeated until the protective coating failed, the number of cycles to failure being shown in the third column of the table. The table also shows, in the last two columns, the total life of each specimen under these cycling conditions, compared with the life of a similarly coated specimen under non-cycling conditions, where such information is available, both in hours.

TABLE 2

| Composition of alloy, wt. percent | Test temperature, ° C. | No. of cycles to failure | Cycled life at test temperature, hours | Non-cycled life at test temperature, hours |
|-----------------------------------|------------------------|--------------------------|----------------------------------------|--------------------------------------------|
| 94.9 W, 5 Cr, 0.1 Pd.....         | 1,317                  | 945                      | 31.5                                   | 60.5                                       |
| 94 W, 5 Cr, 1.0 Pd.....           | 1,317                  | >201                     | >6.7                                   | 47.0                                       |
| 94 W, 5 Cr, 1.0 Pd.....           | 1,400                  | 613                      | 20.4                                   | 21.5                                       |
| 89 W, 10 Cr, 1.0 Pd.....          | 1,400                  | 1,956                    | 65.2                                   | 100                                        |
| 89 W, 10 Cr, 1.0 Pd.....          | 1,500                  | 5.6                      | 17.2                                   | 25                                         |

Some specific methods which we have employed for the manufacture of metal bodies in accordance with the invention will now be described in the following examples.

## EXAMPLE 1

An alloy composed of 90% tungsten and 10% chromium, by weight, was prepared by compacting a mixture of the constituent metals in the appropriate proportions, under hydrostatic pressure of 25 tons per square inch, and sintering the compacts by heating at 1400° C. in moist hydrogen for 16 hours, the sintered compacts being in the form of rods 25 mm. long and 5 mm. in diameter. (The term "moist hydrogen," as used here and in the following examples, is to be understood to refer to hydrogen with a dew point of about 20° C.). This sintering process resulted in the formation of an adherent coating, covering the surfaces of the rods, composed of green chromic oxide, Cr<sub>2</sub>O<sub>3</sub>: it has been confirmed by X-ray analysis that this coating is substantially pure chromic oxide, containing no detectable impurities either in solution or as a separate phase.

The oxidation resistance of the chromic oxide-coating rods, in the as-sintered condition, was investigated by placing the specimens in a platinum boat, heating them in static air at atmospheric pressure, and ascertaining the length of time for which the specimens could be heated to various temperatures prior to failure of the oxide coating, as indicated by the commencement of rapid oxidation of the underlying tungsten. It was found that the oxide coating failed after 5 hours, 2 hours, and 15 minutes at temperatures of 1350° C., 1400° C. and 1500° C. respectively.

## EXAMPLE 2

Rods composed of tungsten-chromium-palladium alloys containing, respectively, 0.1%, 1.0% and 2.0% of palladium, in each case with 5% of chromium, by weight, were prepared by compacting mixtures of the component metal powders under hydrostatic pressure of 35 tons per square inch and sintering at 1400° C. for one hour in moist hydrogen. The specimen rods referred to in this and the following examples were 4 mm. in diameter and 25 mm. long, with rounded ends. The rods were subjected to oxidation tests, in the manner described in Example 1, in the as-sintered condition, and as a result of these tests it was evident that the protective coatings formed during sintering gave a considerable degree of protection to the tungsten, the sintered 93% W-5% Cr-2% Pd alloy, for example, being oxidation-resistant for 434 hours at 1200° C. and for 10 hours at 1450° C.

## EXAMPLE 3

Rods of tungsten-chromium-palladium alloys containing 5% chromium and, respectively, 0.1%, 1.0% and 2.0% of palladium, by weight, were prepared by pressing and sintering metal powder mixtures as described in Example 2, and were then further heated for one hour at 1450° C. in moist hydrogen. The oxidation rates of these rods in air at 1450° C. were determined by heating the rods in static air at atmospheric pressure, and ascertaining the increase in weight, due to oxidation, at hourly intervals: at this temperature, the protective coating on the 0.1% palladium alloy proved to be inadequate, since rapid oxidation of the tungsten occurred. However, in the cases of the 1.0% and 2.0% palladium alloys respectively, the gains in weight were found to be only 0.94 mg./cm.<sup>2</sup>/hour and 1.66 mg./cm.<sup>2</sup>/hour, respectively, the lives of the rod containing 1.0% and 2.0% palladium being 13 hours and 10 hours respectively at 1450° C.

As examples of the lives of these rods at lower temperatures, the protective coating was maintained undamaged on the 0.1% Pd rods for 417 hours at 1200° C., for at least 68 hours at 1300° C., and for 49 hours at 1400° C., and on the 1.0% Pd rods for 434 hours at 1200° C., for 68 hours at 1300° C., and for 22 hours at 1400° C.

## EXAMPLE 4

Rods composed of tungsten-chromium-palladium alloys containing 10% of chromium and, respectively, 0.1% and 1.0% of palladium, by weight, were formed by pressing appropriate mixtures of the constituent metal powders under 35 tons per square inch, and sintering in moist hydrogen for 16 hours at 1400° C. The oxide coating formed during the sintering protected the rods against oxidation, in the case of the 0.1% palladium alloy for 85 hours at 1450° C., and in the case of the 1.0% palladium alloy for 25 hours at 1500° C. and for 14 hours at 1700° C., in each case when heated in air.

## EXAMPLE 5

A rod composed of 89% W-10% Cr-1.0% Pd alloy was prepared as described in Example 4, and the oxide coating formed during sintering was then removed and the rod was heated in air to 1450° C. During the initial heating a chromic oxide coating was formed, which provided protection against oxidation of the tungsten for more than 10 hours at 1450° C. in air.

## EXAMPLE 6

Some rods composed of tungsten-molybdenum-chromium-palladium alloys of compositions, respectively, 58% W, 31% Mo, 10% Cr, 1% Pd and 36% W, 53% Mo, 10% Cr, 1% Pd, by weight, were prepared by compacting appropriate mixtures of the constituent metal powders and sintering in moist hydrogen for 1 hour at 1300° C. The oxide coating formed during the sintering was removed by grinding, and the rods were then heat treated in two stages, the first heating stage being carried out in dry hydrogen (of dew point -40° C.) for one hour at 1400° C. and the second stage in moist hydrogen, again for one hour at 1400° C. It was found that the rods with the lower molybdenum content, provided with an oxide coating in this manner, were more resistant to oxidation than the rods with the higher molybdenum content: thus when heated at 1400° C. in air, the oxide coatings on the 30% Mo rods failed after 2.5 hours, but the coatings on the 31% Mo rods were still undamaged after 6 hours.

## EXAMPLE 7

Molybdenum-based alloy rods, composed of 88% molybdenum, 10% chromium and 2% palladium, by weight, were prepared by pressing the mixed metal powders and sintering for two hours at 1400° C. in moist hydrogen. The oxide coating formed during sintering was removed by grinding, and the rods were reheated in moist hydrogen for one hour at 1300° C. The coating thus formed protected the molybdenum from oxidation for 2 hours at 1300° C. in air.

## EXAMPLE 8

Some tungsten rods were provided with an oxidation-resistant coating by electroplating the surfaces of the rods first with a layer of chromium 0.0005 inch thick, then with a layer of palladium 0.0001 inch thick, and heating the plated rods in moist hydrogen for one hour at 1400° C. During the heating, the chromium and palladium diffused into the surface layers of the tungsten to form a layer of a durable tungsten-chromium-palladium alloy, and a protective coating of chromic oxide was formed on the surface of this alloy layer.

The lives of the protective coatings thus formed on the tungsten rods, when heated in air at 1300° C., were 2 to 2½ hours.

Oxidation tests and life tests carried out on metal bodies in accordance with the invention, as in the above examples, have shown that it appears to be advantageous to carry out a preferentially oxidising heat treatment at relatively high temperatures, for example of at least 1400° C., since such treatment imparts longer lives, at temperatures at least as high as the treatment temperature, to the coated bodies. For example, bodies composed of, or having a surface layer of, tungsten-chromium-palladium alloys with a surface coating of chromic oxide, such as those described in Examples 2 and 3 above, when maintained at a temperature of 1200° C. show oxidation rates as indicated in the examples, which are estimated to be three or four orders of magnitude lower than the oxidation rate of tungsten at the same temperature.

I claim:

1. A small body which is resistant to oxidation at elevated temperatures, consisting wholly of an alloy of tungsten, chromium and palladium in the proportions of 85% to 94% tungsten, 5% to 10% chromium, and 1% to 5% palladium, by weight.

2. A metal body which is resistant to oxidation at elevated temperatures, consisting of tungsten with a surface layer composed of an alloy of tungsten, chromium and palladium in the proportions of 85% to 94% tungsten, 5% to 10% chromium, and 1% to 5% palladium, by weight.

3. A metal body

(a) of which the main constituent consists of at least one metal which is a member of the group consisting of tungsten and molybdenum,

(b) of which at least a surface layer is composed of an alloy consisting of

(I) 5% to 15% by weight of chromium,

(II) 0.01% to 10% by weight of palladium,

(III) and the balance said main constituent,

(c) and which has formed upon the surface of said alloy an adherent, protective coating

(I) consisting essentially of chromium oxide,

(II) the chromium of said oxide being derived from the surface layer of the body,

(III) which oxide has a greater resistance to oxidation than that of the metal body itself.

4. A metal body according to claim 3, wherein the said alloy of which at least a surface layer of the body is composed consists of 5% to 10% by weight of chromium, 1% to 5% by weight of palladium, and the balance tungsten.

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