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VAPOR DEPOSITION OF TUNGSTEN

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The invention relates to a process of producing tungsten in a substantially pure state. More specifically, it relates to the coating of objects with tungsten by reduction of tungsten hexafluoride from the vapor phase.

It is well known that tungsten retains its mechanical characteristics when elevated to very high temperatures, e.g. 2500° C. For this reason such a material becomes very desirable for use as a heat shield means for ballistic missile re-entry bodies, for rocket exhaust nozzles, and the leading edges of supersonic aircraft wings. These are only a few of many examples which could be recited and by which the wide application of the present invention could be emphasized.

In the past, it has been possible to coat certain materials with tungsten by electrodeposition from fused salt baths. However, this process has certain forbidding limitations; several of the most prominent of these limitations being that the surface obtained is generally very rough and uneven, and a thickness greater than approximately 10 mils is difficult to obtain. These limitations have restricted the use of such a process to the laboratory.

There are two methods of tungsten deposition from the vapor phase generally known in the art. One such method utilizes the thermal decomposition of tungsten hexacarbonyl. This method has proved to be unsuitable for many applications, as well as, very expensive. Two factors which limit the application or use of such a process are that the rate of deposition is low, e.g. one mil per hour, and the thickness of tungsten which can be deposited is limited to several mils. In addition, the coating is, in many instances, somewhat stressed and therefore is susceptible to chipping and cracking. The high cost of the hexacarbonyl is the paramount cause of the high cost of this process. The second method of tungsten deposition from the vapor phase involves the reduction of tungsten hexachloride with hydrogen gas. Tungsten hexachloride is a solid at normal room temperature and therefore must be heated to above 225° C. to produce sufficient vapor for the process. Inasmuch as below this temperature tungsten hexachloride is a solid the vapor must be heated above this temperature during its transfer to the deposition vessel from the vaporizing means. This requires heated delivery tubes to prevent condensation of the vapor and consequently results in added expenses. Also, the material or object to be coated must be heated to about 850° C. to obtain an adequate rate of reaction and good adherence between the tungsten coating and material or object being coated. However, the most prominent and undesirable disadvantage of this process is that a substantial portion of the vapor is converted into lower valent chlorides instead of pure tungsten. These undesirable chlorides impede the reactive process, as well as, produce a rough and uneven surface. A still further disadvantage is that the minimum temperature at which the reaction will take place is above 400° C. and this prevents the use of this process to plate many materials. The process appears also to be somewhat affected by

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pressure variations. The above factors combine to make this process inefficient and produces a coating of inferior quality.

Accordingly, one object of the present invention is to provide a process for producing pure tungsten in an improved manner.

Another object of this invention is to provide a process for the production of pure tungsten in a highly efficient manner.

Another object of this invention is to provide a process for the deposition of tungsten wherein lower valent halide compounds are not produced.

Another object of the herein described invention provides a process for producing pure tungsten by deposition from tungsten hexafluoride in the vapor phase.

Still another object of the present invention is to provide an improved process for producing pure tungsten by deposition from gaseous tungsten hexafluoride with hydrogen.

Yet another object of the present invention provides a process which will deposit pure tungsten on any material which is a solid at the reaction temperature.

Still another object of the present invention provides a relatively inexpensive process which will deposit a coating of pure tungsten of substantial thickness on any material which is a solid at reaction temperature and which process is substantially free from the production of lower valent halide compounds.

Still another object of the present invention provides a process for the deposition of pure tungsten which process is insensitive to pressure variations.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description and appended claims.

This invention process calls for the subjecting of the object to be coated to a vapor comprising tungsten hexafluoride and hydrogen gases. This process may be performed by any number of structural arrangements several of which are commercially available.

An example of such a structural arrangement includes a cylindrical ceramic vessel in which the object to be coated is supported. Surrounding the vessel is an electrical heating element or induction coil which is utilized to elevate and maintain the temperature of the object to be coated. The tungsten hexafluoride, a gas at room temperature, and the hydrogen gas each flow through a separate flow meter into the reaction vessel. As the gas mixture flows past the heated object the herein described reaction takes place, that is, substantially pure tungsten is deposited on the surface of the object. It will be understood that many other combinations of structural arrangements will perform this process equally as well as that arrangement just mentioned and that the structural arrangement used to perform the herein disclosed process does not form any part of the invention and is disclosed herein only for the purpose of better describing the process.

Performance of the instant process produces a tungsten coating of a much higher quality than could be anticipated from results of tests of similar processes with other halide compounds. That is, the instant process deposits a coating of substantially pure tungsten on any object which can be raised to the reaction temperature. The deposited coating is of a quality much higher than that heretofore obtained by commercial processes. A smooth evenly distributed layer of tungsten is deposited on an object.

A very important feature of this invention is the increased rate at which the tungsten can be deposited. That is, if this process is compared to similar processes, all normally variable factors being equal, the rate at

which a coating is deposited will be substantially higher. It appears that two factors permit this improved plating rate. Firstly, the absence of side reactions or, more specifically, the production of lower valent fluoride compounds is eliminated, and secondly, the rate of reaction of the tungsten hexafluoride is greater than that of similar compounds.

The reaction of the instant process is entirely a surface reaction. That is, the only reaction is on the surface of the object being coated. This means that there are no lower valent halide compounds formed in the gas itself which would impede the reactive process.

The process has another desirable feature in that it is insensitive to the normal variables which generally affect chemical reactions of this type. The temperature at which the reactive process takes place appears to be the only critical variable. The effects of pressure, in contradistinction to similar processes, has been proven to be substantially negative insofar as the quality of the coating is concerned. The rates at which the tungsten hexafluoride and the hydrogen gas are applied to the object have been shown to not affect the quality of the coating. That is, the amount of tungsten hexafluoride gas and the amount of hydrogen gas that is made available for the reaction does not substantially affect the quality of the coating. Obviously, it would affect the rate at which the reaction takes place and, consequently, the efficiency of the reaction. That is, if the flow of hydrogen were to be entirely stopped the reaction would, naturally cease. If the hydrogen flow is much less than the flow of tungsten hexafluoride the amount of hydrogen determines the amount of tungsten deposited. As a practical matter the most efficient operation of the process dictates that there be an excess of hydrogen. However, as mentioned above, no matter what the rate of flow of hydrogen or tungsten hexafluoride or the relative flow thereof the coating remains of very high quality and the process does not produce lower valent fluorides.

As stated above the only critical variable is the temperature at which the reaction takes place, and the optimum temperature varies with the type of material being coated. However, extensive experimentation has shown that a temperature of approximately 300° C. is the lowest temperature at which the reaction will take place. The term "temperature of reaction" is defined as the temperature of the objects or articles being coated. It has been determined that for most materials, the temperature which most efficiently causes deposition of the tungsten, as well as, that which gives the highest degree of adhesion is approximately 650° C. However, this temperature may be varied depending on the material. There appears to be no definite upper temperature limit to the reactive process. However, the rate of reaction becomes quite rapid at higher temperatures and an even coating thickness is difficult to obtain above about 900° C. Again this temperature varies slightly with the type of material being coated.

The above-mentioned features of the present invention combine to give it an efficiency which heretofore, was not found to be possible in this type of process. In other words, the percentage of tungsten halide that is converted to pure tungsten exceeds that of similar processes. This factor, as well as, the extreme operational simplicity of this process as compared to similar processes make the instant process a very inexpensive and commercially desirable process. The tungsten coating which results from the present reactive process is of substantially improved quality as compared to tungsten which has heretofore been produced commercially.

A number of examples of actual experimental performances of the above-described process will now be set forth to illustrate its uniqueness.

EXAMPLE 1

A molybdenum rocket nozzle insert which had a 1.5

centimeters throat diameter and nozzle inner surface area of approximately 30 square centimeters was subjected to the above process under the following conditions:

5	Temperature of insert.....° C..	650
	Total pressure.....atm..	1
	H ₂ flow rate.....ml./min..	3200
	WF ₆ flow rate.....ml./min..	340
	Length of run.....minutes..	30
10	Tungsten deposited.....inches..	0.023

The prime purpose of this test was to prove that the process performs satisfactorily at atmospheric pressure. The condition of the resulting coating was excellent in that the tungsten was substantially pure, and the deposited tungsten was evenly distributed over the nozzle surface. Notably absent from the reactive process was the production of lower valent fluorides. Adherence between the coating and the nozzle was highly satisfactory.

EXAMPLE 2

A graphite nozzle insert of the same size as the molybdenum nozzle of Example 1 was subjected to the above-described process under the following condition:

25	Temperature of insert.....° C..	750
	Total pressure.....atm..	3/4
	H ₂ flow rate.....ml./min..	1200
	WF ₆ flow rate.....ml./min..	280
	Length of run.....minutes..	15
30	Tungsten deposited.....grams..	30

The main purpose of this test was to show that the reaction performed satisfactorily at an elevated temperature. Again the condition of the resulting coating was excellent. The coating was evenly distributed over the nozzle surfaces. The adherence between the coating and the nozzle was again satisfactory.

EXAMPLE 3

Another graphite nozzle insert substantially identical to the nozzle insert in Example 2 was subjected to the process under the following conditions:

40	Temperature of insert.....° C..	500
45	Total pressure.....atm..	1/2
	H ₂ flow rate.....ml./min..	1650
	WF ₆ flow rate.....ml./min..	350
	Length of run.....minutes..	20
50	Tungsten deposited.....grams..	5

This example proved that the process performs satisfactorily at a temperature less than that of Example 1. Again the resulting coated surface was of excellent quality. Also, the process did not produce lower valent fluoride compounds.

EXAMPLE 4

A steel rod 1 centimeter in diameter and 6 centimeters in length was subjected to this process under the following conditions:

60	Temperature of rod.....° C..	650
	Total pressure.....atm..	1/2
	H ₂ flow rate.....ml./min..	200
65	WF ₆ flow rate.....ml./min..	200
	Length of run.....minutes..	30
	Tungsten deposited.....grams..	7.5

The primary reason for this test was to show that the ratio of hydrogen flow to the tungsten hexafluoride flow did not affect the quality of the coating. The resulting coating was smooth and evenly distributed over the surface of the rod.

EXAMPLE 5

A copper bar having a cross section of 1/2 square centi-

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meter and a length of 5 centimeters was subjected to this novel process under the following conditions:

Temperature of bar.....	°C.....	900
Total pressure.....	atm.....	1/2
H ₂ flow rate.....	ml./min.....	1100
WF ₆ flow rate.....	ml./min.....	150
Tungsten deposited.....	grams.....	9

This process proved that the process could be operated at an elevated temperature and at a high tungsten hexafluoride flow-hydrogen flow ration. Again the coating quality was very satisfactory.

EXAMPLE 6

The interior of a steel container was subjected to the instant process under the following conditions:

Temperature of container.....	°C.....	300
Total pressure.....	atm.....	100
WF ₆ used.....	grams.....	12
Vol. of container.....	ml.....	100
Tungsten deposited.....	grams.....	8

This experiment was performed to test the effect of high pressure on the reaction. It was conclusively shown that the reaction is insensitive and substantially unaffected by the pressure in the testing vessels insofar as the resulting coating is concerned. That is to say, the tungsten coating obtained was evenly distributed over the container with excellent adherence.

EXAMPLE 7

A graphite rod 2 centimeters in diameter and 5 centimeters in length was subjected to this novel process under the following controlled conditions:

Temperature of rod.....	°C.....	650
Total pressure.....	atm.....	0.1
H ₂ flow rate.....	ml./min.....	1000
WF ₆ flow rate.....	ml./min.....	345
Tungsten deposited.....	grams.....	3.5

This experiment had as its primary purpose the performance of the process at sub-atmospheric pressure. The results again proved that the coating was substantially insensitive to pressure variations. The reaction was again, free from the production of lower valent fluorides.

Summary of Examples

The foregoing examples indicate the wide ranges in which this process can be performed satisfactorily. More specifically these ranges are:

	Range
Temperature of object.....	300° C. to 900° C.
Pressure variation.....	0.1 to 100 atm.
Total flow rate.....	400 to 3600 ml./min.
Substrate material.....	Graphite to molybdenum.

In each of the foregoing examples the process was free from the production of non-metallic products of reduction, that is, lower valent fluoride compounds. The adherence between the substrate material and the coating in each of the above examples was very satisfactory, however, it varied slightly with the substrate material and the reaction temperature. The coating was in each example smooth and evenly distributed. The quality of the deposited tungsten was excellent in each case.

The above process can be utilized to form objects of substantially pure tungsten. For example, should it be desired to construct a tungsten tube it is only necessary that a tube with an outer diameter equal to the desired inner diameter of the tungsten tube be coated with tungsten until the thickness of the coating equals the desired tube thickness. It is noted that during the deposition process the ends of the inner tube must be closed to prevent the tungsten from being deposited on the inner surface thereof. After the desired coating is

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obtained the end covers of the inner tube are removed and the inner tube dissolved by an acid to which tungsten is insensitive. For example, the inner tube could be made of copper which is dissolved by nitric acid. As is well known, nitric acid will not adversely affect tungsten and, therefore, a substantially pure coating remains after the tungsten coated copper tube is placed in a bath of nitric acid. As can be easily seen, many intricate shapes and configurations can be obtained by this method. The only requirement is that the coated model or pattern have a surface or opening so that the solvent can come into contact with the model. The substrate material could, also, in some instances, be removed by a grinding operation.

It has also been observed that this process will deposit a coating of tungsten on porcelain. Such a reaction produces a very strong bond between the tungsten coating and the porcelain. This results from reduced tungsten compounds penetrating a few thousandths of an inch into the pores of the porcelain. The adherence between the tungsten and the porcelain has survived severe shock and even crushing of the coated object.

Obviously many 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 may be practiced otherwise than as specifically described.

What is claimed is:

1. The process of coating an object with substantially pure tungsten comprising the steps of heating said object at a temperature above 300° C. then subjecting said object to a vapor comprising tungsten hexafluoride gas and hydrogen gas.

2. The process of depositing a coating of substantially pure tungsten on an object comprising the step of subjecting said object to a gas mixture consisting of tungsten hexafluoride and hydrogen gases, said object being at a temperature between 300° C. and 900° C.

3. The process of coating an object selected from the group consisting of metallic and non-metallic materials with substantially pure tungsten which comprises the step of subjecting said object when heated to a temperature above 300° C. to a gas mixture consisting of tungsten hexafluoride and hydrogen gas.

4. The process of forming an object of substantially pure tungsten which comprises the steps of forming a pattern of a material which is dissolvable by an acid and solid at the reaction temperature than subjecting said pattern of solid material to a gas mixture consisting of tungsten hexafluoride and hydrogen gases so as to form a coated object, during the coating reaction said object being at a temperatures between about 300° C. and about 900° C., and then placing the coated object in a bath of an acid to which tungsten is insensitive thereby dissolving said pattern of solid material, and then recovering from said acid bath a shaped object of substantially pure tungsten.

References Cited in the file of this patent

UNITED STATES PATENTS

1,497,417	Weber	June 10, 1924
2,885,310	Olson et al.	May 5, 1959
2,875,090	Galmiche	Feb. 24, 1959

FOREIGN PATENTS

722,797	Great Britain	Feb. 2, 1955
521,113	Italy	Mar. 25, 1955
742,304	Great Britain	Dec. 21, 1955

OTHER REFERENCES

- Metal Finishing, vol. 50, No. 4, pp. 64-69, April 1952.
 Vapor Plating, Powell, Campbell Conser, pub. John Wiley & Sons, 1955, pages 55-58.
 Materials in Design Eng., p. 99, January 1960.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,072,983

January 15, 1963

Abner Brenner et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 41 and 46, for "tungstem", each occurrence, read -- tungsten --; line 48, for "than" read -- then --; line 52, for "temperatures" read -- temperature --.

Signed and sealed this 8th day of October 1963.

SEAL)
ttest:

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Acting Commissioner of Patents