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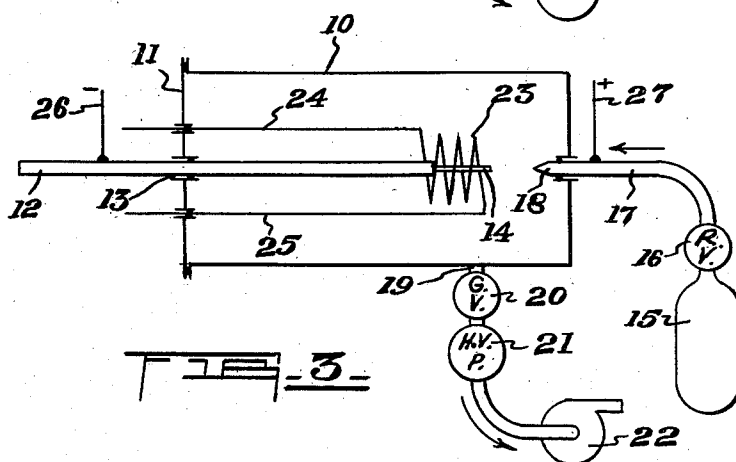
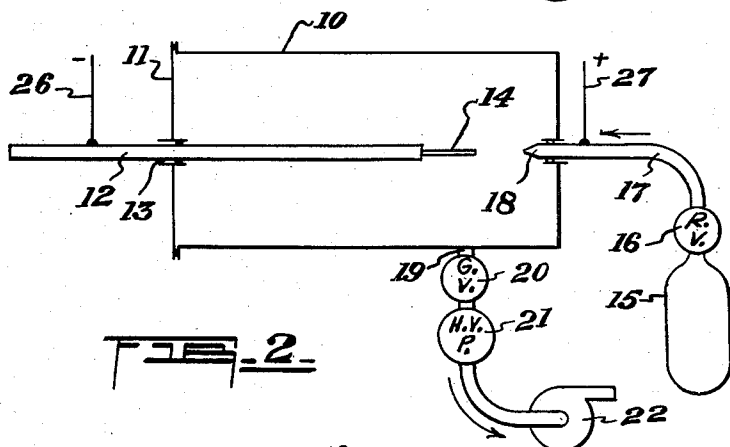
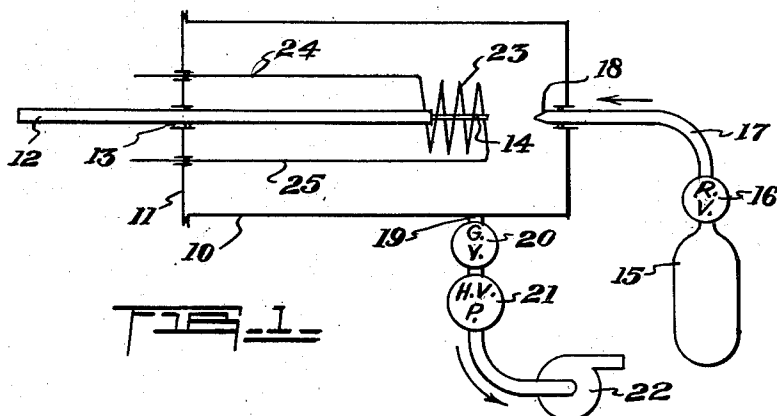
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METHOD FOR PREPARING TITANIUM, ZIRCONIUM AND TANTALUM

Filed Sept. 3, 1954

2 Sheets-Sheet 1



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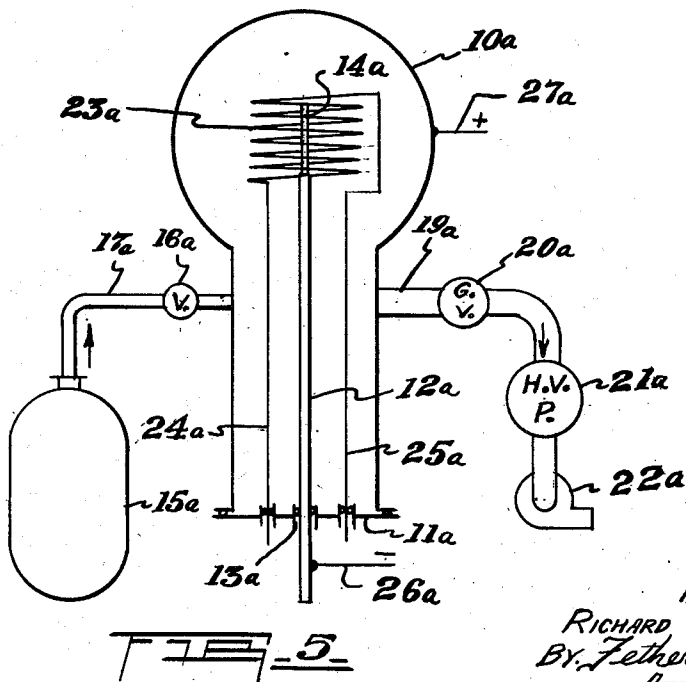
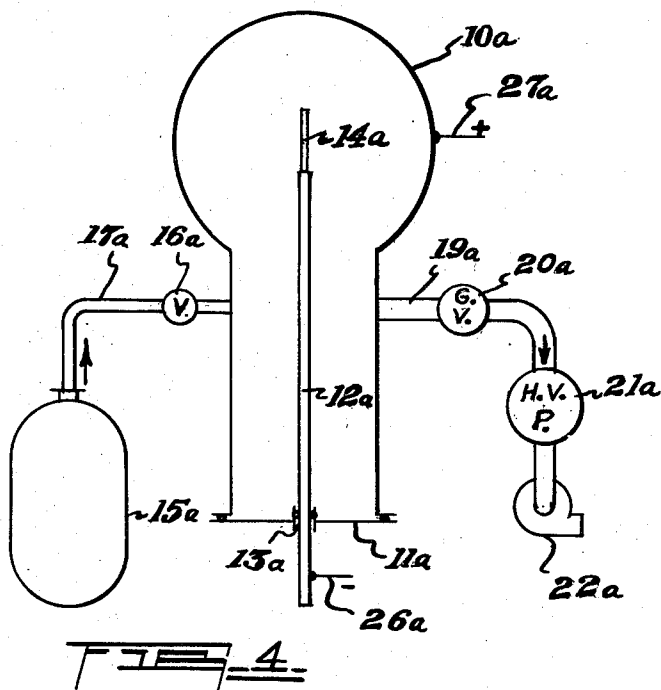
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METHOD OF PREPARING TITANIUM, ZIRCONIUM AND TANTALUM

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Application September 3, 1954, Serial No. 454,093

Claims priority, application Great Britain
September 4, 1953

1 Claim. (Cl. 117—107)

This invention relates generally to a method for preparing metals which form weakly-bonded covalent halides, and, more particularly, to a method for preparing titanium, zirconium, or tantalum, since these are the metals of greatest commercial interest in the above-named group. While my experiments to date have not extended beyond the three metals just named, I believe the methods described in this specification could, without difficulty, be applied to the preparation of the other metals which form weakly-bonded covalent halides.

In the conventional hot-wire or Van Arkel process for the preparation of titanium, the metal is desposited, by thermal dissociation, on a wire raised to red-heat in an atmosphere of the vapour of a weakly-bonded covalent compound of titanium, usually the tetrachloride or tetraiodide. This treatment possesses certain disadvantages: (1) It is virtually impossible to build up a large ingot on the hot wire. (2) The process cannot be made continuous owing to the progressive dilution of the compound (say $TiCl_4$ or TiI_4) vapour by free chlorine or iodine.

I have found that the Van Arkel titanium process can be improved to render it continuous and more productive, and that the improved process may be expanded to embrace the preparation of those metals in addition to titanium which form weakly-bonded covalent halides, for example, zirconium and tantalum.

My contribution to the art may be generally defined as a method for continuously preparing titanium, or zirconium, or tantalum, by removably mounting a small body, preferably a wire or plate, of the desired metal in a closed vessel; establishing a high vacuum within the vessel; heating the small body while directing a halide (a chloride, bromide, or iodide) of the metal into the vessel as a molecular beam which is completely intercepted by the heated body, the body being heated to a temperature in excess of the dissociation temperature of the selected metal halide so that the beam of the latter, upon contacting the body, is broken up into (a) free metal, which is deposited on the heated body, and (b) a free halogen (chlorine, bromine, or iodine). The free halogen is removed as it is formed (e. g., by pumping it off as a gas, or by condensation followed by collection of the condensate); and the body, after an ingot of desirable weight has been formed thereon, is removed and replaced by a fresh body.

The invention embraces a modification of the process of the preceding paragraph. In this modification a small body of the desired metal (titanium, zirconium, or tantalum) is removably mounted in a closed metal vessel which is filled with a gaseous halide (a chloride, bromide, or iodide) of the desired metal, which halide is maintained at a reduced pressure, e. g. about 0.01 mm. to about 1 mm. of mercury. Metal is then electrodeposited on the said small body by an electrolysis which involves the employment of the metal vessel as the anode, the body of the desired metal as the cathode, and the gaseous metal halide

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as the electrolyte, and the passage of a heavy current through the gaseous metal halide.

In drawings which illustrate embodiments of the invention:

5 Figure 1 is a diagrammatic illustration of one embodiment,

Figures 2 and 3 are diagrammatic illustrations of somewhat modified forms of the embodiment of Figure 1,

10 Figure 4 is a diagrammatic showing of modification of the invention dependent upon electrolysis of a gaseous medium, and

Figure 5 is a diagrammatic showing of an embodiment similar to that shown in Figure 4, but modified by the inclusion of induction heating.

15 Considering first the case of Figure 1, reference numeral 10 indicates a closed reaction vessel provided with a detachable end plate 11. A mandrel 12 is passed through a seal 13 in end plate 11 and is centrally disposed within the vessel 10. Mandrel 12 carries at its inner end a plate 14 of titanium. Reference numeral 15 indicates a source of titanium tetrachloride which may be fed from the source through a reducing valve 16 and along a conduit 17 to a nozzle 18, which opens within the reaction vessel and is directed towards the titanium plate 14.

20 The vessel 10 is provided with a means for evacuating it and continuously pumping off any gases formed during the reaction. This means consists of a conduit 19 leading from the vessel, a gate valve 20, a high vacuum pump 21, and a mechanical pump 22. The titanium plate 14 is surrounded by an induction heating coil 23. The high frequency leads to induction heating coil 23, have been labelled 24 and 25.

25 The apparatus shown in Figure 1 could be employed in the following manner in the preparation of titanium from titanium tetrachloride:

30 The closed vessel 10 is first evacuated using the pumps 21 and 22. The titanium plate 14 is then heated by the induction heating coil 23 to a temperature in excess of the dissociation temperature of titanium tetrachloride. The valve 16 is then opened to produce a jet of titanium tetrachloride at nozzle 18. The nozzle 18 is designed to produce a narrow jet which is directed towards and wholly intercepted by the heated plate 14. The pressure within the vessel is kept at a low figure, preferably below .001 mm. of mercury, so that the motion of the molecules of titanium tetrachloride issuing from the jet is rectilinear and they form a molecular beam in their travel towards the plate. When the molecules of titanium tetrachloride contact the plate, the heated plate causes dissociation of the titanium tetrachloride into metallic titanium (which adheres to the heated plate) and free chlorine. The free chlorine is removed as it is formed, via gate valve 20, high vacuum pump 21 and mechanical pump 22. The chlorine produced by the action must be removed so that the desired high vacuum conditions may be maintained inasmuch as they are essential to the maintenance of the molecular beam; and it will be appreciated that the vacuum should be high enough to ensure that a molecule coming from the jet has a high probability of hitting the plate rather than a free gas molecule. The employment of a high vacuum also has the advantage of rendering negligible the probability of the titanium absorbing any damaging quantity of chlorine, oxygen, nitrogen, or other gas, which might be present in the reaction vessel.

35 As the deposit of fresh titanium builds up on the plate 14, the plate-carrying mandrel 12 is slowly withdrawn and is slowly axially rotated to ensure a uniform build up of the titanium. When a titanium ingot of sufficient size has been formed, the mandrel 12 carrying the ingot is removed and replaced by a mandrel carrying a fresh plate. In order that the process may be carried out

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continuously, instead of employing a detachable end plate 11, a vacuum gate may be employed to facilitate removal of the titanium ingot and its replacement with a fresh plate. Alternatively, a reserve mandrel carrying the fresh plate could be rotated into position on a capstan or the like, or any other suitable mechanical arrangement could be employed to change the mandrel so that the process may be made continuous.

In the discussion of Figure 1 given above, and in the discussion of the remaining figures which follows, for purposes of illustration, the preparation of titanium from titanium tetrachloride is described. It should be clearly understood, however, that the process embraces the production of titanium from bromides and iodides thereof and the production of zirconium and tantalum from their chlorides, bromides and iodides. I do not recommend or claim the use of the fluorides of these metals. In case of titanium and titanium tetrachloride has been chosen because of the commercial importance of titanium and the ready availability of titanium tetrachloride. Actually, aside from considerations of availability and economics, I would prefer to work with the tetrabromide or tetraiodide rather than the tetrachloride because of their lower dissociation temperatures. The use of the tetraiodides is also attractive since iodine lends itself to removal by condensation rather than the pumping step illustrated in Figure 1.

The arrangement shown in Figure 2 is generally similar to the arrangement shown in Figure 1. However, it will be noted that induction heating is dispensed with in Figure 2. It is possible to dispense with the induction heating by establishing a marked potential difference between the nozzle 18 and the plate 14. Connections for establishing this potential difference have been indicated at 26 and 27 in Figure 2. The establishment of this high potential difference between the nozzle and plate (with the plate negative), induces a heavy electrical current flow in the stream of gas directed from the nozzle 18 on to the plate 14. Under these circumstances, the wire is heated by positive ion bombardment. The positive ion bombardment has been found sufficient to raise the temperature of the plate to a figure in excess of the dissociation temperatures of the metal halides contemplated by the invention. Once again the titanium tetrachloride (or other metal halide) is broken up into metallic titanium, which adheres to the heated plate 14, and free chlorine, which is once again pumped off as it is formed. The operation of the apparatus of Figure 2 is, therefore, seen to be similar to the case of Figure 1, except for the fact that induction heating is replaced by positive ion bombardment.

The arrangement shown in Figure 3 is simply a combination of the arrangement shown in Figures 1 and 2, i. e. both positive ion bombardment and induction heating are employed to heat the plate upon which the titanium is deposited. The establishment of a potential difference between the plate and the nozzle is not only of value in that it results in heating of the plate, but is also useful in that it insures attraction and adherence of titanium to the plate. When an electrical field and positive ion bombardment are employed, as in the cases of Figures 2 and 3, the vacuum should not be as high as in the case of Figure 1, which depends for its success upon the establishment of a molecular beam of the metal halide. Where an electrical field is employed, as in Figures 2 and 3, I recommend operating at a reduced pressure of from about 1 mm. to about .01 mm. of mercury. A vacuum as high as that employed in Figure 1 would militate against the desired current flow. However, the residual gas pressure must be sufficiently low for the desired ionization of the metal halide.

Turning now to the arrangement shown in Figure 4, 10a is a closed metal vessel having a removable end plate 11a. 12a is a mandrel, 13a a seal and 14a a plate or wire of titanium. 15a is a source of titanium tetra-

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chloride, 17a a conduit leading into the vessel 10a, and 16a is a flow-controlling valve in this conduit. Elements 19a, 20a, 21a and 22a are respectively, a conduit, gate valve, high vacuum pump and mechanical pump for initially evacuating the shell 10a and, at the end of the reaction, drawing off free chlorine produced during the reaction. The arrangement shown in Figure 4 is intended to be run as a batch process although the arrangement can be readily modified for continuous operation. The arrangement of Figure 4 would be operated as follows:

The metal vessel 10a is evacuated, the gate valve 20a is then closed and the valve 18a opened so that the metal vessel is filled with titanium tetrachloride. The titanium tetrachloride should be at a reduced pressure of from about 1 to .01 mm. of mercury. The electrical connections 26a and 27a are then utilized to establish, in the plate 14a, a high negative potential with respect to the metal vessel 10a. The establishment of this potential difference causes a heavy electrical current to pass between the metal vessel 10a and the titanium plate 14a. Once again the titanium plate is heated by positive ion bombardment to a temperature in excess of the dissociation temperature of the titanium tetrachloride. The titanium tetrachloride decomposes into free titanium, which adheres to the plate, and free chlorine. When a batch of titanium tetrachloride has been treated, the mandrel 12a is withdrawn for recovery of the titanium ingot built up upon the plate 14a, and the free chlorine is pumped off and recovered. The process could be rendered continuous by slowly withdrawing the mandrel, replacing the ingot with a new plate where necessary; and by continuously feeding in titanium tetrachloride and pumping off free chlorine.

The arrangement shown in Figure 5 is similar to the arrangement shown in Figure 4 except for the fact that an induction heating coil 23a, having high frequency leads 24a and 25a, is provided to assist in the heating of the plate 14a. This particular arrangement has been found valuable in cases where the dissociation temperature of the metal halide is high, or other conditions militate against raising the plate 14a to the desired temperature. Since the arrangement of Figure 5 is similar to the arrangement of Figure 4, except for the inclusion of the induction heating means, further description of Figure 5 appears to be unnecessary.

It will be noted that the operation of the arrangements of Figures 4 and 5 is essentially an electrolysis procedure wherein the metal shell is employed as the anode, plate 14a is employed as the cathode, and the metal halide, e. g. titanium tetrachloride, is employed as the electrolyte. The positive ions are carried to the cathode where they adhere to form a deposit of metallic titanium.

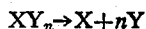
It is particularly interesting to note that this electrolysis procedure involving ionization of the metal halide does not depend for its effectiveness upon thermal dissociation of the metal halide. I have actually determined that the electrolysis procedure may be carried out without any substantial heating of the plate 14a, and definitely without heating it to a temperature anything like the dissociation temperature of the metal halide employed as the electrolyte. Where special conditions make it desirable to effect the electrolysis with the plate cold, precautions must be taken to avoid heating of the plate by positive ion bombardment. The special precautions which may be employed include the water cooling of the plate or employment of a massive mandrel (for heat dissipation) in conjunction with low power dissipation. The special conditions referred to above include the preparation of high purity titanium free of gas inclusions, or the preparation of titanium having special metallurgical properties which would be adversely affected by formation of the titanium at high temperatures.

What I claim is:

A method for continuously preparing a metal selected

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from the group consisting of titanium, zirconium, and tantalum, which comprises removably mounting a small body of the desired metal in a closed reaction vessel; reducing the pressure within said vessel to a value of at most 1 mm. of mercury; heating said body by positive ion bombardment while continuously directing a molecular beam of a halide of the metal through a jet orifice into said vessel and onto said heated body, the cross sectional area of said molecular beam at said heated body being within the surface of said heated body nearest said jet orifice, said metal halide being selected from the group consisting of the chlorides, bromides, and iodides of the desired metal, and the body being heated to a temperature in excess of the dissociation temperature of the selected metal halide; continuously removing from said vessel free halogen formed in the region of said heated body by thermal dissociation of said metal halide in accordance with the equation



wherein:

X is selected from Ti, Zr and Ta,

Y is selected from I, Br and Cl, and

n is an integer corresponding to the valency of X

and periodically removing said body and replacing it with a fresh body when an appreciable quantity of new metal has been deposited on the first body by the thermal dissociation of the metal halide.

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