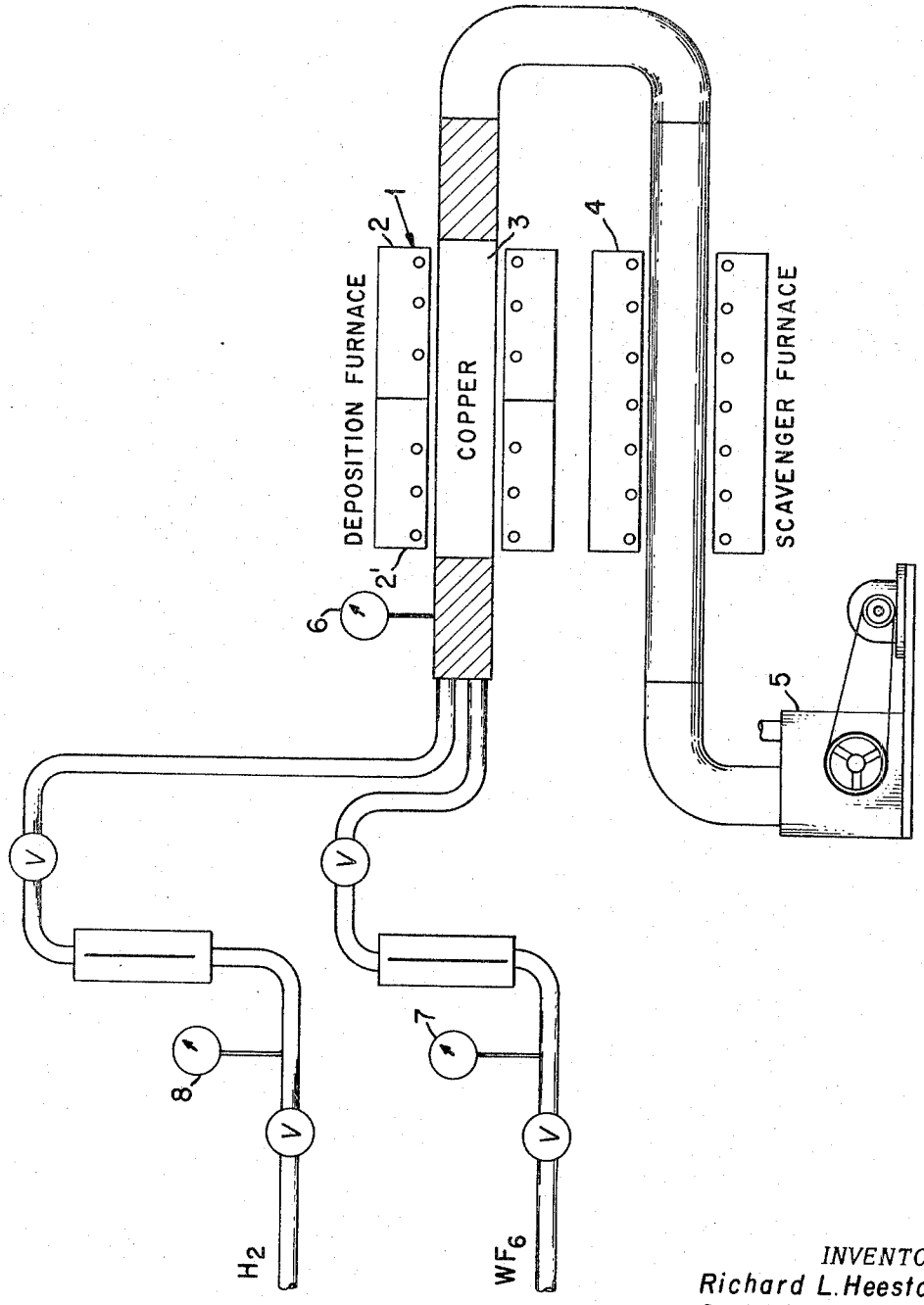
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METHOD FOR MAKING TUNGSTEN METAL ARTICLES

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METHOD FOR MAKING TUNGSTEN METAL ARTICLES

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This invention relates generally to the preparation of metals by vapor phase deposition and more particularly to vapor deposition of tungsten metal by hydrogen reduction of tungsten hexafluoride.

Tungsten metal, with its high melting point, high density, and good corrosion resistance in reducing environments, is a highly versatile metal. Tungsten tubing is particularly useful in highly corrosive environments at elevated temperatures, such as in the presence of alkali metals or reducing gases. With its high melting point it is well suited for parts for rockets to withstand the extreme heat of launching and space exploration.

Conventional metal working and fabrication techniques are, generally, not well suited in the fabrication of tungsten metal. Owing to its various physical, chemical and refractory metal mechanical properties, it is most difficult to work and requires special atmosphere equipment and high temperature furnaces in its fabrication.

Heretofore, tungsten metal sheets were fabricated from metal bars and hot rolled into tubing. The seams could then be arc welded to produce tungsten metal tubing. This was a difficult process which required numerous steps with special equipment operable at high temperatures. Also, tungsten metal has been extruded into tube form. However, the process was expensive due to low material yield and machining of the extruded tube.

Previous attempts to produce tungsten articles, especially seamless tungsten tubing, by such methods as vapor deposition of volatile tungsten compounds have, generally, resulted in articles of short lengths, thin, non-uniform thickness and tubing of only small diameters. Thus, even with such processes, seamless tungsten metal tubing and other tungsten articles of uniform wall thickness, significant lengths, and larger diameters remained difficult or impossible to produce.

It is, therefore, a general object of this invention to provide an improved vapor deposition method for producing tungsten metal articles.

It is also an object of this invention to provide an improved method for making tungsten metal tubing.

Another object of this invention is to provide a vapor phase deposition technique for making seamless tungsten metal tubing.

Still another object is to provide a continuous vapor deposition method for preparing tungsten metal tubing.

A further object is to provide a method for making seamless tungsten metal tubing at relatively low forming temperature.

A still further object of the present invention is to prepare high density seamless tungsten metal articles and tubing having a fine-grained, randomly-oriented grain structure.

Other objects and advantages of the present invention, which will be apparent to those skilled in the art, are accomplished by providing a method of making tungsten metal articles comprising heating a removable support member to at least the reaction temperature of a volatile tungsten metal halide and hydrogen followed by contacting the support member with a reacting mixture of the tungsten metal halide and hydrogen while reducing the temperature progressively from the inlet end and in increments along the axis of the support member to a temperature slightly less than the reaction temperature of the tungsten metal halide and hydrogen while maintaining the remaining portion of said support member at a temperature of at least as great as said reaction temperature. The temperature is reduced at a rate such that a layer of tungsten metal of selected thickness is continuously deposited from one end of said support member to the other. The removable support member is then cooled and removed or dissolved in acid to leave a tungsten metal article. The uniform layer of tungsten metal is deposited from the vapor phase by hydrogen reduction of the tungsten metal halide upon contact of these compounds with the heated surface of the support member.

For purposes of illustration, a preferred embodiment of this invention will hereinafter be shown as a method for producing seamless tungsten metal tubing by vapor deposition of tungsten hexafluoride and hydrogen on a heated mandrel.

It has been found that simply heating a mandrel to the reaction temperature and contacting it with a mixture of tungsten hexafluoride and hydrogen is not sufficient to produce the desired uniform deposit the length of the mandrel, suitable for a high density, uniform, seamless tungsten metal tube. In such a case the metal merely "builds up" for a few inches near the inlet end of the mandrel, producing a non-uniform layer of metal unsuitable for tubing.

In direct contrast, however, it has been found unexpectedly that continuous layers of tungsten metal with fine-grained, randomly-oriented grain structure may be deposited by the novel method described above to form seamless tubing of uniform wall thickness, and that by reducing the temperature progressively along the mandrel, the reduction rate of the tungsten hexafluoride may be controlled closely along the entire length of the mandrel to produce a continuous tungsten deposit of uniform thickness.

One method of the invention may be carried out by using a hollow cylindrical mandrel slightly longer than the length of tungsten tube desired. The mandrel should be of some material which has good heat transfer characteristics, does not react readily with the process gases, and which may be easily removed or dissolved from the tungsten metal tube after deposition. Although a number of materials may be used for constructing the mandrel, such as copper, glass, or graphite, copper in the form of copper tubing is preferred. Copper offers additional advantages in that it is available commercially in a large variety of diameters and because of its ductility it may be drawn to smaller diameters or otherwise shaped as desired.

The hollow cylindrical mandrel, which may be plated with tungsten on the inside or outside as desired, is provided at the inlet end with a source of tungsten hexafluoride gas and a source of hydrogen and at the outlet end an evacuating means, such as a pump, is attached along with a waste gas scavenger and recovery system.

The mandrel may be heated to the reaction temperature by any suitable heating means in which the temperature may be controlled in segments along the length of the mandrel. It has been found that a plurality of clam-shell type furnaces with separate heat control means, arranged in tandem along the length of the mandrel, provide suitable heating means and sufficiently flexible control of heat to reduce the temperature in segments along the mandrel.

In operation, the mandrel system is evacuated to a system pressure between 5 mm. to 20 mm. of mercury, and the entire length of mandrel to be contacted with reacting gases is heated to above the reaction temperature of tungsten hexafluoride and hydrogen. The minimum reaction temperature will, of course, depend upon the pressure of

the system and is about 480° C. at 5 mm. of mercury. Upon contact with the heated mandrel, the reduction rate of tungsten hexafluoride, and therefore, the tungsten deposition rate appears to be too slow at pressures below about 5 mm of mercury. Mandrel temperatures up to about 1000° C. and pressures up to about 20 mm of mercury may be used; however, under these conditions, the deposited tungsten metal grain size increases because of the rapid reduction of tungsten hexafluoride and because tungsten metal tends to "build up" for one or two inches at the gas inlet end of the mandrel. In order to obtain a sufficiently rapid reduction rate of tungsten hexafluoride, while achieving a uniform fine grain tungsten deposit, an optimum temperature of about 650° C. should be maintained at a pressure of about 20 mm of mercury.

These optimum conditions will provide a deposition rate of about 3 mils/hour for about 4 to 6 inch segments of mandrel length on a 0.75 inch diameter mandrel without excessive "build up" at the gas inlet end. The deposition rate also depends on the volumetric ratio of tungsten hexafluoride to hydrogen introduced into contact with the mandrel at reaction temperature. Tungsten hexafluoride to hydrogen ratios of from about 1:50 to about 1:150 have been used successfully. At ratios of less than 1:50, tungsten hexafluoride to hydrogen, the utilization of tungsten hexafluoride was significantly reduced and ratios above 1:150 resulted in a non-uniform deposition of tungsten metal. Although the optimum ratio will also depend on the temperature, pressure, and area of the mandrel, a ratio of about 1:140 is deemed optimum at a temperature of 650° C. using a 0.75 inch diameter mandrel.

Under optimum condition tungsten metal is deposited in uniform thickness at a rate of about 3 mils/hour along the mandrel tube for a distance of 4 to 6 inches from the gas inlet end. As the deposit reaches the desired thickness, the temperature of the furnace adjacent the deposited portion is reduced to a temperature slightly below the reaction temperature of tungsten hexafluoride while the temperature of the remainder of the mandrel is maintained above the reaction temperature. This reduced temperature may be between 350° C. and 500° C. depending on the pressure of the system. It has been found that a temperature of about 400° C. is preferred as this temperature is sufficiently high to prevent thermal shock to the tungsten deposit by cooling the mandrel too rapidly and to maintain a gradual gradient along the mandrel from the higher temperature zone to the lower temperature zone; thus, allowing a more uniform deposit of metal. The temperature is reduced in this manner progressively along the length of the mandrel as a continuous tungsten deposit forms on each segment of the mandrel.

When the tungsten is deposited the length of the mandrel, the furnace may be cooled to room temperature and the mandrel removed or dissolved in acid. Depending upon the mandrel construction material, any suitable solvent may be used to dissolve the mandrel after the deposition step has been completed. Copper mandrels, for example, are readily dissolved in nitric acid leaving a seamless tungsten metal tube having a fine grained, randomly-oriented grain structure and sufficiently dense to be impervious to helium. The fine grain and random nature of the deposit is unique and unknown to the prior art.

Using the method of this invention, tungsten metal tubes ranging between 0.040 inch diameter and 9 inches long to 0.75 inch in diameter and 14 inches long have been prepared with wall thickness varying from 0.001 to 0.060 inch and internal diameter varying no more than 0.001 inch for each tube. The external surface of the tungsten took on the form and texture of the mandrel, i.e., highly polished tungsten tubes were prepared when highly polished mandrels were used. The texture of the deposited (internal) surface of the tungsten tube was much like a chemically or electrically etched surface which could be smoothed by honing.

Attention is now directed to the drawings, the only figure of which is a diagrammatic representation of an apparatus for carrying out the invention. A deposition furnace **1**, comprising a pair of clam-shell furnaces **2**, **2'** arranged in tandem and rheostatically controlled (not shown), is adapted to receive a copper mandrel **3**. Sources of tungsten hexafluoride and hydrogen, individually metered, are connected to the inlet end of the mandrel and a waste gas scavenger **4** and recovery system (not shown) together with a vacuum pump **5** are connected to the exit end of the mandrel. The reaction pressure is controlled by pressure gage **6** and tungsten hexafluoride and hydrogen pressure by gages **7** and **8**.

It will be apparent that this method could be used to produce various other articles having different sizes and shapes. For instance, this method could be used to coat a copper furnace hearth with tungsten metal or it could be used to deposit a tungsten metal layer on a hexagonal support; after which, the hexagon could be cut into a number of tungsten plates. A further extension of this concept would be to use this method to clad fuel elements, which might find use in space reactors, with one of the isotopes of tungsten that has a low neutron adsorption cross section. With the separation of such isotopes from naturally occurring tungsten being quite expensive, this has not been economically feasible with prior art methods due to the low efficiency of such methods. However, with the efficiency of the present method being very good, i.e., tungsten utilization being above 90%, this method would be well suited for cladding fuel elements with an isotope of tungsten of low neutron adsorption cross section.

The invention is further illustrated by the following specific examples.

Example I

A ¾ inch diameter by 18 inches long copper tube, serving as a mandrel, was placed in a pair of clam-shell furnaces arranged in tandem. Sources of tungsten hexafluoride (WF_6) gas and hydrogen were connected to the inlet end of the copper tube and a waste gas scavenger and recovery system together with a vacuum pump were connected to the exit end. The mandrel was heated to 650° C. and the system pressure was lowered to 12 mm. of mercury. The tungsten hexafluoride gas and hydrogen flowed through the heated copper tube mandrel at a flow rate of 25 cc./min. and 2200 cc./min., respectively. Tungsten metal was deposited uniformly along the interior of the heated copper tube for a distance of 4 to 6 inches from the gas inlet. As the deposit reached a desired thickness of about 3 mils, the temperature of the furnace adjacent to the deposited areas of the copper tube was reduced to about 400° C., maintaining the temperature of the rest of the copper tube at about 650° C. In this manner tungsten was deposited on the heated copper tube in 4 to 6 inch segments along the entire length of the copper tube by progressively reducing the temperature of the furnace adjacent to the mandrel area as the tungsten deposit reached a desired thickness. The mandrel was then cooled and dissolved in nitric acid to leave a high density seamless tungsten metal tube ¾ inch in diameter and 14 inches long having a uniform wall thickness of 3 mils.

Example II

A first copper mandrel (¾ inch diameter by 18 inches long) was used in the same manner as in Example I. A thin copper wire, which served as a second mandrel was mounted axially within the first mandrel. The mandrels were placed in a pair of clam-shell furnaces arranged in tandem and heated to 650° C. with the inside mandrel subsequently being heated by radiation from the outside mandrel to about 650° C. The system pressure was lowered to 20 mm. of mercury and the reacting gases, tungsten hexafluoride and hydrogen, in a ratio of 1:40 by volume was passed into the annular space be-

tween the two mandrels. In this manner tungsten was deposited on the inside of the outer mandrel and the outside of the inner madrel and as the deposit reached a desired thickness, the temperature was reduced progressively along the length of the mandrels, as described in Example I to about 450° C. Upon completion of the deposition, the mandrels were cooled and dissolved in nitric acid leaving a high density seamless tungsten metal tube ¾ inch in diameter and 14 inches long having a uniform wall thickness of 3 mils and a tungsten capillary tube 0.004 inch in diameter and 14 inches long.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. The method of making tungsten metal tube on a mandrel by hydrogen reduction of tungsten hexafluoride which comprises:

(a) evacuating said mandrel system to a system pressure between 5 mm. to 20 mm. Hg;

(b) heating said mandrel to a temperature between 500° and 1000° C.;

(c) contacting the surface of said mandrel with a reacting mixture of said tungsten hexafluoride and hydrogen injected along the longitudinal axis of said mandrel from one end, said mixture being in the volume ratio of between 1:50 to 1:150 tungsten hexafluoride to hydrogen; and

(d) reducing the temperature progressively from the said one end along the longitudinal axis of said mandrel to a temperature of about 400° C. while maintaining the remaining portion of said mandrel at said temperature within said range of 500° to 1000° C., said temperature being reduced along said mandrel at a rate such that a layer of tungsten metal of selected thickness is continuously deposited upon said remaining heated portion.

2. Tungsten metal tubing formed by the method of claim 1.

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