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1

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METHOD OF COATING REFRACTORY METALS FOR PROTECTION AT HIGH TEMPERATURES AND RESULTING ARTICLES

Alan Sydney Darling and Gordon Leslie Selman, London, England, assignors to Johnson, Matthey & Co., Limited, London, England

No Drawing. Continuation-in-part of application Ser. No. 16,943, Mar. 5, 1970, now Patent No. 3,657,784, which is a continuation-in-part of abandoned application Ser. No. 631,592, Apr. 18, 1967. This application Mar. 17, 1971, Ser. No. 125,430
Claims priority, application Great Britain, Mar. 20, 1970, 13,599/70
The portion of the term of the patent subsequent to Apr. 25, 1989, has been disclaimed
Int. Cl. B32b *15/04;* **C03b** *5/18*
U.S. Cl. 29—195 **19 Claims**

ABSTRACT OF THE DISCLOSURE

This specification describes an article for use at high temperature, for example in the glass industry, and comprises a refractory core made from niobium, tantalum, chromium, zirconium, vanadium, hafnium, rhenium or alloys thereof, a barrier layer of magnesia and a sheath of a platinum group metal or an alloy based on at least one metal of the platinum group. The oxides of the core metal or alloy are chosen to be less volatile than the oxides of molybdenum at operating temperatures within the range 1100° to 1500° C. A core may also be made from tungsten or molybdenum and in such a case the barrier layer may contain a small quantity of vitreous material, for example borosilicate glass.

This application is a continuation-in-part of Ser. No. 16,943, filed Mar. 5, 1970 and issued as U.S. Pat. 3,657,784. Said Ser. No. 16,943 is itself a continuation-in-part of Ser. No. 631,592, filed Apr. 18, 1967, now abandoned.

This invention relates to the sheathing of refractory metals with platinum group metals, or alloys based on at least one metal of the platinum group. (These alloys will be referred to as platinum base alloys.)

In applicant Selman's British Pat. No. 1,190,266 (Ser. No. 17,306/66) there is claimed an article comprising a core of refractory metal or alloy, not being molybdenum or tungsten or an alloy of molybdenum or tungsten, and a sheath of a platinum group metal or of an alloy based on at least one metal of the platinum group, in which the oxides of the core metal or alloy are less volatile than the oxides of molybdenum at operating temperatures between 1100° and 1500° C. Core metals satisfying this requirement are niobium, tantalum and chromium, or alloys thereof.

A barrier layer may be interposed between, for example, a core of niobium, tantalum or chromium and a sheath of a platinum base alloy.

The barrier layer may comprise:

(a) refractory oxides (i.e. oxides which are themselves refractory; not necessarily the oxides of refractory metals);
(b) refractory carbides;
(c) refractory nitrides (for example, boron nitride and silicon nitride);
(d) refractory sulphides; and
(e) any other refractory compounds which are compatible at the operating temperatures of 1100° C. to 1500° C. with the two materials with which they come into contact.

The above items (a)–(e) include compounds of the rare earth metals.

2

In applicant Selman's British Pat. No. 1,195,349 there is claimed an article comprising a core and a sheath with an interfacial space therebetween in which the partial pressure of oxygen is reduced to a pressure below one micron, the core comprising tungsten or molybdenum or an alloy of tungsten and molybdenum, the sheath comprising a platinum group metal or an alloy based on at least one platinum group metal, and a barrier layer disposed between the core and the sheath to prevent contact between the core and the sheath. The barrier layer may comprise one or more of the above mentioned refractory compounds in reference to the earlier application.

In applicant Selman's co-pending British patent application No. 1,222,434 (corresponding to German patent application No. P 19 16 791.0 and U.S. patent application No. 809,033 filed Mar. 20, 1969 and now abandoned), there is claimed an article comprising a core of a base metal such as molybdenum or tungsten or an alloy thereof and a sheath enveloping the core and formed of a platinum group metal or an alloy based on at least one platinum group metal and having between the core and the sheath a barrier layer formed of a refractory material stable at high temperatures and compatible with, and inert with respect to, the core and sheath and preventing physical contact between them and having within the interfacial space between the core and the sheath an atmosphere of inert gas. The barrier layer may, for example, be a refractory oxide, nitride or carbide which is compatible at high temperatures with both molybdenum and platinum.

A preferred inert gas is argon, but other suitable inert gases are nitrogen and helium. Under conditions of very low oxygen partial pressure, that is less than one micron and at operating temperatures of the order of 1000° C., we have found that many well known and stable refractory compounds which may be used as barrier layers decompose in contact with solid platinum group metals and platinum base alloys.

In contradistinction to many of the well known refractory materials which may act as barrier layers we have now, surprisingly, found that magnesia does not decompose under these conditions.

According to one feature of the present invention, therefore, an article for use at high temperature comprises a refractory core made from niobium, tantalum, chromium, zirconium, vanadium, hafnium, rhenium or alloys thereof, a barrier layer of magnesia and a sheath of a platinum group metal or of an alloy based on at least one metal of the platinum group, in which the oxides of the core metal or alloy are less volatile than the oxides of molybdenum at operating temperatures between 1100° and 1500° C. Core metals satisfying this requirement are niobium, tantalum and chromium or alloys thereof. Articles according to this invention may be used at temperatures of up to 1500° C. and 1600° C.

According to another feature of the present invention an article for use at high temperature comprises a core and a sheath with an interfacial space therebetween in which the partial pressure of oxygen is reduced to a pressure below one micron, the core comprising tungsten or molybdenum, the sheath comprising a platinum group metal or an alloy based on at least one platinum group metal, and a barrier layer of magnesia disposed between the core and the sheath to prevent contact between said core and sheath.

According to another feature of the present invention an article for use at high temperature comprises a core of a base metal such as molybdenum or tungsten or an alloy thereof and a sheath enveloping the core and formed of a platinum group metal or an alloy based on at least one platinum group metal and having between the core and the sheath a barrier layer of magnesia, preventing physical contact between them, and having within the interfacial space between the core and the sheath an atmosphere of inert gas. A preferred inert gas is argon, but suitable inert gases are nitrogen and helium.

In a preferred form of articles according to the present invention magnesia may be uniformly flame- or plasma-sprayed on to the core material or the core material coated or alloyed with a "getter" material for the absorption of oxygen such as titanium, zirconium, hafnium, thorium, vanadium, niobium or tantalum.

A preferred getter is a coating of zirconium 0.003" thick flame- or plasma-sprayed on the core material.

Preferably the magnesia barrier layer is then flame- or plasma-oversprayed to provide a further coating 0.010" thick. Articles in this preferred form having a core of moldbdenum and an outer platinum sheath 0.020" thick have been found to have a life of over 2500 hours at an operating temperature of 1400° C. compared with a life of 2000 hours for a zirconia barrier layer.

A small quantity of a vitreous material, such as a borosilicate glass, which behaves as a viscous material at temperatures above 1000° C. may be flame-or-plasma-sprayed with the magnesia in forming the barrier layer as we have found that this assists adhesion to the core, or getter coated core, material in instances where the core is made from tungsten, molybdenum or an alloy of tungsten and molybdenum.

When platinum thermocouples were heated in contact with zirconia powder under gettered argon, severe reactions occurred at temperatures as low as 1100° C. Similar reactions occur with alumina and thoria. In vacuum similar reactions occur, although at a slower rate than those in argon.

In corresponding tests with magnesia very few signs of reactions between platinum and mangesia have been detected even under conditions of very low oxidising potential where disastrous failure would have occurred in alumina after only a few hours at operating temperature.

After 100 hours of test at 1650° C. in magnesia, under an atmosphere of gettered argon, the calibration of a standard platinum versus 13% rhodium-platinum thermocouple changed by less than 1° C. when retested at the gold point.

A similar thermocouple was run for 450 hours at 1650° C. in magnesia under purified argon. Recalibration at the palladium point indicated a decrease in output equivalent to 4° C., which, at this temperature cannot be considered a serious deterioration. Under similar conditions of test thermocouples immersed in alumina remain intact for a few hours only.

Although aluminum is rapidly taken up from vapours having pressures of the order of 10^{-10} Torr (1 micron$=10^{-3}$ Torr), few signs of magnesium contamination have been detected even when magnesium vapours of the order of 10^{-7} Torr must have been present in the vicinity of the platinum wire surface.

In another method of making an article according to this invention, the core material (niobium, tantalum, chromium, zirconium, vanadium, hafnium, rhenium, molybdenum and tungsten or alloys thereof) is first coated with a layer of metallic magnesium by hot-dipping, galvanising or any other method. The so-coated core is then encapsulated in the sheath material. Thereafter, the encapsulated core is subjected to oxidation treatment so that the magnesium metal is oxidised in situ to magnesia. Oxidation may be carried out at moderately high temperatures by the use of steam or other oxidising atmospheres.

If desired, the ultimate barrier layer of magnesia may be obtained by, for example, first casting molten magnesium into the space between the sheath and the core prior to finally forming the sheath to encapsulate the so-formed core/barrier layer assembly. Another alternative method includes pre-calcining thin sheets of magnesium metal which are tightly wrapped around the core prior to sheathing. The effect of oxidation will be to expand the barrier layer material so that it completely fills the space between the sheath and the core.

What we claim is:

1. An article comprising a refractory core of metal or alloys made from niobium, tantalum, chromium, zirconium, vanadium, hafnium, or rhenium, a barrier layer of magnesia and a sheath of a platinum group metal or an alloy based on at least one metal of the platinum group in which the oxides of the core metal or alloy are less volatile than the oxides of molybdenum at operating temperatures between 1100° C. and 1500° C.

2. An article comprising a core and a sheath with an interfacial space therebetween in which the partial pressure of oxygen is reduced to a pressure below one micron, the core comprising tungsten or molybdenum, the sheath comprising a platinum group metal or an alloy based on at least one platinum group metal, and a barrier layer of magnesia disposed between the core and the sheath to prevent contact between said core and sheath.

3. An article comprising a core of a base metal of molybdenum or tungsten or an alloy thereof and a sheath enveloping the core and formed of a platinum group metal or an alloy based on at least one platinum group metal and having between the core and the sheath a barrier layer of magnesia, preventing physical contact between them, and having within the interfacial space between the core and the sheath an atmosphere of inert gas.

4. An article according to claim **1** wherein the core is made from niobium, tantalum or chromium or an alloy containing at least one of the aforesaid metals.

5. An article according to claim **3** wherein the inert gas is argon, nitrogen or helium.

6. An article according to claim **1** wherein the core material has at least the major portion of its surface coated with a getter material selected from titanium, zirconium, hafnium, thorium, vanadium, niobium or tantalum.

7. An article according to **1** wherein the barrier layer of magnesia is used with a getter material selected from titanium, zirconium, hafnium, thorium, vanadium, niobium or tantalum.

8. An article according to claim **1** wherein the core is alloyed with a getter material selected from titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum, the getter material selected being different from the core material selected from those metals or alloy constituents specified in claim **1.**

9. An article according to claim **2** wherein the barrier layer contains a small quantity of a vitreous material.

10. An article according to claim **9** wherein the vitreous material is borosilicate glass.

11. An article according to claim **2** wherein the core material has at least the major portion of its surface coated with a getter material selected from titanium, zirconium, hafnium, thorium, vanadium, niobium or tantalum.

12. An article according to claim **2** wherein the barrier layer of magnesia is used with a getter material selected from titanium, zirconium, hafnium, thorium, vanadium, niobium or tantalum.

13. A method for making an article for use at high temperatures comprising coating a refractory core of metal or alloys made from niobium, tantalum, chromium, zirconium, vanadium, hafnium, or rhenium, with a barrier layer of magnesia and thereafter applying a sheath of a platinum group metal or an alloy based on at least one metal in the platinum group, in which the oxides of the core metal or alloy are less volatile than the oxides of molybdenum at operating temperatures between 1100° C. and 1500° C.

14. A method of making an article according to claim **13** wherein the barrier layer of magnesia is flame-sprayed onto the core material.

15. A method according to claim 13 wherein the barrier layer of magnesia is plasma-sprayed onto the core material.

16. A method according to claim 13 including coating the core with a getter material selected from the group consisting of titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum, the getter material selected being different from the core material.

17. A method of making an article for use at high temperatures comprising providing a core and a sheath with an interfacial space therebetween in which the partial pressure of oxygen is reduced to a pressure below one micron, the core comprising a metal or alloys made from tungsten or molybdenum, the sheath comprising a platinum group metal or an alloy based on at least one platinum group metal, and disposing a barrier layer of magnesia between the core and the sheath to prevent contact between said core and sheath.

18. A method according to claim 17 wherein, the magnesia contains a small quantity of a vitreous material.

19. A method according to claim 18 wherein the vitreous material is borosilicate glass.

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ALFRED L. LEAVITT, Primary Examiner

J. R. BATTEN, Jr., Assistant Examiner

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