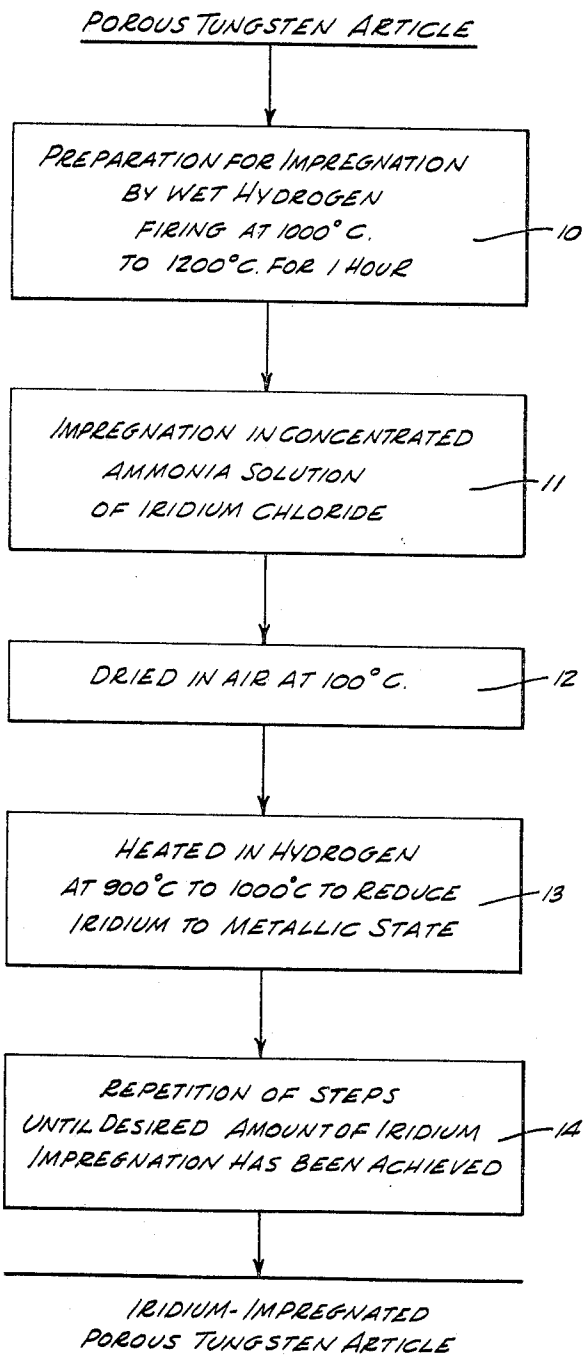
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METHOD OF IMPREGNATING POROUS TUNGSTEN AND RESULTING ARTICLE

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METHOD OF IMPREGNATING POROUS TUNGSTEN AND RESULTING ARTICLE

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U.S. Cl. 117—213 9 Claims

ABSTRACT OF THE DISCLOSURE

A method of preparing a prefabricated article or body of porous tungsten with a gas pervious porous metal deposited on the pore surfacing thereof by wet hydrogen, firing and impregnating the fired tungsten article with a volatile solvent solution of the heat or hydrogen reducible compound of the impregnating metal, drying the impregnated tungsten body and reducing the metal compound to a high temperature resistant free metal coating state with substantial retention of porosity or gas permeability.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Sec. 305 of the National Aeronautics and Space Act of 1958, Public Law 85–568 (72 Stat. 435; 42 U.S.C. 2475).

This invention relates to a method for depositing or impregnating metals into porous tungsten and particularly for impregnating porous tungsten with refractory and noble metals to produce a gas-permeable, high temperature resistant coating upon the porous tungsten.

Refractory metals such as rhenium, molybdenum and tantalum, the noble metals, gold and silver, and the platinum metals, platinum, osmium, ruthenium, iridium and rhodium have been deposited upon tungsten by the use of a sputtering process. However, the sputtering process is complex, requiring the use of high vacuum and high voltage sputtering equipment. Furthermore, by the use of the sputtering process, the internal surfaces of the surface pores of tungsten are not coated with the deposited metal and a layer of impregnant is deposited upon the outer surface only of the porous tungsten. Moreover, the sputtering process often codeposits surface impurities from the vacuum environment on the porous tungsten.

Accordingly, it is a primary object of this invention to provide a low cost, convenient and efficient method for impregnating porous tungsten with high purity metals.

Another object of this invention is to provide a convenient method for depositing a thin, uniform, durable layer of gas-permeable metal upon porous tungsten.

A further object of this invention is to provide a method for impregnating porous tungsten with metals so that the internal surfaces as well as the external surfaces of the outer layers of pores of the porous tungsten are impregnated with porous metal.

Additional objects of the invention will become apparent from the following description, which is given primarily for purposes of illustration, and not limitation.

The accompanying drawing is a flow sheet illustrative of an application of a process or method as described herein.

Stated in general terms, the objects of the invention are attained by preparing a porous tungsten article or body for impregnation by wet hydrogen firing at about 1000° to about 1200° C. for about an hour, impregnating the fired article by submerging it in a suitable solution containing a soluble compound of the impregnating metal, drying the impregnated article in air after recovery thereof from the impregnating solution, heating the dried article, or heating it in hydrogen at about 900° to about 1000° C. to reduce the impregnating metal-containing material to the free metal, and repeating the above-recited impregnation, drying and hydrogen firing steps until the desired amount of metal has been impregnated into the tungsten article. The compound of the metal to be impregnated should be dissolved in a solvent which is volatile and non-reactive with tungsten. The compound should be susceptible to reduction by heat or hydrogen to the metallic state.

A solution suitable for impregnating porous tungsten articles, bodies or electronic parts with iridium, or other impregnating metal, is made of a metal compound in a suitable, non-reactive volatile solvent such as, concentrated ammonia, alcohol, water, nitric acid, hydrochloric acid, or tetrahydrofuran. The impregnant metal compound used should contain no other undesirable, non-volatile metallic elements, or chemical groups, such as sulfate, carbonate or phosphate, which might react with or become a part of the tungsten surface. The halide and nitrate compounds of metals and ammonia and nitroso complexes of metal halides are suitable for making such a solution, although others can be used.

Other examples of suitable solutions are composed of ruthenium trichloride, osmium trichloride, platinum chloride and palladium chloride in hydrochloric acid solutions, rhenium pentachloride in absolute alcohol or tetrahydrofuran, rhodium nitrate in water or dilute nitric acid.

A typical solution is made by adding 0.1 gram of $IrCl_3$ to 3 ml. of concentrated ammonia. The solution is warmed slightly, but not allowed to boil, to dissolve a flocculent precipitate that forms. It is then cooled and tightly stoppered to prevent loss of ammonia.

Porous tungsten parts are prepared for impregnation by wet hydrogen firing at 1000°–1200° C. for one hour, as indicated at **10**. The cooled tungsten is immersed slowly in the ammonia solution in a manner which will permit the entrapped gases in the pores of the tungsten to be displaced by liquid, as indicated at **11**.

An alternative impregnating method is to spray the solution on to the part which can be heated to 50° C. or more to hasten evaporation of the solvent. This method minimizes the amount of metal which is deposited in the interior of the porous tungsten. The tungsten is then placed in an air oven at 100° C. for approximately 30 minutes or until dry, as indicated at **12**. If desired, the dried tungsten may be immersed briefly or sprayed a second time and dried again.

The impregnated iridium compound is reduced to the metallic state by heating the porous tungsten in a non-carbonaceous hydrogen atmosphere at 900° to 1000° C. for ten minutes, or more, as indicated at **13**. If organic solvents have been used, it is often desirable to use wet hydrogen to reduce changes of contamination by the formation of tungsten carbide. The above impregnating process, followed by drying and hydrogen firing, can be repeated until the desired amount of iridium has been impregnated into the tungsten, as indicated at **14**. If an organic solution has been used, it is generally advisable to carry out the 900° to 1000° C. firing in wet hydrogen.

Normally it would be expected that the iridium would be deposited more or less uniformly throughout the pores of the porous tungsten. However, it was found that a major part is deposited as a continuous layer over the tungsten particles which form the outer surface and the outer layer or two of pores without substantially reducing the porosity of the surface. In the case of the iridium example, six impregnations with the aforementioned solution will deposit a layer about 0.5 micron

thick on the surface and in the outer layer of pores corresponding to about 0.3% by weight of iridium. Eleven impregnations produce a surface layer about 1 micron thick with a total addition of about 0.5% by weight of iridium.

After every five or six impregnations, the porous tungsten should be heated to 1500° C. in dry hydrogen for 2 to 4 hours to bond the deposited layer to the tungsten substrate. Tests indicate that the surface layer of about a micron thickness remains in place for at least 25 hours at 1500° C. in hydrogen and 4 hours at 1800° C. in vacuum.

The exact composition of the iridium layer is not known, but it undoubtedly contains some tungsten as an alloy as its crystal structure corresponds more closely to a close-packed hexagonal rather than cubic as in the case of pure iridium and tungsten. This iridium coating has been used to modify the cesium ionization characteristics of a porous tungsten ionizer on a cesium ion beam. Iridium has a higher electron work function than tungsten. Thus an iridium surface emits fewer neutral cesium atoms and prolongs the useful life of a cesium vapor ionizer. An additional benefit results from the fact that sintering a fine pore ionizer, prepared by the method of the invention, over long periods of time may be inhibited by the presence of traces of iridium throughout the body of the porous tungsten.

Obviously many other modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention can be practiced otherwise than is specifically described.

What is claimed is:

1. The method of impregnating the internal and external surfaces of a prefabricated porous tungsten article with a metal selected from the group consisting of refractory metals, noble metals, and platinum metals comprising the steps of preparing the porous tungsten article for impregnation by wet hydrogen firing said article in the order of 1000° C. to 1200° C. for about an hour, impregnating the said fired article with a non-reactive volatile solvent solution impregnant of a heat or hydrogen reducible compound of said metal containing no undesirable non-volatile metallic element, or chemical group capable of reacting with or becoming a part of the tungsten surface, drying the impregnated tungsten article, and heating the impregnated tungsten article to a temperature effecting reduction of said metal compound to free metal deposited upon the porous tungsten article surface without substantially reducing the porosity of the surface.

2. The process of claim **1** wherein the impregnated fired tungsten article is heated in a hydrogen atmosphere.

3. The process of claim **2** wherein the impregnant is a solution containing a compound of a refractory metal.

4. The process of claim **2** wherein the impregnant is a solution containing a compound of a noble metal.

5. The process of claim **3** wherein the impregnant is a solution containing a compound of a platinum metal.

6. The method of claim **1** wherein the impregnant is a concentrated ammonia solution.

7. The method of claim **1** wherein the impregnant is a concentrated ammonia solution containing an iridium salt and the reduction temperature is on the order of 900° to 1000° C. effected in a hydrogen atmosphere.

8. The product produced by the process of claim **1.**

9. The method of claim **1** including the added step of further impregnating the said impregnated tungsten article with said solvent solution after the drying step, or the reducing step, or after each said step.

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U.S. Cl. X.R.

75—208; 117—50, 130, 225, 227, 230

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,489,602 Dated January 13, 1970

Inventor(s) W. E. McKee

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 30, "2475" should be --2457--.
Col. 2, line 57, "changes" should be --chances--.
Col. 4, line 12, "3" should be --2--.

SIGNED AND
SEALED
MAY 12 1970

(SEAL)
Attest:

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