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[54] **PROCESS AND EQUIPMENT FOR THE TREATMENT OF A MATERIAL BY MEANS OF AN ARC DISCHARGE PLASMA**

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[51] **Int. Cl.** **B23k 9/00**

[58] **Field of Search** ..... 219/121 R, 121 P, 76; 75/.5 BB, 10 R; 204/164

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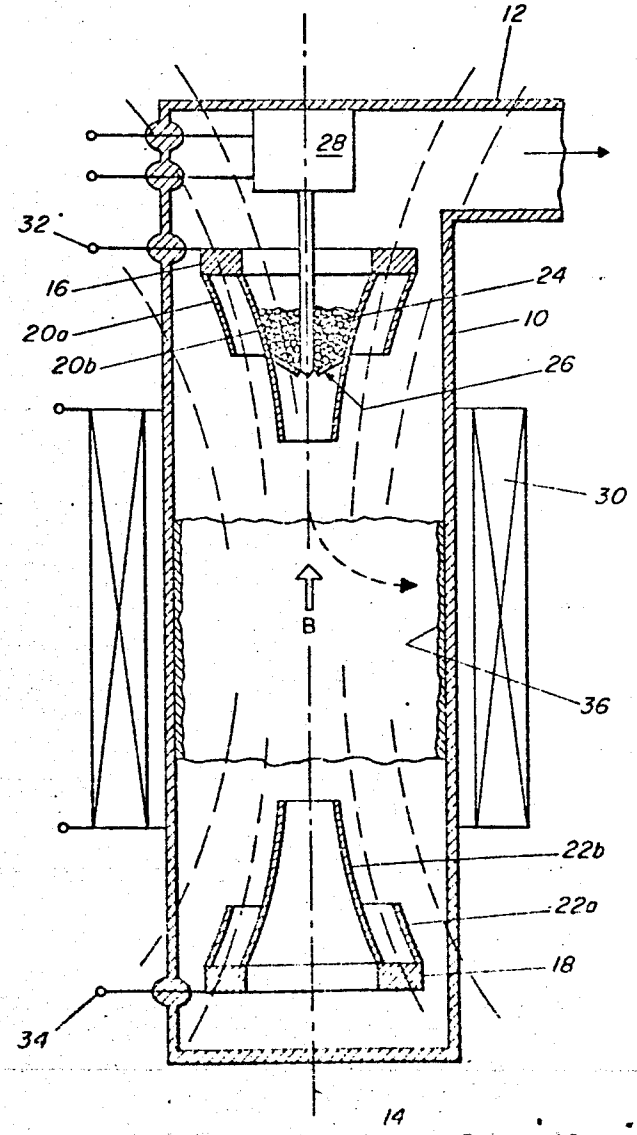
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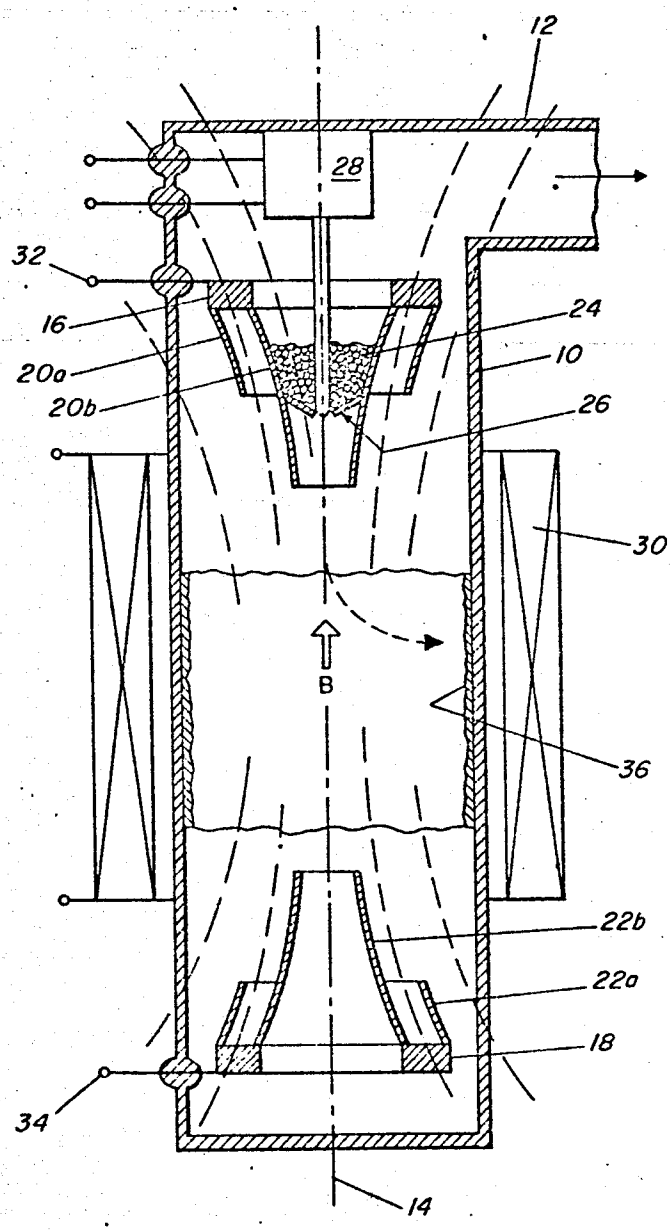
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[57] **ABSTRACT**

Metal compounds are reduced by creating a plasma between two spaced electrodes, which plasma rotates about an axis joining the electrodes, and delivering the reactants to a region of the plasma spaced from the electrodes. The desired reaction occurs near this region, and the plasma is of such a nature that the desired products of the reaction travel in a radial direction out of the plasma. The present invention recovers the desired products of the reaction by causing a halogen or halide to react with the desired product so as to form a metal halide from which the metal is subsequently recovered.

2 Claims, 1 Drawing Figure




12
28
32
16
24
20a
10
20b
26
30
B
36
22b
22a
18
34
14

PROCESS AND EQUIPMENT FOR THE TREATMENT OF A MATERIAL BY MEANS OF AN ARC DISCHARGE PLASMA

CROSS REFERENCE TO RELATED APPLICATIONS

In a process described and claimed in the U.S. Pat. application Ser. No. 307,838 filed Nov. 20, 1972, assigned to the assignee of the present invention, metal compounds are reduced.

SUMMARY OF THE INVENTION

The present invention relates to a process and equipment for the treatment of a material, such as the reduction of metal oxides, by means of an arc discharge plasma burning in a discharge space.

BACKGROUND OF THE DISCLOSURE

Inductive plasma burners for the heating of fine-grained material are known which contain a cylindric discharge vessel into whose front side streams a mixture of a gas and the fine-grained material in axial direction. The stabilization of the discharge plasma is achieved through a tangentially introduced auxiliary current of gas. Such plasma burners are especially used for the melting of powdery or granular materials of high fusing temperatures, such as fireproof oxides or carbides as well as for flame spraying (See German patent publication No. 1,286,241).

Further, there are known plasma burners and equipment for the heat treatment of materials whereby the plasma is produced through an arc discharge burning between two electrodes. Such equipment has an advantage over high-frequency plasma burners, in that the efficiency is higher and the apparatus is smaller and less costly.

U.S. Pat. No. 3,051,639 discloses equipment for hydrocarbon reactions, which employs an arc discharge between a rod-shaped central electrode and an annular electrode arranged at an axial distance from its point. No magnetic field is, however, provided.

U.S. Pat. No. 2,944,140 discloses plasma burners in which the plasma is produced through an arc discharge between a rod-shaped or platelike first electrode, and an annular electrode arranged at a distance from this. In the space between the two electrodes, enclosed by a cylindrical wall, a current of gas is tangentially introduced. For the stabilization of the plasma jet issuing through the opening of the annular electrode, there is provided a "magnetic nozzle" which is formed through a magnetic coil that may be arranged either between the electrodes or on the side of the annular electrode that is facing away from the platelike electrode. In the latter case the cross-section of the coil, consisting of a tube, through which flows a cooling agent, may at first somewhat diminish and then again gradually enlarge with increasing distance from the annular electrode.

In a plasma burner disclosed in U.S. Pat. No. 2,945,119 which likewise works with a "magnetic nozzle," the plasma jet produced through an arc discharge between a platelike electrode and an annular electrode passes through a quartz tube—fixed to the central opening of the annular electrode—into wall of which two spaced annular electrodes are inserted. The annular electrodes are connected with a direct-current supply for producing an auxiliary discharge. Between the annular electrodes is arranged a cylindric magnetic coil, connected with a direct-current source, enclosing the quartz tube, whose length is considerably smaller than the axial distance from the annular electrode.

There is further known from the German publication 1,932,703 equipment for the heat treatment of materials through an arc plasma, whereby the arc discharge burns between a tapered conical anode and a plasma jet serving as cathode, axially projecting into the anode, which is produced through a linear plasmatron. The anode is enclosed by a magnetic coil, or is itself developed as a magnetic coil in order to produce a substantially axial magnetic field which exerts with the radial electric field between the plasma jet and the anode an azimuthal force on the arc in order to let it rapidly rotate, so that the temperature in the reaction area will be more uniformly distributed. The pressure in the reaction space enclosed by the anode may be equal to atmospheric pressure, smaller than it, or greater than it. On reduced pressure the discharge may be diffuse, whereas on higher pressures there develops an arc discharge. The material that is to be treated is introduced through a laterally obliquely inserted tube approximately between the axis and the circumference of the anode into the upper part of the space enclosed by it. Underneath the anode is provided a freezing device.

Finally, it is known from scientific publications (Physics Letter, 24A, No. 6, Mar. 13, 1967, p. 324/325; Z. Naturforsch. 23*a*, 251–263, 1968 and 24*a*, 1473–1491, 1969) that between two annular electrodes, arranged at a distance from one another, between which lies a relatively strong magnetic field, there can be produced a stable low-pressure arc discharge that has some unusual properties. The conditions for the existence of such a discharge are, however, relatively critical, e.g. it is a prerequisite for the existence of such a discharge that the electron density lies in the range between about 5×10^{15} and $3 \times 10^{16} cm^{-3}$.

It is a disadvantage of the known processes and equipment for the treatment of materials by means of a plasma, produced through an electric discharge between two electrodes, that contamination of the treated material with electrode material is practically unavoidable. Moreover, there exists practically no zone of uniform temperature and density; on the contrary mostly the attempt is made to approximate such a zone through a rapidly rotating discharge channel.

The present invention has as a major objective to obtain a process and equipment for the treatment of material by means of an arc discharge plasma, whereby a contamination of the material with electrode material is prevented and a stable discharge is assured, in the presence of a zone of uniform, very high temperature.

BRIEF DESCRIPTION OF THE INVENTION

The invention includes a process characterized by a combination of the following conditions:

a. the average pressure in the discharge space containing the electrodes is kept below atmosphereic pressure;

b. a magnetic field is produced which runs substantially parallel to the axis forming the connection line between the electrodes, and which has in at least one part of a range of such a high value that the product $\omega\pi$ of the electron gyration frequency in the plasma ω and the time π within which on an

average an electron transmits its impulse to the ions of the plasma is greater than 1, and that the arc discharge plasma in this range as a whole in itself rotates around a central magnetic field line to which the plasma is substantially symmetrical;

c. the material to be treated is brought into a part of the range close to the central magnetic field line in which is fulfilled the condition of $\omega\pi > 1$; and

d. the treated material is recovered from the space lying radially outside of this range by means of formation of a volatile metal halide.

Under the above conditions, there occurs a great radial pressure gradient which results in high pressures in the axial range. Thereby contamination emanating from the electrode is kept away from the part of the discharge space which lies between the electrodes. On the other hand, surprisingly, the material introduced into the space between the electrodes, preferably at an axial distance from them in the proximity of the axis, is actually not transported in axial direction, but it permeates the rotating discharge in radial direction, so that the treated material is obtained in pure state from the part of the discharge space which lies outside of the plasma, e.g. after it has been centrifuged onto the inside wall of the discharge vessel. Unexpectedly, the discharge is also not so strongly disturbed by the foreign or untreated material as to cause instabilities. We have found that the relatively high electron temperature in the uninfluenced discharge, to be sure, decreases with the introduction of foreign material, but that the electron density which is required for the stability and existence of the discharge is hardly influenced by the introduction of the material.

BRIEF DESCRIPTION OF THE DRAWING

The attached FIGURE shows in cross-sectional elevation the preferred apparatus of the invention, an arc discharge plasma vessel for treatment of particulate material in accordance with the present process.

DETAILED DESCRIPTION OF THE INVENTION

A preferred application of the present process is for the reduction of metal oxides, such as tantalum oxide, titanium oxide, aluminum oxide for recovery of the pure metal. Preferably, a relatively coarse-grained starting material (e.g. with particle size up to 100 μm and more, preferably between 20 and 80 μm, such as 50 μm) is used. The particle size is preferably also relatively uniform.

Preferred apparatus for executing the process of the invention contains a discharge vessel-connected with a vacuum pump system,--including: an annular first electrode; a second electrode, substantially symmetrical to the vessel axis and arranged at a distance from the first electrode, a magnetic coil coaxially enclosing the space between the electrodes, which is capable of producing in the range of the vessel axis a magnetic field of at least 10 kG (kilo-Gauss); and means for introducing material to be treated through the annular, first electrode into the range of the discharge space between the two electrodes, near the vessel axis preferably at distance axially from the electrodes. Alternative embodiments will also be described hereafter.

The apparatus schematically presented in the drawing including a substantially cylindric vacuum vessel **10** composed, for example, of quartz, ceramic, or any other non-magnetic material. The vacuum vessel **10** is closed at one end, and connected at the other end through a connecting duct **12** with a vacuum system (not shown) which permits evacuation of the vacuum vessel **10**, or alternatively to fill it with a desired gas under a specified pressure, to drain the accumulating gases, and to maintain such a pressure that a stable discharge is assured.

Inside of the vacuum vessel **10** are arranged coaxial to its axis **14**, two annular electrodes **16** and **18**, which may be of aluminum, for example. From the radial inner and outer rim of the electrodes **16** and **18** project each approximately tapered conical walls **20***a*, **20***b*, and **22***a*, **22***b*, respectively, of insulating material, e.g. quartz or ceramic, which define a channel of annular cross section. Preferably, each inner wall **20***b* or **22***b*, axially projects farther toward the center of the discharge vessel than its respective outer wall, **20***a* or **22***a*.

In the space enclosed by the wall **20***b* is provided means for the dosed introduction of particulate material **24**, e.g. finely-grained or powdery, that is to be treated. The feeding is preferably achieved axially symmetrically with respect to axis **14** of the vessel **10** in order to assure uniform influence on the material through the discharge plasma. The means for feeding the material in the illustrated embodiment may be needle valve **26**, adjustable through an electro-magnetic or other control means **28**, and permits measured introduction of the material **24** into a range near the axis of the vacuum vessel **10**. Since wall **20***b* projects axially from the electrode **16** into the discharge space enclosed of the vacuum vessel **10**, the material to be treated may be introduced into the plasma at considerable axial interval from the electrodes **16** and **18**. This, together with the special kind of discharge, help to prevent contamination of the material with electrode material, as will be further explained.

The central part of the vacuum vessel **10** lying between the electrodes **16** and **18** is enclosed by a cylindric magnetic coil **30**, which permits the production of a relatively strong magnetic field B. The intensity of the magnetic field should be at least so great that the product $\omega\pi$, of the gyration frequency ω of the free electrons in the plasma and the time π within which on an average an electron transmits its impulse to the ions of the plasma, is greater than 1 at the pressure conditions existing in the discharge space. In practice the intensity of the magnetic field will be at least 10 kG, preferably at least 20 kG; good results were obtained at field intensities between 30 and 60 kG.

The magnetic coil terminates preferably bilaterally at an axial distance from the electrodes, so that the magnetic field lines diverge in the range of the electrodes as indicated through dash-lines. The walls **20***a*, **20***b*, and **22***a*, **22***b* are preferably so shaped (thus tapered conically and similar to a rotated hyperbola), that they follow substantially the course of the magnetic field lines, and that the charge carriers in the discharge are therefore compelled onto paths which run parallel to the electrode walls.

The electrodes **16** and **18** are provided with corresponding terminals **32** and **34**, respectively, which are connected with a current source (not shown), preferably a direct-current source that is capable to supply sufficient current for the discharge. The magnetic coil **30** in operation is connected with an energy supply (not shown). The magnetic coil **30** may be a super-

conductive coil so that it will not require any energy supply in continuous service.

In the operation of the illustrated apparatus the material to be treated **24**, e.g. finely granular or powdery tantalum oxide (or titanium oxide or the like) which is to be reduced, is placed within the space enclosed by the wall **20***b*. The vacuum vessel is then evacuated through the pump duct **12**, and subsequently filled with a desired gas (e.g., hydrogen, air or an inert gas) under an inflation pressure between about 1 and 10 torr, preferably between about 3 and 5 torr (measured at room temperature). With the magnetic field B cut in, there is then ignited between the electrodes **16** and **18** an arc discharge by means of a high-tension impulse. During arc discharge the needle valve **26** is opened and material **24** is fed in measured doses into a range of the discharge near the vessel axis. From the axial range the material is driven radially outward through the hot, current-carrying plasma tube which arises between the electrodes due to the discharge. There results an extremely intense and a uniform interaction with the plasma, and the material is centrifuged against the outside wall of the vacuum vessel **10**. The treated material, e.g., reduced metallic tantalum, is thereby accumulated at the inside wall of the vacuum vessel **10**, as shown at **36**.

In one specific embodiment of the invention the magnetic coil **30** had a length of about 30 cm; the magnetic field B produced through the coil **30** had a field intensity of about 50 kG and between the electrodes **16** and **18** burned a tubular, stable arc discharge with a current of about 2 kA and an approximate arc-drop-voltage of about 300 V. The distance of the electrodes was about 60 cm, the average diameter of the electrodes was about 6 cm. The work was done in pulsed operation, the duration of the impulses was of the order of milliseconds.

When tantalum oxide or titanium oxide, respectively, was used as the material to be treated, the material settled at the wall of the vacuum vessel in the form of metallic tantalum or titanium, respectively, of high purity. The effect of the reduction in relation to the applied electric energy is very high, so that the production cost of produced material is very much cheaper than that of comparable, commercial processes. Good yields were obtained with finely granular starting material of a particle size of about 50 μm.

The described process and apparatus have particular application in the preparation of chemical elements from their compounds, particularly for the recovery of metals. Those metals which cannot be produced from their ores through reduction with carbon, therefore are of particular significance, such as titanium, zirconium, vanadium, tantalum, and aluminum. The present process and apparatus can also be used for the preparation of chemical compounds, especially when these can be produced only through strongly endothermic reactions. Moreover, various materials which exist in fusible form can be treated; also liquids of low vapor pressure; or vapors, gases, and mixtures or dispersions of such materials.

The concept "annular electrode" is meant herein to comprise also electrode forms which topologically are equivalent to a circular ring, thus e.g., perforated electrodes which substantially have the form of a disc, a rectangle, an ellipse, a triangle, and so on.

With the aid of the drawing, we have described a preferred embodiment of the present invention. But from this preferred embodiment there can be made modifications. In some respects, however, certain disadvantages may be encountered. Instead of the annular electrode **18**, there may be used a coaxial rod-shaped electrode. The developing plasma discharge is then hollow only in the upper part. In principle, it is also possible to make both electrodes compact, e.g., rod-shaped, and even to arrange them unsymmetrically with respect to the cylindric magnetic coil **30**. The electrodes may also be arranged at a relatively great distance from the magnetic coil. In this case the essential conditions for the present process of $\omega\pi > 1$ will only be fulfilled in a part of the range lying between the electrodes, and will develop only there the plasma discharge which rotates around its axis in the form of a column. Since the plasma discharge is then not hollow, it is not possible to introduce the material to be treated on a burning discharge into the range of the axis of rotation of the plasma discharge, but it becomes first necessary to bring a certain quantity of the material into the range of the axis of rotation, e.g., letting it drop and then only ignite the discharge around the free-falling material. This requires necessarily a relatively complicated control of the course of the process, and the magnetic field is not utilized to its maximum, which fact may lead to quite substantial decreases in efficiency, particularly on account of the high field intensities. The circumstances are more simple if the upper electrode—as shown in the drawing—is annular and coaxial to the magnetic field, but arranged so far from this that the conduct of the arc current through the magnetic field is not yet incurred in the proximity of the electrode, and that at the electrode is then initiated a discharge channel, rotating around the axis of the magnetic field, which passes over into discharge form used for treating the material only in the range in which the condition of $\omega\pi > 1$ is fulfilled. Since in this case the desired discharge is not hollow, the discharge is preferably only ignited when the material is already in the range on the axis around which then is formed the ignited, desired discharge.

When the material produced in the above described manner, which usually deposits itself on the inside wall of the discharge vessel enclosing the plasma, is capable of forming a volatile metal halide, the metal is removed from the discharge vessel preferably by having it converted into the volatile metal halide through a halogen or halide introduced into the discharge vessel, and that the metal halide is removed from the area, and then decomposed to form the pure metal.

By "volatile metal halide" we mean herein a metal halide which can be converted into vapor form without decomposition at moderate temperatures, e.g., up to about 500°C, preferably at temperatures between about 200° and 300°C. Suitable metals are such as chromium, niobium, silicon, tantalum, titanium, uranium, vanadium, and zirconium.

The halogen or halide used for extracting the metal from the apparatus should fulfill the following conditions:

1. lowest possible boiling or sublimation point of the metal halides;
2. thermal decomposability to halogen (or metal halide) and metal at temperatures as low as possible;

3. selective extraction effect on metal mixtures such as can occur when using relatively impure starting materials, such as ores.

Example

As starting material for the preparation of titanium we use ilmenite ($FeTiO_3 + Fe_2O_3$), whereby at the inside wall of the discharge vessel which encloses the plasma (usually a quartz tube) there settles substantially a mixture of titanium and iron. For the extraction of the titanium we select iodine as extraction agent (on account of the low boiling point, about 377°C, of TiI_4). Iodine fulfills also the two other conditions; it forms with the titanium TiI_4 thermally decomposable at about 1000° to 1200°C, and with iron it forms FeI_2 which boils only at a temperature somewhat above 600°C. The iodine is introduced into the discharge space in vapor form. At about 200°C it acts on the mixture of titanium and iron, and forms TiI_4 which at this reaction temperature is already sufficiently volatile to allow to have it pumped off. Any FeI_2 possibly formed is not volatile at 200°C and remains in the apparatus. The pumped off TiI_4 is decomposed on a hot surface at 1000° to 1200°C, consisting preferably of titanium metal. The iodine that is freed thereby can be recycled into the process.

The extraction process of the invention is considerably more simple to execute than a mechanical removal of the metal and still has, moreover, the following advantages:

a. through control of the operational parameters (e.g., temperature of formation and decomposition of the metal halides) the process can be selectively applied to various metals. This achieves, in addition to the extraction, simultaneously also a purification;

b. the process can in general be executed at relatively low temperatures;

c. certain embodiments allow continuous operation, i.e., it is not necessary to switch off the discharge during the extraction of the recovered metal.

In many cases, however, a discontinuous operation will be preferable, i.e., in that a metal deposit of a certain thickness is first produced on the inside wall of the discharge vessel, the discharge is then interrupted, and from this metallic deposit there is finally removed the desired metal from the apparatus through conversion into a metal halide.

Instead of iodine, also bromine, chlorine, and fluorine can be used.

Instead of a pure halogen, it is also possible to introduce into the apparatus a halide of a metal that is capable to give off a part of its halogen atoms to the treated material, and which thereby leads to an extractable halogen compound that is volatile in the above sense.

We claim:

1. In a process for the treatment of a metal compound capable of forming a volatile metal halide, which process includes the following steps: (a) producing an arc discharge plasma in a region of a discharge vessel between two axially spaced electrodes (b) maintaining the average pressure in said region at less than one atmosphere; (c) producing a magnetic field running substantially parallel to the axis forming the connection line between said electrodes the value of which in at least one part of said region has such a high value that the product $\omega\pi$ of the electron gyration frequency ω in the plasma and the time π within which on an average electron transmits its impulse to the ions of the plasma is greater than 1, and that the arc discharge plasma in said region as a whole in itself rotates around a middle magnetic field line to which the plasma is substantially symmetrical; and (d) bringing said metal compound into a part of said region close to the mid point of said magnetic field under said condition of $\omega\pi > 1$, whereby said plasma effects a chemical reduction of said metal compound and said reduced metal compound travels to a space lying radially outside of said region; wherein the improvement comprises recovering said reduced metal compound from the space lying radially outside of said region by (i) introducing a halogen or halide into said vessel and contacting said reduced metal compound therewith, whereby said reduced metal compound is converted into a vaporous volatile metal halide, (ii) removing said volatile metal halide in vapor form from said vessel, and (iii) further treating said volatile metal halide such as decomposing said volatile metal halide to obtain substantially pure metal.

2. The process of claim 1, wherein said metal compound is a titanium-furnishing metal compound; and said halogen or halide comprises vaporous iodine.

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