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METHOD OF PRODUCING METALLIC BODIES

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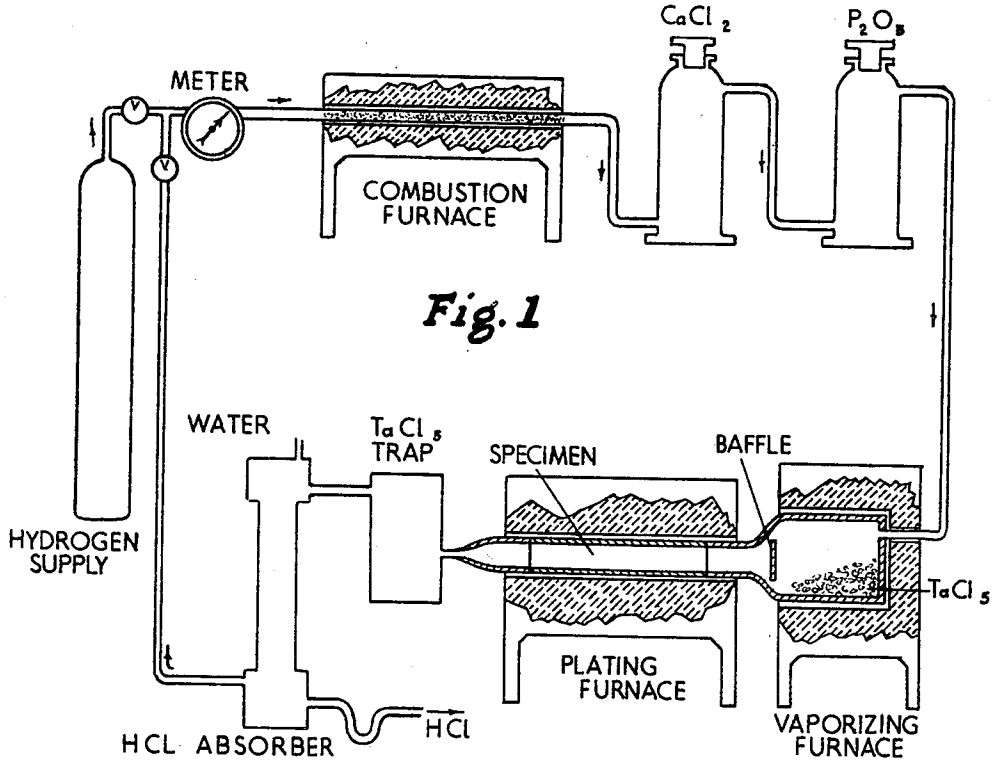


Fig. 1

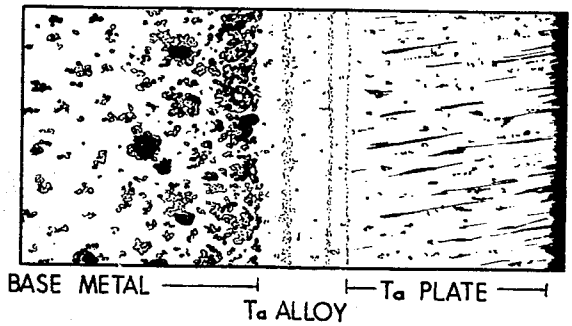


Fig. 2

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METHOD OF PRODUCING METALLIC BODIES

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11 Claims. (Cl. 75—84)

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This invention relates to the production of dense acid-resistant plates of tantalum or columbium upon a base metal to which the plating is bonded. By the process of this invention it is possible to produce articles consisting of a base metal completely protected by an integral coating of tantalum or columbium which renders the article immune to attack by strong acid. By the process of this invention it is also possible to produce metallic tantalum or columbium.

It should be understood at this point that where the term "tantalum" is used, it refers also to columbium and alloys of tantalum and columbium, ranging from all tantalum to all columbium, unless it be apparent that specific reference is made only to the element tantalum.

It is known that compounds of tantalum such as the halides, particularly the chloride, are decomposed at elevated temperatures in the presence of hydrogen to produce more or less impure metallic tantalum. The tantalum so produced by the prior art methods has been, to our knowledge, loose material which has no adhesion to the base upon which it was deposited. These prior art methods have been practicable only upon extremely small scale production of tantalum, and it has not been possible heretofore to form a dense plating of tantalum upon a base metal under controlled conditions whereby the plating firmly adhered and formed a permanent protective coating. The present process is an improvement on the heretofore known methods of halide reduction which results in the deposition of a smooth, dense, acid-resistant and impervious plating of tantalum upon base metals which may not be acid-resistant.

As base materials a wide variety of metals and alloys are suitable. By way of example it may be mentioned that satisfactory results have been obtained with: copper, copper plated metals, molybdenum, nickel-iron alloys, copper-nickel alloys, both those rich in copper and those rich in nickel, and various steels, particularly chrominum-nickel steels of the "stainless" type. By this invention tantalum may also be deposited as a plating upon a base of metallic tantalum. It will be obvious that the method of our invention will not be applicable to metals or alloys which melt below the minimum temperature for the operation of our invention, which will later be shown to be about 500° C.

In brief, this invention comprises volatilizing a suitable tantalum or columbium compound, for example, a tantalum halide, and especially the chloride, in an atmosphere of purified hydrogen, conveying the tantalum halide-hydrogen mixture

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to the metal surface to be plated without prematurely decomposing the halide, and then causing the halide to decompose in such manner that the tantalum formed by the reaction bonds to the metal surface and forms a dense adherent plating thereon. There are a large number of factors affecting the production of a protective metal plating upon a base metal, and each of these factors must be held within carefully restricted limits if satisfactory plating is to be assured. In the plating of a base metal with columbium it is obvious that a columbium compound would be employed, and by the use of a mixture of a tantalum compound and a columbium compound a mixture of the two metals will be plated on the base metal.

It has been found that the temperatures to which the halides may be subjected before utilization in the plating procedure are quite limited. The common halides of tantalum and columbium have boiling points as follows:

Halide	Boiling Point
	° C.
Tantalum:	
Bromide	320
Chloride	242
Fluoride	229.5
Columbium:	
Bromide	270
Chloride	240.5
Fluoride	229

As long as the halide-hydrogen mixture is maintained at temperatures above the boiling point of the halide, any proportion of halide may be obtained in the vapor so far as quantity only is concerned. Below the boiling point an amount of halide proportional to its vapor pressure at such lower temperatures may be carried by the hydrogen.

The upper temperature limit to which the hydrogen-halide mixture may be subjected before plating is quite critical. It has been found that if these halides are heated above about 500° C. to about 600° C. prior to the desired deposition, the tantalum or columium halide is decomposed with the production of powdery tantalum or columbium and the corresponding halogen acid. This powdery metal has no useful value as a protective coating, and it has been found that the acid thus formed by premature decomposition may attack the base metal which it is desired to protect. Because of this fact it is necessary that in carrying out the process of this invention the hydrogen-halide mixture be maintained at tem-

peratures below this decomposition point until the atmosphere contacts the surface which is to be plated. For best results, it is desirable to release the halide at a temperature close to its boiling point and to prevent the hydrogen-halide mixture from reaching a temperature greatly in excess of this value until it contacts the base metal upon which the plating is to be deposited.

In plating extended sections of material with an acid-proof coating, the atmosphere flow must be adjusted so as to secure this condition. This means that the temperature of the body being plated cannot exceed certain limits, which will be set forth in more detail below, in order that this premature decomposition may be avoided.

Unlike many plating reactions, that involved in the deposition of tantalum and columbium is largely not a replacement reaction wherein one metal is replaced by another but is a straight deposition reaction wherein the metal halide is decomposed by hydrogen. The first action on many metal surfaces may be replacement, but the reduction reaction with hydrogen quickly becomes predominant. If the metal halide concentration in the plating atmosphere is excessive, some of the metal halide passes through the system without decomposition and deposition of metal. Theoretically the reaction by which the major portion of the metal is deposited may be represented by reference to the theoretical reaction involving tantalum chloride and hydrogen. This reaction is as follows:

$$2TaCl_5+5H_2=2Ta+10HCl$$

We have found that, as long as the proper temperature conditions are maintained, the ratio of hydrogen to halide in the plating atmosphere may vary over fairly wide limits. However, for the production of strongly adherent places of appreciably thickness over extensive surface areas, sufficient hydrogen should be present to combine with essentially all of the acid radical released by the decomposition of the metal halide during the deposition reaction. Optimum results are produced on most base metals when the inlet gas contains at least twice the theoretical amount of hydrogen necessary to combine with the acid radical set free by the decomposition of the metal halide. The preferred ratio, therefore, of hydrogen atoms to metal atoms in the inet gas is at least 10 to 1. When the concentration of hydrogen in the atmosphere is too low, thinner, more or less porous coatings may be obtained which are generally unsatisfactory for acid resistance. Hydrogen concentrations in excess of 10 to 1 ratio set forth above may be used with excellent results; however, too high a concentration of hydrogen tends to decrease the speed with which the desired coating is produced. The hydrogen chloride produced by the deposition exerts a back pressure on the decomposition reaction, of course, but it has been found that the maintenance of the gas at the 10 to 1 ratio given above produces satisfactory results in most cases.

It is within the scope of this invention to remove the hydrogen chloride from the hydrogen in the exit gas by suitable scrubbing or chemical means and then return the purified hydrogen to the plating system.

It is also within the scope of this invention to condense metal halide which has not been decomposed, and reintroduce it into the system to be revolatilized.

The temperature of the metal or alloy being plated also requires careful consideration. As noted before, tantalum and columbium halides appear to initiate spontaneous decomposition by hydrogen at about 500° C. to 600° C. However, the deposition produced by this spontaneous decomposition tends to be loose, nonadherent and porous, these properties being undesirable in producing a protective plating. The plating atmosphere, therefore, should not be permitted to exceed this temperature until it contacts the base upon which the coating is to be produced. The minimum temperature at which smooth, thin coatings are obtained depends, to a large extent, upon the particular base metal being used. For example, very satisfactory coatings can be produced on copper and molybdenum at a temperature of about 500° C., and this temperature is preferred in the deposition of these metals on molybdenum. A temperature of about 800° C. is preferred for depositing coatings on iron; a temperature of about 1000° C. is preferred for nickel. Under proper conditions, temperatures as high as 1300° C. may be used for coating most metals which, of course, have sufficiently high melting points. Thus, coatings may be obtained over the general range of from about 500° C. to about 1300° C.

At the higher temperatures in this range the alloying action between the deposited tantalum or columbium and the base metal may become excessive and produce a rough alloyed coating which does not possess the desired acid-resistance. Even if alloying action is not rapid, the coating is apt to be rough and uneven and is so nonuniform that its performance cannot be predicted. Of more importance is the fact that when these high temperatures are used at the surface being plated, the halide may be decomposed before it reaches the surface, thereby preventing effective plating. Optimum plating temperatures for the practice of this invention appear to be mainly in the range of about 500° C. to about 1150° C. with the more rapid plating taking place at the higher temperatures. However, some base metals cannot be heated to the higher temperatures without melting, alloying excessively or undergoing undesirable structural changes. In these cases it is necessary to plate more slowly at the lower temperatures since the rate of deposition is dependent upon the plating temperatures and upon the hydrogen halide and the metal halide content of the gas above the surface being plated; in general, lower plating temperatures favor more ductile deposits. The plating temperature may be adjusted with respect to the gas composition to secure a uniform coating over an extended surface. It will be obvious to those skilled in the art, with the aid of the present specification, to choose the appropriate ratios of hydrogen to halide and temperatures, depending upon the base metal which it is desired to coat or plate.

The hydrogen used for the plating reaction of this invention also requires careful control. The tantalum and columbium halides used in the plating reaction hydrolize very easily. Any oxygen or water vapor present in the hydrogen reacts with the halides to form oxy-compounds which are unsuitable for plating. As a consequence, the hydrogen used for this plating must be purified, as by passing the hydrogen through a combustion unit of either the catalytic or noncatalytic type, and then drying it thoroughly before using. Care must also be exercised to insure that oxygen from other sources is eliminated from the reaction system. Oxygen-containing compounds should be removed from the metal

halide, and the surface of the base metal should be suitably cleaned to eliminate all traces of oxides and scale. In fact, the presence of dissolved oxygen in the base metal may, in some instances, prevent the formation of satisfactory coatings. Other reducing gases such as carbon monoxide and methane are not satisfactory for this plating. Other gases such as nitrogen, carbon dioxide, or hydrocarbons, should be excluded from the plating atmosphere because of the affinity of tantalum and columbium for these gases at elevated temperatures and the difficulty of removal of any gaseous element from tantalum and columbium except hydrogen.

In applying a protective coating of tantalum or columbium according to this invention, it will be apparent that the base metal or alloy must not melt, soften to a great extent, or undergo undesirable changes in structure at the plating temperatures (500° C. or above). In addition, the tantalum or columbium must bond to the base metal so as to produce adherent platings. Copper, nickel, molybdenum, nickel-iron alloys, copper-nickel alloys and various plain carbon and alloy steels have been found to be suitable base metals for deposition of a tantalum and columbium plate. In plating various base metals, the base may be provided with a suitable electrodeposited coating or layer of copper and the tantalum or columbium deposited on the copper layer in accordance with our invention. It is believed that a very slight alloying action between the tantalum or columbium plate and the base metal is desirable to secure the desired bond, and this is offered as a possible explanation of the method by which bonding occurs, although this is not intended to limit the invention. Nickel and high nickel alloys, such as Monel metal, are particularly good base materials, since the tantalum plate, as produced under the conditions of this invention, bonds to nickel in a very effective manner. Figure 2 shows the type of bond obtained with nickel. Other metals produce a similar type of bond, although it is apparent that the bond strength may not be as high, or may be higher, depending upon the base metal.

Having thus described the general features of the invention, a particular example will be explained to illustrate the operation of the process. For the purpose of illustration, reference is made to Fig. 1 of the accompanying drawing in which the various refinements of the operation have been eliminated and only the basic essentials of the invention shown. In this example the invention is employed to plate a section of the inner wall of a metallic tube with tantalum, whereby this section may be rendered acid-proof. As illustrated in the drawing, hydrogen from any desirable source, for example, a tank, as illustrated, is passed first through a meter, thence through a combustion furnace which may desirably be furnished with catalytic packing to reduce the temperature of reaction, thence through a preliminary drier containing, for example, calcium chloride, and thence into a final drier which is desirably filled with phosphorus pentoxide. The purified hydrogen then passes in succession through two furnaces, the first for vaporizing the plating agent, for example, tantalum chloride, and the second in which the plating reaction is carried out. The effluent gas and vapor are desirably passed through a trap for catching the unused tantalum chloride, and a condenser for recovering the hydrogen chloride. The resulting hydrogen is then available for recycling in the system.

In operating the apparatus described above, the specimen to be plated is placed in position in the plating furnace and the hydrogen turned on. When the hydrogen has flowed through the apparatus for a sufficient length of time to provide a pure hydrogen atmosphere, the heating of the plating furnace is begun. The temperature of the various portions of the heated section is adjusted with respect to the gas supply (of hydrogen and tantalum halide) which is to be used so as to secure the desired uniformity of deposit. When the desired temperature conditions are obtained in the plating furnace, the vaporizing furnace is then heated to a temperature at which the desired rate of tantalum halide volatilization is obtained. This rate may be such with respect to the flow of hydrogen that the ratio of hydrogen atoms to tantalum atoms in the entrance gas is about 10 to 1. When this mixture is passed over the section to be plated, a metallic plate is formed on the base metal and is bonded thereto. The plating reaction is continued until the desired thickness of plate is deposited; then when the halide supply is cut off, as for example, by ceasing to heat the vaporizing furnace, the plated article is allowed to cool in the purified atmosphere.

It appears that for reasonable thicknesses of plate the amount of plate deposited increases linearly with time. In all cases care must be taken that the tantalum chloride is not heated above about 500° C. to 600° C. before contacting the surface to be plated in order to avoid spontaneous deposition of the undesirable form of tantalum which slowly deposits in this temperature range. The tube prepared by this process, upon removal from the apparatus, will have a dense, adherent, acid-resistant tantalum plating upon the section which has been treated. The plating produced by this invention is smooth and impervious to attack by such reagents as hydrochloric acid and aqua regia at normal temperatures. Inasmuch as tantalum cannot readily be electrodeposited to satisfy such severe requirements, the process disclosed permits the production of lined pipes and vessels and plated parts of intricate design which are satisfactorily resistant to acid attack. Articles produced by this plating process are less costly than articles of solid tantalum, yet are as satisfactory for many purposes. In the plating of many articles it is desirable to heat the base metal by induction. In this manner the heat may be concentrated in the article being plated and there is less tendency for the plating atmosphere to decompose spontaneously prior to contact with the metal surfaces and produce a porous deposit or to plate on the furnace walls.

While the coating produced by the method of this invention is adherent to the base metal, it is possible to plate a thick coating of tantalum or columbium upon a thin piece of base metal, and then remove the base metal by selective attack in an acid whereby a tantalum or columbian shell may be produced and used as a source of the metal. This tantalum or columbium may be processed according to any of the known methods of treatment. Owing to the presence of hydrogen during the deposition, a certain amount of hydrogen is taken up by the deposited metal. For many purposes this does not interfere with the uses to which the plated article may be put. However, if it is desired to

remove the hydrogen, the procedure disclosed in the patent to Austin, No. 2,015,509, may be employed, for example.

Fig. 2 illustrates, at a magnification of about 500, the cross section of a tantalum plate upon a nickel base as produced according to our invention. The etchant used attacks the nickel particularly near the junction with the tantalum alloy. The polishing scratches appearing in the tantalum zone were left there deliberately in order to show the difference in physical properties of the three zones. It appears that the initial portion of the tantalum deposited on the base forms an alloy with the base metal. Thereafter a substantially pure plate is laid down. In the case of the plate upon nickel, it appears that a series of intermetallic compounds are formed, judging from the banded structure between the base metal and the tantalum plate.

It is to be understood that a columbian plate may be formed in the same manner as the tantalum plate. If a tantalum-columbium plate is desired a mixture of tantalum halide and a columbian halide may be employed; the ratio of the halides being such as to yield the desired ratio of the metals.

It is to be further understood that the foregoing description is merely illustrative of the invention and that various modifications will suggest themselves to those skilled in the art, and may be made without departing from the spirit and scope of the invention.

We claim:

1. The method of depositing an integrally bonded, protective coating on a metal base having a melting point above about 500° C. which comprises forming a mixture of hydrogen and the vapor of a volatile metal halide selected from the group consisting of tantalum halides, columbium halides and mixtures thereof, the mixture of hydrogen and volatilized metal halide being substantially free from carbon-containing gases, water vapor and oxygen, the amount of hydrogen present in said mixture being sufficient to combine with essentially all of the acid radical released by the decomposition of the metal halide when the metal halide is heated to a temperature above about 500° C., maintaining the mixture of hydrogen and volatilized metal halide at a temperature above the volatilization temperature of the metal halide but below about 500° C., heating the metal base to a temperature between about 500° C. and 1300° C., and passing the said mixture of hydrogen and volatilized metal halide into contact with the heated metal base.

2. The method of depositing an integrally bonded, protective coating on a metal base having a melting point above about 500° C. which comprises forming a mixture of hydrogen and the vapor of a volatile metal halide selected from the group consisting of tantalum halides, columbium halides and mixtures thereof, the mixture of hydrogen and volatilized metal halide being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to metal being about 10:1, maintaining the mixture of hydrogen and volatilized metal halide at a temperature above the volatilization temperature of the metal halide and below about 500° C., heating the metal base to a temperature between about 500° C. and 1300° C. and passing the mixture of hydrogen and volatilized metal halide into contact with the heated metal base to produce a smooth, dense, impervious and adherent plate of the metal on the metal base.

3. The method of depositing an integrally bonded, protective coating on a metal base having a melting point above about 500° C. which comprises forming a mixture of hydrogen and a volatilized tantalum halide, the mixture being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to metal being about 10:1, maintaining the mixture at a temperature above the volatilization temperature of the tantalum halide but below 500° C., heating the metal base to a temperature between about 500° C. and 1300° C. and passing the mixture into contact with the heated metal base to produce a smooth, dense, impervious and adherent plate of tantalum on the metal base.

4. The method of depositing an integrally bonded protective coating on a metal base having a melting point above about 500° C. which comprises forming a mixture of hydrogen and volatilized tantalum chloride, the mixture being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to tantalum being about 10:1, maintaining the mixture at a temperature above the volatilization temperature of tantalum chloride but below about 500° C., heating the metal base to a temperature between about 500° C. and 1300° C. and passing the mixture into contact with the heated metal base to produce a smooth, dense, impervious and adherent plate of tantalum on the metal base.

5. The method of depositing an integrally bonded protective coating on a molybdenum surface which comprises forming a mixture of hydrogen and volatilized tantalum chloride, the mixture being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to tantalum being about 10:1, maintaining the temperature of the mixture at a temperature above the volatilization temperature of tantalum chloride but below 500° C., heating the molybdenum surface to a temperature of at least about 500° C. and passing the mixture into contact with the heated surface.

6. The method of depositing an integrally bonded protective coating on a copper surface which comprises forming a mixture of hydrogen and volatilized tantalum chloride, the mixture being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to tantalum being about 10:1, maintaining the temperature of the mixture at a temperature above the volatilization temperature of tantalum chloride but below 500° C., heating the copper surface to a temperature of at least about 1000° C. and passing the mixture into contact with the heated surface.

7. The method of depositing an integrally bonded, protective coating on a nickel surface which comprises forming a mixture of hydrogen and volatilized tantalum chloride, the mixture being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to tantalum being about 10:1, maintaining the temperature of the mixture at a temperature above the volatilization temperature of tantalum chloride but below 500° C., heating the nickel surface to a temperature of at least about 1100° C. but not exceeding about 1300° C. and passing the mixture into contact with the heated body to produce a smooth, dense, impervi-

ous and adherent plate of tantalum on the nickel surface.

8. The method of producing columbium which comprises forming a mixture of hydrogen and volatilized columbium halide, the mixture of hydrogen and columbium halide being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to columbium being about 10:1, maintaining the temperature of the mixture at a temperature above the volatilization temperature of the columbium halide but below 500° C., passing the said heated mixture over a metal base heated to a temperature between 500° C. and 1300° C., whereby the columbium halide is decomposed and columbium is deposited on the metal base, and separating the deposited columbium from the metal base.

9. The method of producing a metallic body of the group consisting of tantalum, columbium and mixtures of tantalum and columbium which comprises providing a metal base having a melting point above about 500° C., forming a mixture of hydrogen and the vapor of a volatile metal halide selected from the group consisting of tantalum halides, columbium halides and mixtures thereof, the mixture of hydrogen and volatilized metal halide being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to metal being about 10:1, maintaining the mixture of hydrogen and volatilized metal halide at a temperature above the volatilization temperature of the metal halide but below about 500° C., heating the metal base to a temperature between about 500° C. and 1300° C., passing the mixture of hydrogen and volatilized metal halide into contact with the heated metal base to produce a smooth, dense, impervious and adherent plate of the metal on the metal base and separating the deposited plate from the metal base.

10. The method of producing a tantalum body which comprises providing a metal base having a melting point above about 500° C., forming a mixture of hydrogen and the vapor of a volatile tantalum halide, the mixture of hydrogen and volatilized tantalum halide being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to tantalum being about 10:1, maintaining the mixture of hydrogen and volatilized tantalum halide at a temperature above the volatilization temperature of the tantalum halide but below about 500° C., heating the metal base to a temperature between about 500° C. and 1300° C., passing the mixture of hydrogen and volatilized tantalum halide into contact with the heated metal base to produce a smooth, dense, impervious and adherent tantalum plate on the metal base and separating the deposited tantalum from the metal base.

11. The method of producing a tantalum body which comprises providing a metal base having a melting point above about 500° C., forming a mixture of hydrogen and the vapor of a volatile tantalum chloride, the mixture of hydrogen and volatilized tantalum chloride being substantially free of carbon containing gases, water vapor and oxygen, the atomic ratio of hydrogen to tantalum being about 10:1, maintaining the mixture of hydrogen and volatilized tantalum chloride at a temperature above the volatilization temperature of the tantalum chloride but below about 500° C., heating the metal base to a temperature between about 500° C. and 1300° C., passing the mixture of hydrogen and volatilized tantalum chloride into contact with the heated metal base to produce a smooth, dense, impervious and adherent tantalum plate on the metal base and separating the deposited tantalum from the metal base.

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