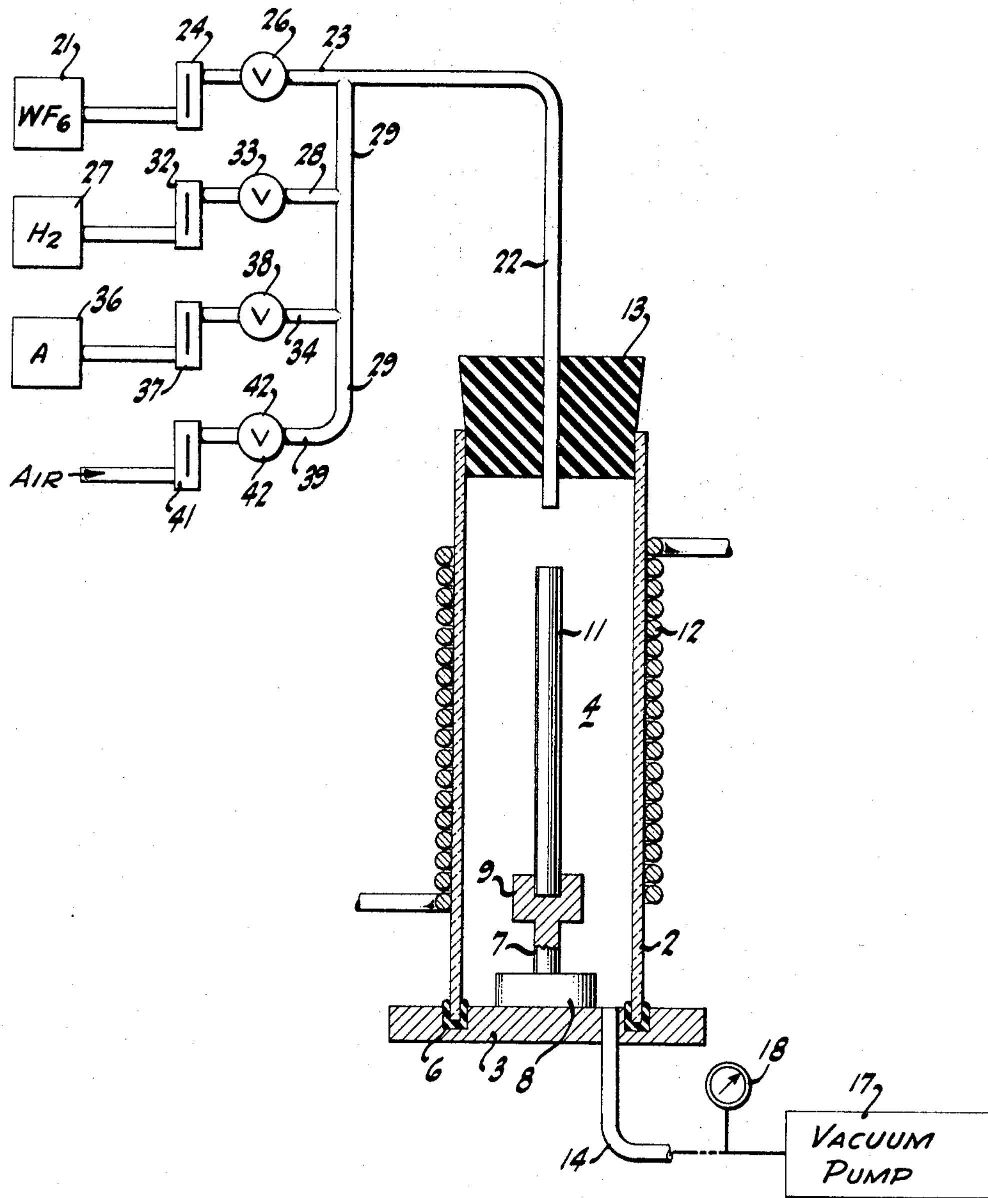
Feb. 23, 1971 R. A. HOLZL 3,565,676

CHEMICAL VAPOR DEPOSITION METHOD

Filed April 1, 1968 2 Sheets-Sheet 1

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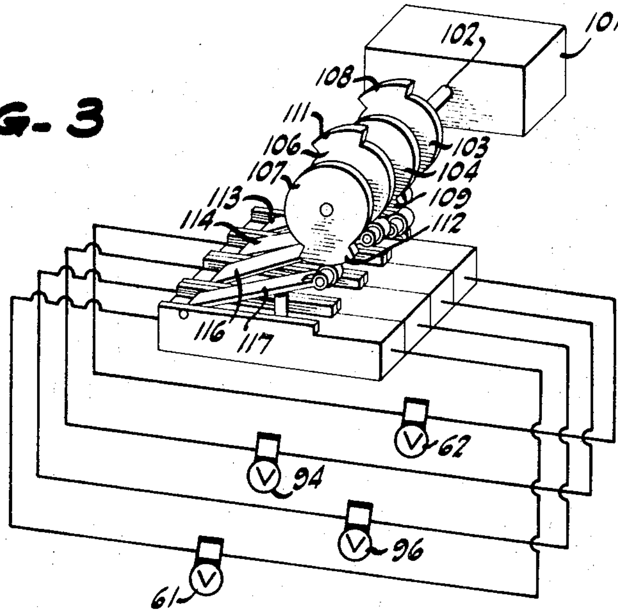
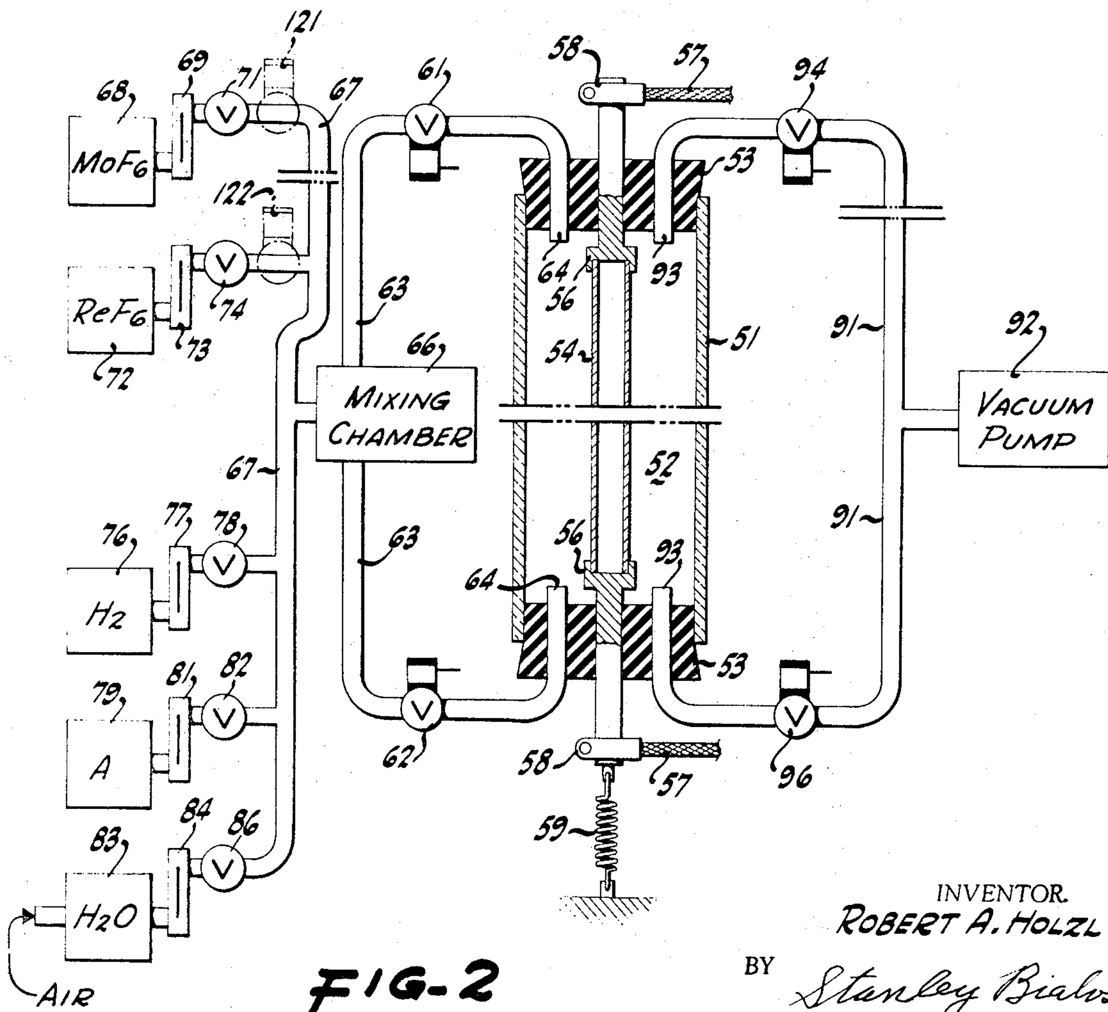
Filed April 1, 1968 2 Sheets-Sheet 2

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3,565,676

# CHEMICAL VAPOR DEPOSITION METHOD

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U.S. Cl. 117—107.2 6 Claims

## ABSTRACT OF THE DISCLOSURE

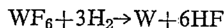
In a chemical vapor deposition process wherein refractory material is coated on a hot surface from the hexafluoride state, a controlled amount of oxygen or oxygen-producing material introduced into the system during the deposition process controls residual fluorine content and provides markedly improved physical characteristics to the resultant deposited coating.

This invention relates to the thermochemical deposition of material, also referred to as chemical vapor deposition (hereinafter designated as CVD), and more particularly to a method of imparting improved physical properties to such material deposited on a shaped substrate or mold by CVD.

CVD is well known; a most common method of forming a coating or plating of such material on a mold or substrate is from a so-called hexafluoride system. In such type of system a coating is deposited onto a heated surface contained in an enclosed reaction chamber into which a gaseous hexafluoride of the material, such as tungsten, molybdenum, rhenium and various mixtures thereof, is continuously introduced in the presence of a reducing agent, such as hydrogen. The gas flow is generally effected by means of a vacuum applied to the reaction chamber. There are various types of physical methods for effecting the deposit in the reaction chamber.

All such physical methods are applicable to a hexafluoride CVD system, as well as to other CVD systems, as they do not depend upon the character of the chemical reactants. Likewise, the invention hereof is not dependent on the particular type of physical method which is employed in effecting CVD, although preferred types of flow systems are disclosed herein by way of example. It is applicable to any type of hexafluoride CVD system wherein the deposition of the refractory material results from decomposition of the material from the hexafluoride state.

In such hexafluoride system wherein the material to be deposited on the hot surface is affected by a reducing agent, such as hydrogen, two types of reactions occur. For example, in the case of tungsten (W) the principal and normal reaction is as follows:



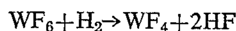
$$WF_6+3H_2 \rightarrow W+6HF$$

The hydrogen fluoride (HF) is a gas at the usual temperature at which the tungsten (W) deposit is effected; and consequently, it escapes from the reaction chamber with the spent gases as the reaction chamber is exhausted under vacuum.

It has been found pursuant to this invention, that an extremely minor amount of fluorine becomes entrapped in the deposited tungsten, which produces a detrimental effect (note the paper by J. V. Festa and J. C. Danko on page 349 of the book publication, "Proceedings of the Conference on Chemical Vapor Deposition of Refractory Metals, Alloys, and Compounds," at Gatlinburg, Tenn., Sept. 12–14, 1967, published by American Nuclear Society, Incorporated, Hinsdale, Illinois (Copyright



1967). This detrimental effect is believed to be due to a secondary reaction as follows:



$$WF_6+H_2 \rightarrow WF_4+2HF$$

The $WF_4$ (tungsten tetrafluoride) is non-volatile at the deposition temperature (usually about 600 to 700° C.) of metallic tungsten and becomes trapped as a solid impurity in the deposited tungsten, thus impairing strength. Moreover, objects formed of CVD tungsten are frequently employed in extremely high temperature environments in the order of 1800 to 2500° C.; and at such elevated temperatures, the solid tungsten tetrafluoride is volatile and escapes as a gas from the tungsten, thus rendering the tungsten porous by formation of voids, further weakening the same. Illustrative of such porosity or voids is the print of a photomicrograph (100 power) on page 408 of the aforementioned book publication.

Although the above equation of the secondary reaction depicts the formation of tungsten tetrafluoride ($WF_4$), other tungsten fluorides below the gaseous hexafluoride state may be formed at the deposition temperature, such as $WF_3$ and $WF_2$. They are also solids at the deposition temperature and gases at higher temperatures. They are all hereinafter referred to as subfluoride in contradistinction to the hexafluoride which is a gas at the deposition temperature.

Summarizing the invention, it comprises continuously introducing into the CVD hexafluoride system a controlled amount of oxygen or oxygen-forming material during the deposition process. This is contrary to expectations because the introduction of oxygen has heretofore been considered detrimental. The oxygen controls the quantity of residual fluorine entrapped as solid subfluoride in the deposited coating by oxidizing the subfluoride to a gaseous state during CVD, thus allowing escape of the fluorine from the system.

As will be discussed hereinafter in greater detail, it has been found pursuant to this invention that in the case of tungsten the quantity of oxygen should be such as to provide some trace amount of subfluoride in the metal to prevent grain growth of the tungsten, particularly at elevated temperatures, but that sufficient oxygen be employed to fix the subfluoride content below a maximum quantity to preclude the aforementioned deleterious void formation. An advantageous range of residual fluorine in the deposited tungsten (calculated on the amount of fluoride by weight) is about 8 to 25 parts per million (p.p.m.), desirably between 10 to 20 p.p.m.

In the case of other types of deposits, such as rhenium and tungsten co-deposits or alloys, rhenium and molybdenum co-deposits or alloys, rhenium, and molybdenum, the same chemical reactions occur but the aforementioned void formation has not been found to be a problem. However, it has been found that the entrapped fluorine content should be kept below about 25 p.p.m. to impart ductility to the metal. Above about 25 p.p.m., such metal will be markedly brittle. This is not a factor with respect to pure tungsten deposits because of the inherent brittleness of tungsten.

From the preceding, it is seen that the invention has as its objects, among others, the provision of an improved method and apparatus for controlling residual fluorine in a hexafluoride deposition system to impart markedly improved properties to CVD material, and to improved products made by such method and apparatus as a result of such residual fluorine control. Other objects of this invention will be apparent from the following more detailed description and accompanying drawings in which:

FIG. 1 is a schematic sectional elevation of a conventional unidirectional flow CVD system adapted for deposition of tungsten, but which includes the novel means

hereof for continuously introducing oxygen into the system during the deposition process;

FIG. 2 is a similar view of an alternate form of system wherein the material is deposited in tapered layers, and illustrating co-deposit of molybdenum and rhenium;

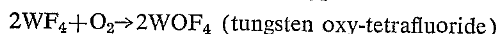
FIG. 3 is a schematic view of a switching system for automatically controlling the deposition cycle of the apparatus of FIG. 2;

In greater detail, the invention hereof, as previously mentioned, is not dependent on any particular type of physical CVD system. A physical method frequently employed is that of effecting steady, constant flow of the reactants through the chamber in a single direction past the hot surface. In this method when the fresh gaseous reactants are introduced into the chamber, they will react more readily to deposit material on the portion of the hot surface that is closest to the point of gas introduction (inlet or upstream end of the surface) than they will react to deposit material on the portion of the hot surface that is farthest from the point of gas introduction (the outlet or downstream end of the surface). This is because the gaseous reactants are continuously depleted of their plating capability as they flow past and deposit material on the hot surface. Consequently, the resultant coating will be tapered which is particularly objectionable where the hot surface is relatively long in the direction of the gas flow.

Another method, as exemplified in U.S. Pat. 3,031,388, dated Apr. 24, 1962, has been developed whereby a short portion of a long cylindrical object is heated, limiting deposition to said short portion, thereby minimizing taper in the deposit. The heating mechanism is then traversed down the length of said object causing the deposition area to travel correspondingly, eventually resulting in a substantially uniform deposit to be effected along the entire length of the object.

Additional physical methods are disclosed and claimed in assignee's copending application by Robert A. Holzl (the applicant hereof), Frederick A. Glaski and James R. Humphrey, Ser. No. 620,164, filed Mar. 2, 1967, now abandoned, for "Vapor Deposition Method and Apparatus"; and by Frederick A. Glaski and James R. Humphrey, Ser. No. 645,278, filed June 12, 1967, for "Method and Apparatus for Vapor Deposition." In the method of the former application, a uniform coating is obtained by forming the coating in very thin layers effected by rapidly filling the reaction chamber with the reactants at such high velocity while pocketing the reactants therein, as to cause each layer to be deposited substantially uniformly. In the latter application and as shown in FIG. 2 hereof, the method is adapted particularly for relatively long objects and is effected by forming the coating also in layers which are tapered but wherein the flow of the reactants is alternately reversed through the reaction chamber to cause the layers to taper in opposite directions and thus compensate for the taper.

It is believed that the addition of oxygen during the deposition of the metal, controls residual fluorine content by oxidizing the solid subfluoride to a gaseous state in accordance with the following equation in which tungsten tetrafluoride ($WF_4$) is considered typical of subfluoride:



$$2WF_4+O_2\rightarrow 2WOF_4 \text{ (tungsten oxy-tetrafluoride)}$$

The tungsten oxy-tetrafluoride ($WOF_4$) is volatile at deposition temperatures, and hence flows out of the CVD reaction chamber.

Any oxygen source can be employed, such as pure oxygen, air, or substances that will produce oxygen at the deposition reaction temperature, such as carbon dioxide. Consequently where oxygen is referred to herein it is employed generically to include all oxygen sources. Because of availability and consequent economy, air is preferred. In the case of metals such as rhenium, and molybdenum, and codeposits of these metals together or with others, water saturated air for some reason, not presently ascertainable, produces best results and is consequently preferred. However, in the case of pure tungsten deposits, air at ambient conditions has been found to produce best results, and is hence preferred.



The invention has been found to produce markedly improved physical properties to pure tungsten deposits where void formation and grain growth has been a problem heretofore. Normally, without the controlled addition of oxygen into the CVD system, the entrapped or interstitial fluorine content (calculated on the amount of fluorine) is about 50 to 100 p.p.m.; and in this respect all fluorine contents herein are calculated on the amount by weight of elemental fluorine, and not fluorine compounds or salts. Also, all fluorine determinations herein are made in accordance with the Photometric-Pyrohydrolysis method established by General Atomic Division of General Dynamics Corp., and which is described in the U.S. Publication "Chemist Analyst" 55, 71–73 (July 1966).

At such normal relatively high fluorine content of 50 to 100 p.p.m., void formation occurs in tungsten when it is used in high temperature environments, as can be noted from the middle of three companion photomicrographs on page 277 of the aforementioned book publication, "Proceedings of the Conference on Chemical Vapor Deposition" etc., as well as from the aforementioned photomicrograph on pages 408. With too little fluorine content, it has been found pursuant to this invention, that substantial grain growth occurs, causing weakness in the tungsten. Such grain growth is depicted by the right hand photomicrograph on page 277 of the aforementioned book.

To obviate grain growth in tungsten, the amount of oxygen introduced into the CVD system hereof should not be so excessive as to oxidize all the subfluoride, as it has been found that there should be at least about 8 p.p.m. residual fluorine in the tungsten to prevent grain growth, and desirably at least about 10 p.p.m. Above about 25 p.p.m. residual fluorine, void formation will be substantial. Hence, there should be a sufficient quantity of oxygen introduced to hold the fluorine content in the tungsten below about 25 p.p.m., and desirably below about 20 p.p.m. Thus, the fluorine content in tungsten should be held to about 8 to 25 p.p.m., and desirably about 10 to 20 p.p.m.

These ranges in tungsten can be readily obtained by controlling the amount of oxygen introduction with reference to the amount of gaseous tungsten hexafluoride into the CVD system The amount of oxygen (calculated on the basis of pure oxygen) should not vary more than about 0.2 to 0.6% by volume standard (standard temperature and pressure conditions—STP) of the amount of tungsten hexafluoride gas standard, introduced into the system to obtain a range of about 25 to 8 p.p.m. residual fluorine, and desirably about 0.3% standard of the amount of tungsten hexafluoride to obtain the close trace range of about 10 to 20 p.p.m. fluorine content. Based on amount of air introduction, this means from about 1.0 to 3.0% air by volume standard based on the volume of tungsten hexafluoride, and desirably about 1.5% by volume. The aforementioned oxygen range for tungsten is well below that at which poor plating of the tungsten occurs.

As was described above, the effect of controlled oxygen addition to pure CVD tungsten overcomes problems heretofore encountered, namely, void formation and grain growth. With respect to other CVD metals, such as rhenium, molybdenum, and particularly co-deposits or alloys of rhenium and molybdenum, and rhenium and tungsten, the presence of rhenium obviates these problems which are encountered with deposit of tungsten alone. Nevertheless, the introduction of a controlled amount of oxygen into such CVD systems improves the physical properties of the metal deposit in a different manner, namely, by imparting ductility thereto, up to as

much as 15 to 20% increase in ductility. However, the metal deposit becomes markedly brittle if the fluorine content is not controlled below a maximum quantity which is critical. To impart ductility for such metal deposits other than tungsten, the fluorine content should also be less than about 25 p.p.m., which is also the maximum for tungsten, and desirably to be safe, less than about 20 p.p.m. However, the lower limit of fluorine is immaterial in contradistinction to the minimum amount of fluorine content required for pure tungsten to prevent grain growth.

Hence, the maximum fluorine content in both instances is generic. To obtain the proper fluorine control for the aforementioned metallic deposits other than pure tungsten alone, the maximum amount of oxygen introduced into the CVD system is relatively immaterial as long as it does not exceed the amount at which poor plating will occur. In other words, it is immaterial if all the residual fluorine in these metals is eliminated by oxidation, but to prevent poor plating the oxygen addition should not exceed about 8% by volume standard of the total volume standard of hexafluoride gas or gases.

However, to insure that the residual fluorine content for the aforementioned metals other than tungsten is less than about 25 p.p.m., the amount of oxygen introduced into the system should be at least about 0.2% by volume standard of the total volume standard of hexafluoride gas or gases, which is the same as for tungsten alone. As an illustration, if the gases are molybdenum hexafluoride and rhenium hexafluoride to provide a codeposit of molybdenum and rhenium, the amount of oxygen introduced should be at least 0.2% by volume standard of the volume standard of the total amount of gaseous hexafluorides to provide a maximum of about 25 p.p.m. residual fluorine content, and desirably more to decrease the residual fluorine content substantially below 25 p.p.m. because the lower the better for these metals other than tungsten.

The following are illustrative of typical CVD systems, and typical examples illustrative of the invention.

Referring to FIG. 1, it illustrates a conventional form of apparatus wherein the method of this invention can be conducted by the conventional unidirectional flow of the reactants. The apparatus comprises conventional glass tubing **2** of about 1½ in. inside diameter, usually of quartz or "Vycor" glass, removably mounted on a support base **3** to form a conventional deposition reaction chamber **4**. Inasmuch as a vacuum is applied to the reaction chamber in the deposition or plating process, a peripheral seal **6** of suitable material such as a rubber gasket, is provided in a groove in base **3** to engage over the lower end of tube **2** and seal the same.

A work holder **7**, provided with a disc-shaped end **8** for stable support on base **3**, is removably mounted on such base; and desirably, although not essential, work holder **7** is rotated by suitable mechanism (not shown) about an upright axis so that during the deposition process, all of the surface of the object to be plated will be uniformly exposed to the reactants. At its upper end, work holder **7** is provided with a horizontal support table **9** provided with a recess for holding the object **11** to be coated, which in the embodiment illustrated is a mold or mandrel in the form of a molybdenum rod, which when plated on its exterior surface forms a tube when the mandrel is subsequently removed. An induction heating coil **12** is conventionally positioned about tube **2** at the zone of mandrel **11** to impart the requisite heat to the mandrel for effecting the chemical vapor deposition on the exterior surface thereof. A conventional rubber stopper **13** is removably secured in the top end of tube **2**; and vacuum line tubing **14** is connected to a vacuum pump **17** which provides a constant vacuum source. A suitable vacuum gauge **18** is connected in line **14**.

In accordance with conventional vapor deposition technique, a source **21** of tungsten hexafluoride ($WF_6$) is connected to tubing **22** by means of tubing **23** in which is connected a conventional flow meter **24** and a manually operable control valve **26** to control the meter for presetting its rate of flow. Tubing **22** provides a line for conducting reactants into the reaction chamber **4**, and is removably gripped in stopper **13**.



A source **27** of hydrogen ($H_2$) is also connected to tubing **22** by means of tubing **28** and a manifold tube **29** connected to tubing **23** beyond valve **26**. A conventional flow meter **32** and manually operable control valve **33** are also provided to control the hydrogen flow in line **28**. Also connected to tubing **22** through manifold **29** and tubing **34** is a source **36** of an inert purging gas, desirably argon, with another conventional flow meter **37** and a manually controlled valve **38** connected in tubing **34**. Finally, means is provided for introduction of atmospheric air into reaction chamber **4** by means of inlet tubing **39** connected to manifold **29**, and also having therein a conventional flow meter **41** and manually operable control valve **42**.

Except for the valve controlled means for introduction of air, the system is conventional for all systems in which there is unidirectional flow of the reactants effected by vacuum pump **17**; and as is conventional in such systems, the work is heated up to a desired temperature by induction heating coil **12**, and the reactant gases are caused to flow continuously through the reaction chamber **4** at the desired quantities depending upon the reactants. Before the deposition process is initiated, the reaction chamber is desirably flushed with argon, and after such flushing, the supply of argon is shut off. Although FIG. 1 illustrates tungsten fluoride as one of the reactants for plating of mold **11** with tungsten, it can be other reactants or a mixture of reactants.

## EXAMPLE I

The following is a typical operating example for the plating of mold **11** with tungsten.

First of all, with vacuum pump **17** operating, and all valves closed except the argon control valve **38**, argon is caused to flow through the chamber at 2 standard liters per minute as measured by flow meter **37**. The vacuum is shut off and, the argon pressure in the chamber is allowed to rise to approximately 1 atmosphere whereupon the vacuum is again applied to the chamber and argon is again allowed to flow into the chamber to repeat the flushing cycle. This flushing or purging cycle is continued intermittently a number of times (4 or 5) to insure that all residual air had been removed from the chamber prior to initiation of CVD.

After approximately 15 minutes of cycled purging, the source of argon is shut off by valve **42** and mold **11** is heated to the usual deposition temperature for tungsten of about 650° C. The pressure applied is 18 in. of mercury (vacuum). Mold **11** is a molybdenum rod 14 in. long and 0.296 in. in diameter. The tungsten hexafluoride is caused to flow at 475 cc. standard per minute, the hydrogen at 250 cc. standard per miuute, and the air (substantially dry atmospheric air) at 8 cc. standard per minute. This results in an amount of oxygen of about 0.34% by volume standard of the volume standard of the tungsten hexafluoride. The deposition time is 90 minutes which results in plating of the mandrel with a tungsten coating of about 0.040 in. in thickness.

After the period noted, the reaction chamber is flushed with argon as before and the mold allowed to cool. After such cooling, the coated molybdenum mold is removed from the reaction chamber and the molybdenum is removed from the tungsten coating by dissolving in aqua regia, which does not attack tungsten. The resultant free upstanding tubing provides an extremely suitable cathode for a thermionic electron tube because it is capable of withstanding extremely high temperatures in the order of 1800–2000° C. It is substantially free of void formation, and has a residual fluorine content of about 15 p.p.m.

Also, there is no substantial grain growth when the tubing is heated to such elevated temperature.

As previously pointed out, the invention hereof is not dependent on any particular form of apparatus or flow system for effecting CVD; and as illustrative of another type of apparatus reference is made to FIGS. 2 and 3 which disclose a system of the type disclosed in assignee's aforementioned copending application by Frederick A. Glaski and James R. Humphrey, Ser. No. 645,278, in which the flow of reactants is periodically reversed to avoid the tapering effect of unidirectional flow of the reactants, by plating the mold in layers to compensate for such tapering and thereby cause the plated coating to be of substantially uniform thickness.

In subsequent Example 2, the mold or mandrel is plated with an alloy of rhenium and molybdenum and these are shown in FIG. 2, but other metallic hexafluorides may be employed in their place. The apparatus comprises conventional glass tubing **51** of quartz of "Vycor" clamped in a conventional manner to a suitable support (not shown). Tubing **51** forms reaction chamber **52** through which flow of the reactants is effected. Conventional rubber stoppers **53** are removably fastened in the respective ends of chamber **52**. Mandrel **54** is resistance heated in the chamber by the passage of electric current directly therethrough from solid copper conducting rods **56** passing through the respective stoppers **53**, and which are connected to copper cables **57** by means of clamps **58**; the mandrel being clamped between the ends of rods **56**. To allow for expansion of the parts under heat, the lower rod **56**, shown in FIG. 2, is placed under tension by means of coil spring **59**, to thus insure that it can move slightly through the associated stopper as expansion occurs.

For controlling flow of reactant gases into chamber **52**, an automatically operated electromagnetically controlled inlet valve **61** is connected to one end of the chamber, and another similar inlet valve **62** is connected to the opposite end. These valves are also connected in tubing **63** for the conduction of the reactant gases and which have extensions **64** extending through the respective stoppers **53**. Also connected in tubing **63** is an enlarged chamber **66** which serves as a mixing chamber for the reactants.

Mixing chamber **66** is connected to manifold inlet tubing **67** which is, in turn, connected to a source of reactants comprising source **68** of molybdenum hexafluoride connected to a conventional flow meter **69**, with a manually operable control valve **71** in manifold **67** after flow meter **69**. Similar, a source **72** of rhenium fluoride is connected to conventional flow meter **73** and another manually operable control valve **74**; and a source of hydrogen **76**, flow meter **77** and manually operable valve **78** are also similarly connected to manifold **67**. As previously explained when a CVD apparatus is started, it is usually desirable to purge the same with an inert gas; and for this purpose, a source of argon **79** is connected to flow meter **81** and to manually operable valve **82**.

In a molybdenum hexafluoride and rhenium hexafluoride system, it is desirable that the air containing the oxygen be saturated with moisture as was previously mentioned; and for this purpose, the air is introduced through a water bath in a chamber **83** which is connected to flow meter **84** in turn connected to manually operable control valve **86**.

Means is provided for alternately periodically effecting flow of the reactants through the respective ends of reaction chamber **52** comprising tube **91** connected to a constant source of vacuum provided by vacuum pump **92**. Tubing **91** has extensions **93** extending through and gripped by the respective stoppers **53**. The exhaust of reactants from one end of chamber **52** is automatically controlled by electromagnetically operated exhaust valve **94**; and similarly, exhaust from the opposite end of chamber **52** is controlled automatically by electromagnetically operated exhaust valve **96**. From the preceding it is seen that periodic reversal of flow of reactants through reaction chamber **52** can be effected by operating the inlet and exhaust valves in such manner that inlet valve **61** and exhaust valve **96** are open when inlet valve **62** and exhaust valve **94** are closed, and vice versa.

Means is provided for automatically operating the respective sets **61, 96** and **62, 94** of electromagnetically controlled valves in proper sequence. Referring to FIG. 3, a conventional, electrically operated motor-timer **101** is provided connected to drive shaft **102** which has cam discs **103, 104, 106** and **107** fixed for rotation therewith; the respective cam discs having cams **108, 109, 111** and **112** which, respectively, open and close spring-pressed switch arms **113, 114, 116** and **117** to open and close the sets of valves in the sequence pointed out above.

## EXAMPLE II

The following is a typical example of the plating of mandrel **54** with a molybdenum and rhenium co-deposit.

As in Example I, reaction chamber **52** is purged first with argon by flushing the chamber repeatedly for about 15 minutes; the argon flow through the chamber being at two standard liters per minute under a high vacuum of about 28.5 inches of mercury (vacuum). After such purging, the mandrel is heated to a deposition temperature of about 875° C. by alternating current resistance through leads **57** and the connector rods **56**. Although the temperature can be controlled in any suitable manner, it is controlled by an infra-red radiation pyrometer.

Hydrogen flow of about 2750 standard cc. per minute, as controlled by flow meter **77** and valve **78**, is then introduced into the chamber. The deposition cycle is initiated by adjusting valve **71** to effect flow of molybdenum hexafluoride at the rate of 400 standard cc. per minute; then valve **74** is adjusted to effect flow of rhenium hexafluoride at the rate of 20 standard cc. per minute; and valve **86** is adjusted to allow a flow rate of water saturated air at 7.5 cc. per minute. At such flow rates, the volume of oxygen standard is about 0.36% of the total volume standard of the rhenium hexafluoride and the molybdenum hexafluoride. These flow rates are generally established in about 25 seconds at which time the automatic solenoid valve control system is activated; the pressure being about 28.5 inches of mercury (vacuum).

In this connection, valves **61** and **96** are simultaneously closed and valves **94** and **62** simultaneously opened alternately to cause the reactant gas mixture flow to reverse direction through the chamber with the flow in each direction about 15 seconds. After about 45 minutes of the cyclic deposition of a co-deposit of rhenium and molybdenum, the plating of mandrel **54** is terminated by closing valves **71, 74, 78** and **86**; and the argon flow is again resumed at about 2 standard liters per minute while repeating the cyclic flushing or purging process with all the other valves **71, 74, 78** and **82** closed, for the purpose of removing all active gases from the chamber. The coated mandrel **54** is allowed to cool in the argon atmosphere.

The reverse flow principle effects deposition of the rhenium and molybdenum, in vary thin layers adjacent ones of which tapered in opposite direcitons so as to provide an overall coating of substanially uniform thickness, as is explained in the aforementioned assignee's copending application, Ser. No. 645,278.

The deposition is continued for about 45 minutes, resulting in the deposition of about 140 layers. Mandrel **54** is stainless steel tubing approximately 72 in. long and 0.068 in. in diameter, and the overall thickness of the deposited molybdenum-rhenium coating is about 0.010 in. Its composition is about 7% rhenium and it contains about 15 p.p.m. residual fluorine. A free-standing molybdenum-rhenium tube is finally produced by pulling the mandrel out of the tube from one end. The tube has about 25% increase in ductility compared to a simi-

lar tube which is formed without the introduction of a minor amount of oxygen into the system, and is suitable for use as a sheath for a high temperature thermocouple probe capable of withstanding temperatures in the order of 2000° C.

EXAMPLE III

The following is a typical example wherein tubing is made by the alternating flow system of FIGS. 2 and 3 but wherein an alloy of tungsten and rhenium is formed by flow of tungsten hexafluoride along in one direction, and then flow of rhenium hexafluoride alone is effected in the same direction. Then the direction of both the tungsten hexafluoride alone and the rhenium hexafluoride alone is reversed, and the reversals continued alternately to build up a coating or plating of the desired thickness. The apparatus is the same as in FIGS. 2 and 3 except that the mixing chamber 66 is omitted and additional automatically controlled valve **121** and **122** (shown in phantom lines in FIG. 2) are employed after valves **71** and **74**, respectively, and which are sequentially operated to provide for separate flow of the respective hexafluorides.

Tungsten hexafluoride is in the chamber **68** in place of molybdenum hexafluoride; and as with respect to Example II, chamber **52** is first flushed with argon. The following are the run conditions for the instant example:

Reaction chamber size—1½ in. inside diameter, and length 36 in.
Mandrel material—stainless steel 0.083 in. outside diameter and 24 in. long
Mandrel temperature—1000° C.
Vacuum—28.5 in. mercury (absolute)

Mandrel is initially heated in hydrogen plus argon in conventional manner to clean surface of oxides prior to the coating of the mandrel. Flushing with argon flow; same as in Example II at rate of 380 cc. per minute standard.

Hydrogen flow—1000 cc. per minute standard
Tungsten hexafluoride flow—250 cc. per minute standard
Rhenium hexafluoride flow—200 cc. per minute standard
Saturated air flow—50 cc. per minute standard

Volume of oxygen is about 5.0% standard of volume of rhenium hexafluoride, and about 4.0% standard of volume of tungsten hexafluoride.

Duration tungsten hexafluoride flow—20 seconds in each direction
Duration rhenium hexafluoride flow—5 seconds in each direction

Tungsten hexafluoride and then rhenium hexafluoride were run successively in one direction, and then run successively in reverse direction.

Duration of CVD with sequential flow in alternate opposite directions—65 minutes
Rhenium content of alloy—26.6%

The number of layers formed is approximately 312, and the overall thickness of the resultant tungsten-rhenium coating is about 0.036 in.; and such coating has an average of about 7.0 p.p.m. residual fluorine. The mandrel being of stainless steel is removed by pulling it out of the coating; and the resultant free-standing rhenium-tungsten tube exhibits room temperature ductility in that it can be plastically deformed in the "as deposited" state by bending as much as 15°, and still return to its original shape. The resultant tubing is suitable as a high temperature thermocouple probe sheath; and the same alloy is suitable for the manufacture of crucibles in which chemical reactions may be conducted.

The above examples are merely exemplary; and as previously explained, the method hereof is applicable to any type of CVD system wherein the platings or deposit of high refractory metals such as tungsten, rhenium or molybdenum and various co-deposits or alloys thereof is from the hexafluoride state. All that is required is to introduce into the CVD system a continual flow of oxygen or oxygen-forming material in a quantity to control the residual fluorine content in the manner described. In this connection, the oxygen will oxidize the subfluoride to the gaseous state at all deposition temperatures usually employed for CVD deposit of such refractory metals or combinations thereof.

I claim:

**1.** In the coating of a surface of an object by chemical vapor deposition wherein the gaseous hexafluoride of refractory metal selected from the group consisting of tungsten, molybdenum, rhenium and mixtures thereof, and hydrogen are reacted in a chamber under a vacuum and the metal is deposited in substantially non-oxidized state onto said surface by application of heat thereto, the improvement of minimizing void formation and grain growth in tungsten and imparting increased ductility to other of said deposits which comprises effecting flow of a controlled amount of oxygen in said chamber, the amount of oxygen being in the range of about 0.2 to 8% by volume standard of the volume standard of the metal hexafluoride.

**2.** The method of claim **1** wherein the amount of oxygen provides an amount of residual fluorine in said deposited coating of below 25 parts per million.

**3.** The method of claim **1** wherein the gaseous metal hexafluoride is tungsten hexafluoride, and the amount of oxygen is about 0.2 to 0.6% by volume standard of the volume standard of the tungsten hexafluoride to provide a residual fluorine content in the deposited tungsten of less than about 25 parts per million to obviate substantial void formation in the tungsten when used in a high temperature environment and above about 8 part per million to preclude substantial grain growth of the tungsten.

**4.** The method of claim **1** wherein said metals are molybdenum and rhenium.

**5.** The method of claim **1** wherein said metals are tungsten and rhenium.

**6.** In the coating of a surface of an object by chemical vapor deposition wherein gaseous tungsten hexafluoride and hydrogen are reacted in a chamber and substantially pure tungsten is deposited onto said surface by application of heat thereto, the improvement of controlling residual fluorine content in such coating which comprises conducting such reaction by effecting flow of oxygen in said chamber, the amount of oxygen being about 0.3% by volume standard of the volume standard of the tungsten hexafluoride resulting in an amount of residual fluorine in the deposited tungsten of about 10 to 20 parts per million.

**References Cited**

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