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DISSOCIATION-DEPOSITION APPARATUS
FOR THE PRODUCTION OF METALS
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Fig. 3.

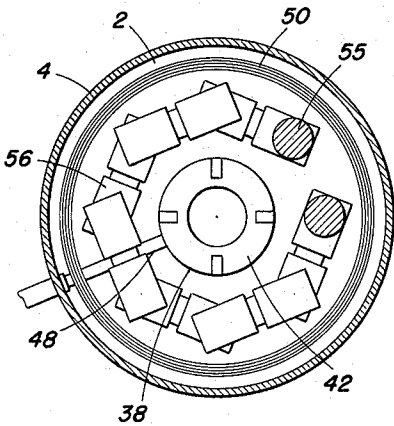


Fig. 2.

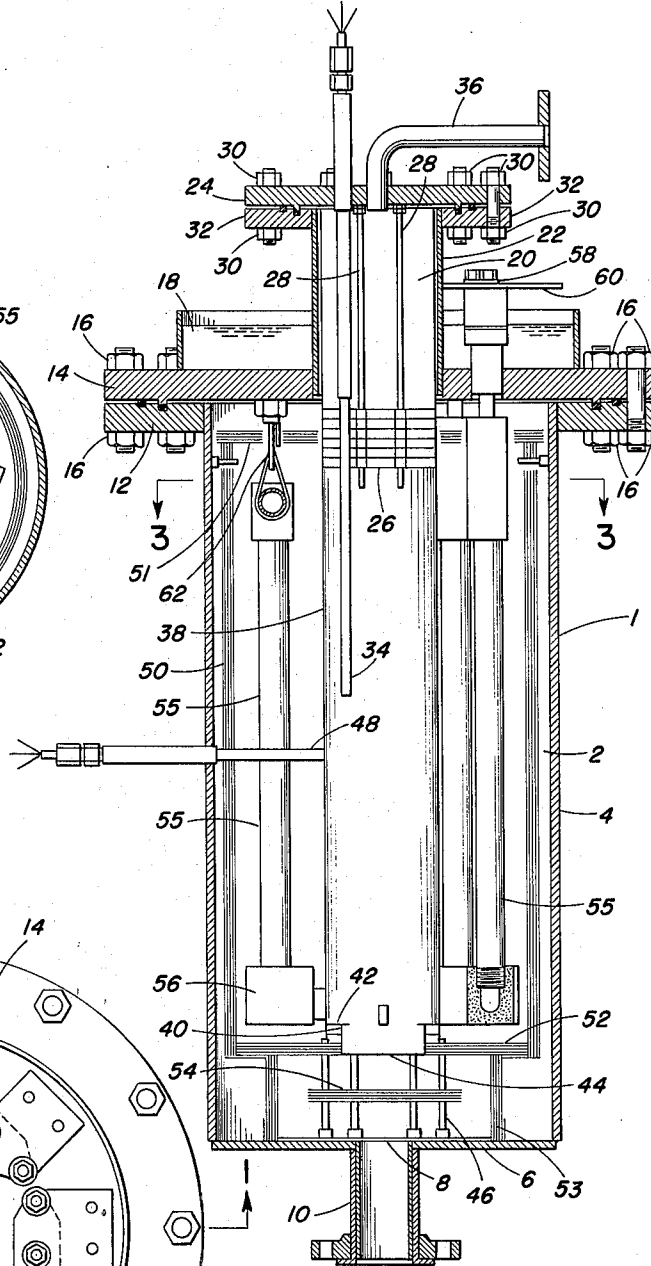
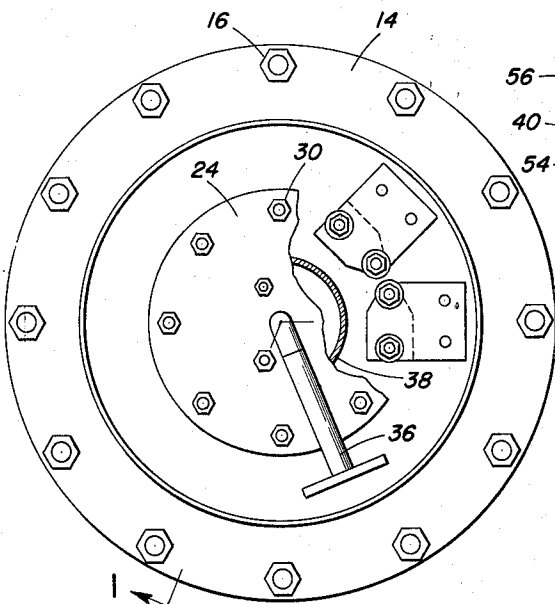


Fig. 1.

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1

3,243,174

DISSOCIATION-DEPOSITION APPARATUS FOR THE PRODUCTION OF METALS

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1 Claim. (Cl. 266—24)

This invention relates to apparatus for the production and recovery of iodide metals. More particularly, the invention contemplates the provision of improved apparatus for obtaining metallic elements such as titanium, hafnium, zirconium and chromium from their corresponding iodides by thermal decomposition and dissociation of the metal iodide on a heated dissociation-deposition surface.

It is now well established that metals such as titanium, hafnium, zirconium and chromium, among others, can be recovered in high purity form by contacting their corresponding iodides in the vapor phase with a heated dissociation filament or surface maintained at a temperature above the decomposition temperature of the metal iodide, with consequent dissociation of the metal iodide at the dissociation-deposition surface and concomitant deposition of the pure metal thereon. Assuming that an atmosphere of the metal iodide vapor is maintained in contact with the heated dissociation-deposition surface, either by feeding from an external source or by formation in situ from crude metal and iodine liberated during the dissociation reaction, the deposition of pure metal can be effected on a continuous basis and substantially high-purity metal formed.

Thus, the foregoing principles have been applied to produce these metals by decomposition of their corresponding iodides at directly heated filament wires or rods. Deposition on resistively heated filaments of this type requires close control and regulation of the power input to compensate for variations in the resistive load caused by the gradual buildup of deposited material thereon. Furthermore, employment of this "hot-wire" technique has demonstrated that, due to the limited deposition surface available, the dissociation-deposition reaction proceeds extremely slowly, and certain of the resulting iodide metals thus produced tend to be coarsely crystalline, brittle and spiny in structure.

There has been suggested in more recent years a modification of this principle involving a somewhat enlarged dissociation-deposition surface. It has been proposed, for example, to provide a heating and deposition assembly disposed within a reaction vessel and composed of graphite or other material; the apparatus comprising a graphite resistor and shell surrounding said resistor and in contact therewith through a joint support and connecting member. In this system the shell is an integral part of the heating unit and the electrical circuit. Indeed the centrally disposed resistor is grounded to the deposition surface or shell which, in turn, is grounded to the reaction vessel or chamber, thus making the graphite deposition surface an appreciable fraction of the total resistance of the circuit.

However, in employing this apparatus, whether the metal is deposited on a shell of graphite or other material, it would be necessary, not only to remove the heating deposition unit from the containing vessel, but to dismantle it as well, in order to separate the shell with its deposit from the heating coil and other components of the unit. In addition, it is then necessary that the unit be reassembled with a new shell, making certain that the numerous points are sufficiently tight to secure good electrical contact throughout, in that a poor contact could readily terminate a run prematurely and

2

even ruin the unit. Further, such prior methods and apparatus as this normally provide that the pressure in the space defined between the centrally disposed resistance and the inner shell wall be identical with that between the outer surface of the shell and the walls of the reaction chamber to avoid mechanical stresses on the shell; and to effect this, suitable passage through the pervious graphite of the shell, or other means is provided; thus permitting attack by iodine and vapors on the entire resistance heating system, while also permitting deposition of metal on both sides of the shell and centrally disposed graphite resistance member. Such deposition even if limited to the outer shell results in substantial contamination of the dissociated metal product not only through direct contact, but by reaction with any oxygen, which unavoidably leaks into the apparatus to form carbon monoxide which could introduce both carbon and oxygen as contaminants into the deposited metal.

Accordingly, the present invention provides a novel and commercially feasible furnace for producing high-purity metals of chromium and of the metals of Group IV of the Periodic Table by radiant or indirect heating from externally positioned heater elements surrounding a shell member formed, most desirably, of titanium, molybdenum or where iodide chromium is desired, of high-chromium stainless steel or the like; upon the interior surface of which deposition occurs from a dynamic flow of the corresponding gaseous metal iodide transmitted through the interior of said deposition shell. Accordingly, iodination of relatively impure titanium bearing material and vaporization of the resulting titanium tetraiodide are carried out separately from the successive dissociation and deposition steps.

The titanium tetraiodide thus prepared may, if desired, be relieved of certain amounts of impurities, metallic and nonmetallic, prior to introduction thereof into the dissociation-deposition furnace by, for example, fractional distillation or fractional sublimation.

The present invention, however, both as to its organization and mode of operation, together with further features and advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is an elevational view of the apparatus of the present invention with portions broken away to show the interior structure thereof.

FIGURE 2 is a view of the upper end of applicant's apparatus as embodied in FIGURE 1, with portions removed to disclose the interior structure.

FIGURE 3 is a cross-sectional view taken through line 3—3 of FIGURE 1.

Referring now more particularly to the drawings, the invention involves a thermal decomposition-metallic deposition furnace apparatus indicated in its entirety by 1, adapted as noted hereinabove for the production of chromium, hafnium, zirconium and, most desirably, titanium. The apparatus 1 comprises a heating vessel 2, the side wall 4 of which is disposed, illustratively, in a cylindrical manner, and closed at its lower end by bottom wall 6 welded or otherwise suitably integrated with the vertically disposed cylindrical side wall 4. Disposed centrally in the aforesaid bottom wall 6 is an orifice 3 serving as a vapor exhaust port or outlet communicating with the vapor outlet conduit 10, the function of which will be referred to and described in further detail in due course hereinafter. Secured to or formed integrally with the upper peripheral edge of the aforesaid cylinder 4 is outwardly directed flange 12, adapted for engagement with the cover 14.

In the illustrated embodiment, this engagement is effected by means of lock-bolts 16. The cover 14 serves as the base upon which lies the oil bath 18. The cover 14

3

is also disposed about the lower end of a tubular well 20 which latter member is delimited by the well wall 22 and the cover plate 24; its lower boundary being defined by diffusion or distribution baffles or plates 26 which serve as and are constituted to form radiation shields which are integrally attached to and supported by post members 28 which are in turn bolted to the under surface of the aforesaid cover plate 24. This plate member 24 is removably attached by suitable means, e.g. bolts 30, to the laterally-directed flange 32 which is suitably secured in fixed or integral relation with the aforesaid well wall 22 as, for example, by welding or other suitable means. Defining a passage through said cover plate 24 are a thermocouple 34 and the vapor inlet conduit 36 for transfer of gaseous metal iodine, e.g. titanium iodide, from a boiler (not shown) where the aforesaid iodide has been initially heated to the gaseous state. The thermocouple 34 is disposed in a substantially vertical position within the furnace 1 and passes through the diffusion plates 26. The vapor inlet conduit 36 is terminated at a point approximately flush with the under surface of the cover plate 24. Also disposed in such a manner as to terminate at a point flush with the under surface of the cover plate 24 is the dissociation-deposition shell or chamber 38 which is normally and substantially cylindrical in conformation and is removably mounted in the apparatus 1. The upper and outer surface of the shell or chamber 38 is in substantially contiguous but slidable relation with the inner surface of the well wall 22. A similarly substantially flush relationship exists between the periphery of the diffusion plates 26 and the inner surface of the aforesaid deposition shell 38; the latter member being extended vertically downward from this point in substantially parallel relation to the side wall 4 of the vessel 2.

The dissociation-deposition shell 38 defines a restricted passage 40 toward its lower end providing an overhang 42 terminating in an exit port 44. The shell 38 is supported by contact of this overhang 42 with a plurality of upwardly directed support members or posts 46 which thus serve as guides for the shell 38 and aid in its stabilization against lateral disturbance. The exit port 44 faces the orifice or mouth 8 of the vapor outlet conduit 10. A thermocouple 48 is disposed in substantially horizontal position to define a passage through the side wall of the vessel 2, and vertically disposed radiation barrier shields 50, positioned in spaced parallel alignment to the side enclosing surface 4 of the closed vessel 2 thus minimizing heat loss and reflecting heat toward the outer surface of the deposition shell or cylinder 38. Other barrier shielding members 51 and 52 are positioned horizontally adjacent the cover wall 14 and bottom wall 6, respectively. The bottom barrier wall 52 engages and supports the vertically disposed side barrier shielding 50 which in turn engages and supports the upper barrier shielding 51. Additional radiation shielding members 53 are disposed vertically about the space provided between the exit port 44 of the deposition shell 38 and the exhaust port 8 of the vapor outlet conduit 10 to support the bottom barrier shielding wall 52 and thus the entire radiation barrier shielding erected in the heating vessel 2 and referred to above but not including the diffusion plates 26. Suitable shielding elements are also mounted horizontally (54) on the shell-supporting posts 46 between said exit port 44 and the exhaust port or mouth 8 of the conduit 10 to aid in further insulation of the bottom wall 6 and the aforesaid conduit 10.

The thermocouple 48 which passes through the side wall 4 and side wall radiation barrier shield 50, as described above, terminates in contact with the outer surface of the deposition shell 38. Positioned between the vertically disposed shell 38 and radiation shield 50 are the plurality of heating elements or rods 55, formed of graphite and connected in series by means of graphite connector blocks 56 (FIG. 3) which are alternately po-

4

sitioned at respective ends and bridge the rods 55 to provide the continuous series connection terminating at the electrode terminals 58 as illustrated in FIGURE 1. These terminals 58 are bolted for support to the laterally extending arm 60 which is secured at one end with the well wall 22. The terminals 58 traverse the cover wall 14 and are cooled by the oil bath 18. The graphite heating elements 55 are, in turn, removably attached to the under surface of the cover 14 by suitable securement means such as that seen transversing the upper barrier shield 51 and designated by the numeral 62 in FIGURE 1.

For the purpose of effecting a more detailed understanding of the significance of the aforesaid apparatus in relation to the dissociation-deposition procedure in which it is employed, the following description of preferred operating conditions is rendered in concert with the drawing. Thus, titanium tetraiodide having been prepared is heated initially to the gaseous state, in a suitable boiler (not shown). The gaseous titanium tetraiodide is then transmitted by positive pressure means as a dynamic flowing body of vapor through the vapor inlet conduit 36, and thence into the tubular well 20 within the shell cylinder 38. Passing downwardly the titanium tetraiodide vapor is dispersed and diffused around the radiation shielding baffle or diffusion plates 26 and is then received within the main body or actual dissociation-deposition portion of the shell 38 wherein the temperature is maintained at a level above the decomposition point for titanium tetraiodide.

This decomposition temperature is initiated and sustained by the indirect or radiant heating of the shell 38 by the graphite resistance elements 55 surrounding the aforesaid shell cylinder 38. The rate of dynamic flow is controlled by the heat input to the boiler. Electrical power to the electrode terminals 58 and thus to the resistance elements 55 is supplied by a direct or alternating current generator (not shown) adjusted to effect the desired temperature as measured by a platinum-rhodium thermocouple 48 or preferably by a tungsten-molybdenum thermocouple 34 positioned in the deposition chamber or cylinder 38. Desirably, the resistances are placed in series with the field winding of the generator and varied through standard relay systems and motors which in turn are actuated by a recording controller.

The gaseous titanium tetraiodide, thus introduced, upon contact with the inner surface of the shell 38, is decomposed and metallic titanium of uniquely high-purity deposited upon the aforesaid shell surface. The apparatus or system 1 is evacuated or outgassed by the suitable vacuum means operating through the exhaust port or orifice 8 into the vapor outlet conduit 10 prior to introduction of the titanium tetraiodide therein. The shell cylinder 38, particularly where metallic titanium is the desired product, is itself preferably formed of titanium. Other materials which result in minimal contamination of the deposited metal and which provide a suitably non-reactive surface at the necessary dissociation temperatures and from which the deposited metal, i.e., titanium, zirconium or hafnium, may be readily removed, can be employed for the purpose of this invention, e.g. molybdenum, or tungsten; or high-chromium stainless steel, quartz, silica, or high-silica glass in the case of chromium. In addition to the deposition of metallic titanium in our preferred embodiment, there is evolved dissociated iodine, which, with unreacted titanium tetraiodide is drawn through the exit port 44 of the shell 38 and through the aforesaid orifice 8 into the vapor outlet conduit 10, and conducted therethrough to a conventional cooled collector and condenser device (not shown) for recovery of process materials for reuse. The remaining gaseous impurities are exhausted from the system by the aforesaid vacuum means. The conduits 36 and 10 from the boiler and to the condenser respectively are insulated and heated at a temperature sufficient to maintain the gaseous flow

5

in the vapor state. The insulation or radiation barriers 50, 51, 52, 53 and 54 of the furnace are most effective when formed of molybdenum, although zirconium brick compositions (Zirconia, Norton Company, Worcester, Mass.), and high-temperature alumina-kaolin clay compositions (J-M3000, Johns-Manville Co., New York, New York) can also be desirably employed. Optionally, a pre-heater may be inserted within the tubular well 20 to elevate the temperature of the titanium tetraiodide from that of the boiler to a point adjacent but below the decomposition temperature maintained within the main portion of the shell cylinder 38 beneath the heat shielding baffles 26. It will be evident, however, that certain of the heat received by the lower and main portion of the shell cylinder 38 from the graphite heating elements 55 will be conducted to the upper portion of the shell cylinder 38 present in the tubular well 20 and this conducted heat is sufficient normally to accomplish the purpose served by a pre-heater. In any event, in view of the elevated temperatures attained in the well 20 and vessel 2, the adjacent oil bath 18 is used to cool the electrode terminals 58 as noted above and is, in turn, water-cooled. When iodide chromium is prepared the temperature gradients for vaporization, dissociation and deposition of chromium vary materially from those employed with the metals of Group IV of the Periodic Table, i.e. hafnium, zirconium and titanium. In this regard, reference is made to the co-pending U.S. application Ser. No. 579,970, filed April 23, 1956, now abandoned, by John M. Blocher, Jr., and Alfred C. Loonam, and entitled "Process for Production of Iodide Chromium."

Having thus described the subject matter of the invention, what it is desired to secure by Letters Patent is:

Apparatus for use in the production of a metal by thermal decomposition of the corresponding metal halide thereof; said apparatus comprising a heat insulated furnace, a substantially cylindrical dissociation-deposition chamber formed of titanium metal positioned therein in removable and slideable engagement therewith; a plurality of resistance heating elements connected in series and formed of graphite for indirectly heating said dissociation-

6

deposition chamber to a temperature sufficient to cause dissociation of metal halide therein and deposition of high-purity metal on the interior surface thereof; said heating elements being positioned within the aforesaid furnace and exterior to and surrounding said dissociation-deposition chamber in spaced relation to said chamber, and substantially isolated from contact with said metal halide; together with a vapor inlet conduit positioned at one end of said chamber for introducing gaseous metal halide into and through said dissociation-deposition chamber, and an exit port and conduit at the other end of said chamber for conducting dissociated gaseous iodine, unreacted metal halide and associated metallic and nonmetallic impurities therefrom.

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